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Documenting the pesticide processes module of the ARS RZWQM agroecosystem model†‡

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Abstract: We describe the theory and current development state of the pesticide process module of the USDA-Agricultural Research Service Root Zone Water Quality Model, or RZWQM. Several processes which are significant in determining the fate of a pesticide application are included together in this module for the first time, including application technique, root uptake, ionic dissociation, soil depth dependence of persistence, volatilization, wicking upward in soil and aging of residues. The pesticide module requires a large number of parameters to run (as does the RZWQM model as a whole) and it is becoming clear that RZWQM will find most interest and use as part of a 'scenario' in which all data requirements are supplied and the predictions of the system compared with a real (usually partial) data set. Such a scenario may then be modified to examine the response of the system to changes in inputs. It also has significant potential as a technology transfer or teaching tool, providing detailed understanding of a specific agronomic system and its potential impacts on the environment.
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1 INTRODUCTION

The behavior and fate of pesticides in the environment is determined by an interlocked system of processes so complex that computer simulation modeling is the only means of attempting to understand it.[2–6] Modeling pesticide water pollution processes began with agricultural nonpoint pollution research in the 1970s.[7–9] Early successes include CREAMS, the first widely used pesticide agricultural field water-transport model,[10] its successor GLEAMS,[11] and PRZM,[12,13] the most important model used for pesticide water pollution risk prediction in the USA.[14,15] Many models are now available, each of which may have some specific advantage for a given application. The amount of computer power available to the average user has increased enormously in the last two decades, and the upper limits on model complexity are now constrained, not by the capabilities of hardware, but by the amount of human effort available to construct the more complete models which such equipment allows, and to develop the detailed input data sets required. The increased 'reality' (and therefore complexity) desired by researchers is in tension with practical needs.[3,5,16] For regulatory and resource conservation agencies, models have become increasingly important tools for environmental risk assessment. The development of procedures in which models are used in conjunction with field and laboratory tests to expand those tests to a full probability-of-risk distribution has been an active research area, particularly within industry.[5,14,17–20]

RZWQM development was begun in 1985 and it was first released in 1992. The fundamental advance of RZWQM at the time was its ability to simulate hydrology and chemical transport as driven by the intensity of individual precipitation events.[1,21] This can provide a more realistic description of many pesticide transport and dissipation processes that depend on rainfall intensity or any parameter that cannot be represented well by a 24-h average.

In its original release, the RZWQM pesticide module contained nearly every conceivable pesticide dissipation/degradation process. The result was so

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complex that the model never achieved a user base among pesticide scientists. The release described here represents a thorough revision in which processes accounted for are restricted to those for which database default parameter values can be provided, or for which field data are known to exist, or for which we felt a user might have data; or for which a user might at least be able to make a reasonable estimate. Some of the latter have been kept because they clearly should be accounted for, and we hope some research may be done to fill these gaps. We have also incorporated developments in pesticide environmental science which have occurred since the original version of the model was released, eg, some of the findings and recommendations of the FOCUS and FIFRA modeling worksgroups.[14,15,18,19]

RZWQM is still a 'research' model.[5] It does not yet have an erosion component (one is in preparation based on the GLEAMS erosion model) and so it is of limited utility in describing runoff of sediment-transported pollutants. Not all of the pesticide processes have been completely verified or tested against field observations. Nevertheless, RZWQM has developed a small cadre of pesticide scientists who are exploring its potential ability to describe more realistically pesticide fate and behavior in agricultural crop/soil systems. This potential for greater realism is due to the model including the most complete inventory of algorithms of those processes known to be important in determining this behavior:

- Application target
- Pesticide formulation
- Soil sorption kinetics
- Pesticide acid/base properties
- Root uptake
- Washoff from foliage and crop residue
- Increased persistence in the vadose zone
- Upward leaching due to wicking
- Half-lives for each compartment
- Aerobic and anaerobic soils
- A new mixing model for runoff
- Volatilization from moist soil
- Binding (aging) of pesticides in soil

As will become clear, although we know each of these factors can be important, our knowledge of some of them is incomplete.

2 COMPARTMENTS AND PROCESSES

On days when no precipitation or irrigation occurs, RZWQM calculates changes on a daily time-step basis, tracking changes in four interacting environmental compartments: crop foliage, plant residue, soil surface and soil subsurface (Fig 1). Plant 'residue', a layer of dead crop or other plant matter immediately overlying the surface of the soil, may be either detritus used to control erosion, or thatch underlying turf. The soil surface is the interface between the soil and the atmosphere; in RZWQM it includes the top 1-cm depth of soil. The soil subsurface or root zone is the soil from a depth of 1 cm to the bottom of the soil profile.

Transport processes between compartments and major pesticide dissipation/degradation processes within compartments are shown in Fig 1. The root zone is divided into horizons with distinct properties based on the input soil profile, and the horizons are subdivided into numerical layers or nodes for computation purposes. The physics of soil water and solute movement and macropore flow are described in Malone *et al.*[21]

3 PESTICIDE CARRYOVER, SELECTION AND APPLICATION

3.1 Pesticide carryover

Pesticide may be placed in each soil horizon to simulate initial concentrations which are carryover from the period prior to simulation. The mass of the pesticide present on crop residues may also be input, in units of $\mu g\ cm^{-2}$ land area. It is assumed that no crop or weed plants are present at the beginning of a simulation.

3.2 Pesticide selection and daughter and granddaughter product specification

Users may select an active ingredient from a menu of pesticides and default values for pesticide-specific parameters are loaded. These values may be edited, or a new user-defined pesticide may be created. Some processes are turned on by additional parameter input. RZWQM currently handles up to three pesticides, including transformation products. Multiple applications of each pesticide may be made.

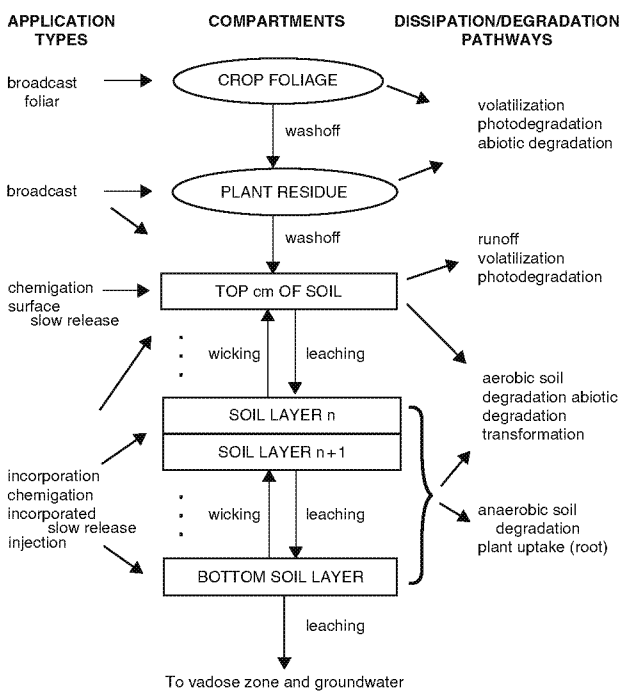

Figure 1. Location of application residues and dissipation/degradation pathways in the compartments of the RZWQM model.

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The formation of degradation or metabolite chemical species can be a significant part of the environmental impact of a pesticide.[22,23] For users who have information on conversion rates or who wish to experiment with product formation and dissipation, RZWQM provides three choices: parent–daughter, parent–2 daughters, or parent–daughter–granddaughter tracking. The properties of the product(s) must be specified—in effect, the daughter or granddaughter becomes one of the maximum of three 'pesticides' tracked. Input requirements are 'Ancestry codes' (1 = parent; 2 = daughter; 3 = granddaughter) defining the source compound of each product, and the specific compartment and transformation process(es) generating the daughter or granddaughter products. The user may specify transformation fractions which specify the fraction of parent(daughter) degradation which forms daughter(granddaughter) product (ie a yield coefficient).

Each day of the simulation, RZWQM adds daughter and granddaughter product to the existing amounts in each compartment by calculating their production from parent by the specified transformation processes. For example, for a daughter product:

$$[\mathrm{D}](t) = [\mathrm{D}](t-1) + F_{\mathrm{D}}\left(\frac{M_{\mathrm{D}}{}^{\mathrm{mol}}}{M_{\mathrm{P}}{}^{\mathrm{mol}}}\right) \times [\mathrm{P}](t-1)(1-\mathrm{e}^{-k_{\mathrm{D}}}) \quad (1)$$

where the brackets [] indicate concentrations ($\mu\mathrm{g\,g^{-1}}$) of products in the specified compartment and P and D indicate parent and daughter, t and $t-1$ indicate the current day and previous day, respectively. The molecular mass ratios M^{mol} correct the concentrations for the change in molecular mass with transformation, and the fractions F are the conversion fraction. If the dissipation rate of a metabolite in a compartment is slower than its formation rate then it will accumulate in that compartment. Note: if 'aerobic soil degradation' is selected as a transformation process, RZWQM generates metabolite with the same rate constant in both surface and subsurface soil layers. This is a simplification because the soil at the surface experiences extremes of moisture and temperature.[24,25]

3.3 Method of application

For each application of a pesticide the user selects an application method, which determines which Compartments initially receive the pesticide (see Fig 1).

3.3.1 Broadcast—leave on surface

This method applies a uniform spray from above the crop canopy, and the canopy (if present) intercepts a fraction of the spray equal to 1 minus the canopy land cover fraction $F_{\mathrm{f}}^{\mathrm{lt}}$ (calculated by the plant model), giving an applied foliage concentration C_{f}^{A} per unit of land area ($\mu\mathrm{g\,cm^{-2}}$). The application rate of pesticide A, in units of $\mathrm{kg\,ha^{-1}}$, is multiplied by an application efficiency F_{ae} (fractional) and converted to $\mu\mathrm{g\,cm^{-2}}$ by multiplying by a conversion factor of 10($1\,\mathrm{kg} = 10^9\mu\mathrm{g}$; $1\,\mathrm{ha} = 10^8\mathrm{cm}^2$):

$$C_{\mathrm{f}}^{A} = 10A\,F_{\mathrm{ae}}(1 - F_{\mathrm{f}}^{\mathrm{lt}}) \quad (2)$$

F_{ae} may be input by the user.

There is much evidence that broadcast spray applications are rather inefficient. Willis and McDowell[26] reviewed studies of foliar application efficiency and give average deposition efficiencies (the fraction of the application rate actually deposited) as 62 (±27)% for 'ground' sprayers and 45 (±20)% for aerial application. However, pesticides with zero vapor pressure or formulations such as wettable powders with low volatilization rates can approach 100% deposition.[27,28] In the absence of specific values from the literature, RZWQM assumes a ground sprayer is used and gives a default pesticide deposition efficiency F_{ae} of 0.6, unless the vapor pressure of the pesticide is zero, in which case the deposition efficiency is 1.0. It is recommended that the user consider changing the F_{ae} to 0.45 for aerial application.

The fraction of pesticide which passes through the canopy is intercepted by crop residue, if present, which also has an associated light transmission fraction $F_{\mathrm{f}}^{\mathrm{lt}}$ calculated by mass of plant residue on the surface, giving an initial crop-residue concentration of pesticide per cm^2 of land area C_{r}^{A}:

$$C_{\mathrm{r}}^{A} = 10AF_{\mathrm{ae}}F_{\mathrm{f}}^{\mathrm{lt}}(1 - F_{\mathrm{r}}^{\mathrm{lt}}) \quad (3)$$

The remaining pesticide not intercepted by crop foliage and/or plant residue is assumed to reach the soil surface. In a real situation such a deposit would be a very thin deposit right at the surface of the soil. However, a depth of mixing >0 must be defined, and RZWQM assumes the pesticide is mixed evenly throughout the topmost layer, which by definition is one centimeter in depth. Thus the initial concentration of pesticide in this surface layer ($\mu\mathrm{g\,g^{-1}}$dry soil) is

$$C_{\mathrm{sl}}^{\mathrm{A}} = \frac{10AF_{\mathrm{ae}}F_{\mathrm{f}}^{\mathrm{lt}}F_{\mathrm{r}}^{\mathrm{lt}}}{\rho_{\mathrm{b,sl}}} \quad (4)$$

where $\rho_{\mathrm{b,sl}}(\mathrm{g\,cm^{-3}})$ is the dry bulk density of the soil in layer 1.

3.3.2 Broadcast—incorporate down with tillage implement

This method applies the pesticide as above, but the chemical that reaches the soil surface and plant residues is incorporated. Pesticide on plant residue is incorporated in proportion to the degree to which plant residues are incorporated. The 'Incorporation' option assumes that a field cultivator is used, which is assumed to have an effective depth of 10 cm; the applied pesticide is divided equally between all layers within that depth. Default deposition efficiency is the

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same as for Broadcast. Both the tillage implement and incorporation depth can be modified in the 'Management' section of the model.

This assumption of even mixing of incorporated pesticides throughout the effective depth of the cultivator is a simplification—incorporation by tillage implements typically results in a zone of high concentration remaining near the surface, with concentration decreasing with depth,[29–32] and may also leave streaked zones of different pesticide concentrations along the path of the incorporation.[33,34]

3.3.3 Foliar application

The entire application is deposited on the crop foliage, regardless of the amount of foliage and plant residue present. This option does not simulate any real application technique (except perhaps wiper applicators),[35] but may be used in a 'virtual experiment' to examine the behavior of foliar-applied pesticides alone. Default deposition efficiency is the same as Broadcast.

3.3.4 Application in irrigation water

This method allows for application of pesticides in irrigation water. Since RZWQM is one-dimensional, furrow and drip irrigation, which fertilize sites within a field, will not be represented well (see Benjamin *et al*[36]), but sprinkler chemigation (including center-pivot chemigation, which has been developed for a wide variety of materials) should be simulated adequately. At present pesticide application to foliage in irrigation water is not considered. The default deposition efficiency is 100%.

3.3.5 Microencapsulated (slow release)—surface or incorporated

This method provides for a slow-release pesticide placed in the top 1 cm of soil or mixed uniformly within the 'secondary plow zone'. The term 'microencapsulated' is misleading: this feature may be used for other controlled-release formulations or for any formulation type with a known active ingredient release rate. This option only allows the user to specify a linear release, although other forms of release of active ingredient, such as exponential, can occur.[37] The percentage of active ingredient released per day is user-specified. This is released into the soil water at the start of each computational day, equilibrates and joins any pesticide already present. The deposition efficiency is 100%.

3.3.6 Soil surface

This method simulates an application in which all of the applied pesticide deposits on the soil surface, even if plant residue or crop foliage are present. An example of this is a shielded sprayer applying herbicide onto the soil below the crop canopy. It also allows for another virtual experiment in which one simulates what happens to that fraction of the pesticide which is initially deposited on the soil surface. Again, the chemical is treated as though mixed evenly throughout the topmost, 1-cm-thick soil layer, and the default deposition efficiency is 0.6.

3.3.7 Fumigation—injected into the plow layer

This method causes RZWQM to check for the knife injector depth, which is input, along with the specification of a 'NH_3 Applicator' in the 'Tillage Management' section. The pesticide is then added uniformly to the soil layer with index number n which is closest in depth to that of the knife. The deposition efficiency is 100%.

3.4 Time of application

The time of application may be absolute (a specific date is input) or relative to planting, crop emergence or harvest (a time offset is input). When an offset is input the application time is triggered by planting emergence or harvest date, which allows for multi-year simulation procedures with varying planting, emergence or harvest dates between years. The offset is crop-specific, so that one can have a specific timing sequence for each crop used in a rotation.

4 PESTICIDE TRANSPORT BETWEEN COMPARTMENTS

4.1 Foliar and plant residue washoff

Pesticides on crop foliage or plant residue may be washed onto the soil by rainfall. Washoff can be a major source of transfer between foliage/residue and soil compartments, even for extremely insoluble pesticides, if rainfall occurs shortly after application.[38–40] If runoff occurs during such an event, it can significantly increase runoff concentrations,[41–43] but, because half-lives on foliage are typically very short, rainfall must occur shortly after application.[44]

In most washoff studies rainfall amounts are more important than rainfall intensity, and there appears to be a fraction of the deposit which is most 'available' for washoff and is most readily washed off. Willis *et al*[45] developed an empirical equation which relates the fractional loss of the foliar deposit to (a) the fraction of the deposit that is washable and (b) the amount of rainfall. Since rainfall, plant and residue concentrations, and soil surface concentrations in the top centimeter of soil are all in the same mass per unit area units, the equation for each increment of rainfall $I_R \Delta t$ may be written as:

$$C_f = C_f^o F_f^{wo} \exp_e(-P_f^{wo} I_R \Delta t) \quad (5)$$

where P_f^{wo} is the rainfall washoff coefficient (units are mm^{-1}), F_f^{wo} is the fraction of pesticide which is readily washable and I_R is the rainfall rate ($mm\ h^{-1}$). These are input as 'plant canopy washoff' and 'residue washoff' coefficient and power parameter, respectively. $I_R \Delta t$ is the cumulative rainfall (mm) during a time segment, and eqn (5) is invoked in each time segment that rain occurs. A similar equation is used for washoff of pesticides intercepted by crop residue,

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Table 1. Default values used for washoff parameters for both plant residue and crop foliage

Pesticide solubility range	Washoff fraction F_f^{wo}, F_r^{wo}	Washoff power term P_f^{wo}, P_r^{wo}	Experimental pesticides and pesticide classes in literature (see Willis *et al*[45])
(mg liter^{-1})	(%)	(mm^{-1})	
<10	100	0.002	Pyrethroid, organochlorine
10 – <100	100	0.005	Organophosphorus
100 – <1000	100	0.013	
1000 – <10^4	100	0.033	Carbamate, organophosphorus
10^4 – <10^5	100	0.085	Organophosphorus
10^5 – 10^6	100	0.2	Organophosphorus

using subscripts r instead of f. The pesticide removed from foliage or plant residue is transferred to the top centimeter of soil where it joins pesticide already present, and may be further mobilized by leaching or runoff.

Apart from the work of Willis and coworkers, few measurements of these parameters are available; these are given in the RZWQM database. On the basis of that work, a generic set of parameters is proposed, based on the solubility of the active ingredient. In the absence of input data the values in Table 1 are default. Malone *et al*[46] calibrated these parameters for atrazine and alachlor on long-term no-till corn residue and found $P_r^{WO} = 80$ and $F_r^{WO} = 0.15$ and 0.45 for atrazine and alachlor, respectively.

4.2 Plant uptake

RZWQM at present considers only root uptake, which is a function of pesticide concentration in soil solution in the vicinity of the roots, the amount of water uptake by the roots, and the ease of transport of the solute pesticide molecule through the root cell membranes. The latter has been characterized by measuring the ratio of the concentration of the pesticide in the plant transpiration stream C_{ts} to the concentration in adjacent soil water C_w; the ratio is called the 'transpiration stream concentration factor'[47] K_{tscf}:

$$K_{tscf} = \frac{C_{ts}}{C_w} \tag{6}$$

If plants actively absorb pesticides by some physiological process K_{tscf} will be greater than unity, but most measurements[48] indicate $K_{tscf} < 1$. Briggs *et al*[49] conducted laboratory studies on uptake of 18 pesticides by roots of laboratory-germinated barley, and developed the following exponential equation relating K_{tscf} to the pesticide octanol–water partitioning coefficient (K_{ow}):

$$K_{tscf} = 0.784 \exp_{10}\left[-\frac{(\log_{10}(K_{ow}) - 1.78)^2}{2.44}\right] \tag{7}$$

K_{tscf} was <1 for all the chemicals studied.

During any time segment, plant water uptake U_w is dependent on the growth stages and phenology of the plant and environmental conditions. The amount of water uptake by plant roots from each layer in the root zone is calculated by the plant growth submodel. Pesticide uptake by the plant U_p is calculated based on the above equations and the pesticide concentration in the soil water:

$$U_p = U_w C_w K_{tscf} \tag{8}$$

4.3 Leaching within the soil root zone: convection and dispersion

The leaching model is described in a companion paper to this one[21] as well as previous reports.[46,50] Leaching has been the subject of intense theoretical and experimental investigation for the past two decades.[3–5,51–54] In RZWQM, the hydrologic model computes the mass movement of water between layers (it may be upward or downward depending on the moisture potential differences between layers), and the pesticide module computes the concentrations of pesticides that are present in the water that is moved. Pesticide in water that flows below the bottom of the soil profile is 'lost' from the system. Because the hydrology model allows for the presence of 'stagnant' water in soil micropores it includes a diffusion component (eg see Walker and Crawford,[55] and Hartley and Graham-Bryce[56]) that determines macropore/micropore redistribution of solutes. Malone *et al*[46] have investigated this component with blocks of undisturbed soil under no-till corn.

5 SOIL SORPTION

At a given time only pesticide which is in solution in 'mobile' soil water (mesopores and macropores) can be moved by water transport. Soil is a very heterogeneous (in all dimensions and at all scales) mixture of interacting inorganic and organic chemical and biological systems. A pesticide molecule in the soil/water mixture is subject to a large variety of potential transformations,[57–59] and adsorption/desorption is possible at a variety of surfaces and phases.[60,61]

Figure 2 diagrams pesticide soil sorption processes and acid/base equilibria in solution that are modeled by RZWQM. Acidic or basic pesticides may form ionic species, anions and cations, respectively. Multi-ionic species (diacids, dibases, zwitterions) are not considered. Up to a 'three-site' sorption model, consisting of instantaneous equilibrium, 'kinetic'

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(slower) sorption/desorption, and irreversible binding may be used. The chemistry of the pesticides and soil conditions will determine user inputs and which of the processes will apply.

5.1 Equilibrium sorption

In Fig 2 near-instantaneous, reversible equilibria are symbolized by double-headed arrows labeled with the equilibrium constant, capital (italic) K. Processes with rates slow enough such that equilibrium may not be established during water transport are symbolized by single-headed arrows labeled with the process rate constant, lower-case (italic) k.

To calculate that part of a pesticide which is mobile we need to calculate the concentration in the soil water. The simplest model is an instantaneous, simple soil sorption equilibrium defined by an equilibrium constant K_d.

$$K_d = \left(\frac{C_S}{C_W}\right) \tag{9}$$

When eqn (9) is combined with the mass balance equation,

$$m_p = C_s^{\Sigma} + \frac{\theta}{\rho_b} C_w^{\Sigma} \tag{10}$$

where m_p is the total mass (mg) of pesticide per gram of soil (dry weight), θ is the soil volumetric moisture content ($cm^3 cm^{-3}$) and ρ_b is the dry soil bulk density ($g\ cm^{-3}$), the solution concentration may then be calculated as

$$C_w = \frac{M_p \rho_b}{K_d \rho_b + \theta} \tag{11}$$

If an amount of soil moisture ΔW moves out of this soil layer into an adjacent layer, it transports a mass of pesticide $\Delta W \cdot C_W^{\Sigma}$ out of the layer. Equations (9)–(11) must be calculated for each layer in the soil. The terms in eqn (9) are all related by the process parameters shown in Fig 2.

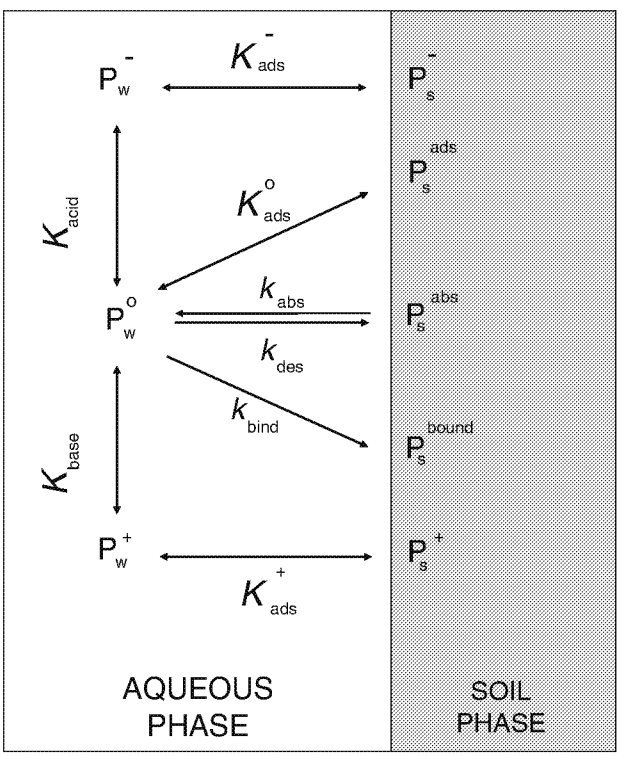

Figure 2. Acid/base equilibria and instantaneous and 'kinetic' soil sorption reactions in soil water and at the soil/water interface. P symbolizes the pesticide molecule and superscripts 0, + and − indicate neutral, cationic and anionic species, respectively. Double-headed arrows indicate near-instantaneous equilibria; paired arrows indicate slower reversible reactions. Although not shown, ionized species may also undergo fast/slow sorption steps and binding.

5.2 Acid/base equilibria and sorption

Almost a third of all pesticides are either ionic or partially ionized within the normal range of soil pH, and the resultant ionic species will absorb quite differently from the neutral forms.[62,63]

Acid and base ionic equilibrium constants can be defined in a variety of ways; in RZWQM we use the definitions[62,64]

$$K_{acid} = \frac{C_w^- \cdot C_w^{H+}}{C_w^o} \quad K_{base} = \frac{C_w^+ \cdot C_w^{OH-}}{C_w^o} = \frac{C_w^+ \cdot K_w}{C_w^o \cdot C_w^{H+}} \tag{12}$$

where C_w^o, C_w^+, C_w^- and C_w^{H+} indicate water-phase concentrations of neutral, cationic and anionic pesticide forms and hydrogen ion, respectively. $K_w = C_w^{H+} \cdot C_w^{OH-} = 10^{-14}$ is the dissociation constant for water, and C_w^{H+} is calculated as 10^{-pH}. For most ionizable pesticides, values for K_{acid} and K_{base} are in the RZWQM data base, in the form of pK_a and pK_b, the negative of the base-10 logarithms of K_{acid} and K_{base}, respectively.

Values for 'pK_a' and 'pK_b' in the literature are not always defined as in eqn (12) (for example see Weber[65] and Hartley and Graham-Bryce[56]). Thus the user who wants to input values for these parameters in RZWQM

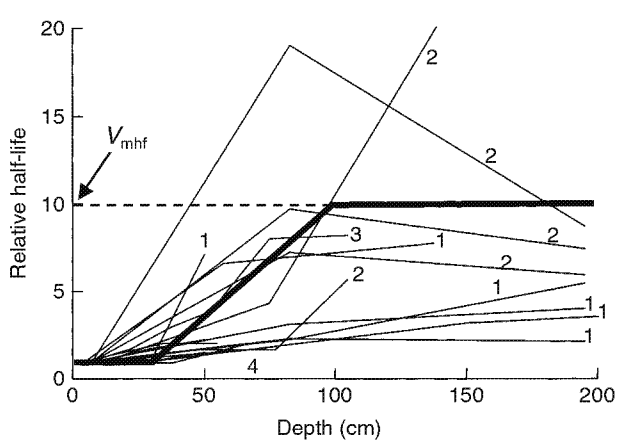

Figure 3. Half-lives of (1) alachlor, (2) atrazine (including unpublished data of Jayachandran and Moorman), (3) fluometuron and (4) chlorsulfuron, measured at different depths and divided by the half-life near the surface. The heavy line is given by eqs (28)–(30) with $V_{mhf} = 10$.

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must be certain that the definition used conforms to eqn (12).

If a pesticide exists in both ionic and neutral states in soil water, its sorption will be a result of two simultaneous sorption equilibria. K_0 as defined in eqn (9) becomes the ratio of the sum of the concentrations of the two pesticide species:

$$\text{for acids:} K_d = \frac{C_S^0 + C_S^-}{C_W^0 + C_W^-}$$

$$\text{for bases:} K_d = \frac{C_S^0 + C_S^+}{C_W^0 + C_W^+} \tag{13}$$

combining eqns (12) and (13) gives, for acids:

$$K_d = \frac{C_{ns}^{H+} K_{ads}^o + K_{ads}^- K_{acid}}{C_{ns}^{H+} + K_{acid}} \tag{14}$$

and for bases:

$$K_d = \frac{K_w K_{ads}^o + K_{base}\, C_{ns}^{H+} K_{ads}^+}{K_w + K_{base} C_{ns}^{H+}} \tag{15}$$

Since adsorption equilibria occur near the soil surface, the near-surface hydrogen ion concentration, C_{ns}^{H+} has been used in these equations in place of C_w^{H+}; this is defined, approximately, as

$$C_{ns}^{H+} = 10^{-pH+1.8} \tag{16}$$

where the 1.8 term is an approximate correction for apparent increased acidity near the soil surface due to the net negative electrostatic charge there.[66] More analysis of this 'surface acidity' phenomenon is needed. For example, the 1.8 term likely varies from soil to soil, depending on the inorganic and organic chemistry of the surface. Substituting C_{ns}^{H+} into eqn (21) and rearranging gives, for acids, an expression for the ratio of concentrations of anion and neutral species near the soil surface: $C_w^-/C_w^o = 10^{(pH-1.8-pKa)}$. Thus, when the soil pH is about four or more units above the pK_a, the pesticide near the surface is essentially all anionic and K_d will approach K_{ads}^-. If the soil pK_a is near or above the soil pH (such a pesticide will be a very weak acid) then K_d will approach K_{ads}^o. Similarly, for bases, near the soil surface, the ratio of concentrations of cation and neutral species $C_w^+/C_w^0 = 10^{(14+1.8-pH-pKb)}$. For example, if a soil has a pH of 5 then the pesticide will be essentially cationic at the soil surface if the pK_b is about 9 or less; essentially neutral if pK_b is greater than about 13.

Equations (14) and (15) require values for the adsorption constants for the individual species P^o and P^+ or P^-. The database (based primarily on the data of Hornsby *et al*[62]) has a single K_{oc} value which was taken from literature values and meant to provide only a first-approximation estimate when combined with soil organic carbon content. We make the simplifying assumption that anions and cations are, like neutral species, principally adsorbed by soil organic matter. If the pesticide is an acid or base, then the default K_{oc} is a combination of neutral and ionized species adsorption–and also a function of the pH of the 'source soil' in which K_{OC} was measured. A field for this pH has been built in the RZWQM database. However, for many pesticides a default source soil pH of 6—an appropriate value for US soils—has had to be assumed.

Based on observed K_{oc} for pesticides which are strong acids and bases, the organic carbon soil sorption coefficient for anions, K_{oc}^-, is assumed equal to 10 and the organic carbon sorption coefficient for cations, K_{oc}^+ is 10^5 (see Green and Karickhoff[63]). Given these assumptions, the overall K_{oc} for each soil layer is then calculated by calculating organic carbon sorption coefficients for the neutral species using eqns (14) or (15). The details are given in the RZWQM documentation chapter.[1] This feature of RZWQM needs a detailed evaluation; an exploratory trial is reported in Ma *et al*.[67]

5.3 Organic carbon and Freundlich sorption constants

The value of K_d for a pesticide in different soils has been observed to be approximately proportional to the amount of organic matter present in the soils.[60,68–70] Thus, once K_d is measured in a soil of known organic carbon content, one can calculate a soil organic carbon sorption coefficient K_{oc}, proposed by Goring,[71] which is approximately constant for all soils and may be used to estimate K_d in any other soil of known organic carbon content:

$$K_d = K_{oc} \cdot F_{oc} \tag{17}$$

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

Equation (17) is an approximation.[61,63] When K_d and F_{oc} are measured in a variety of soils for a pesticide, calculated K_{oc} are not constant but vary typically over a factor of two or three to 50, depending on the variety of the soils. However, this range is usually smaller than the range for K_d in the same soils. K_{oc} in soils with very low F_{oc} may show the effects of clay surfaces.[70] This effect is ignored in RZWQM, but it probably should not be (eg see Werkheiser and Anderson[72]). Clay sorption is probably less a factor in near-surface soils with 0.1% or more organic matter, but may be more important in vadose zone and aquifer soils.

In all the above a linear adsorption isotherm is assumed. For sorption data covering concentration ranges of an order of magnitude or more, the empirical Freundlich equation[60,61] is popular because it fits such sorption data well, being essentially a log/log regression equation (but see Gustafson and Holden[73] and Wauchope and Russell[74])

$$\ln(C_s) = \ln[K_{oc}^f F_{oc}] + (1/n)\ln(C_w) \tag{18}$$

where $(1/n)$ is the traditional way of symbolizing the slope. K_{oc}^f, the Freundlich organic carbon sorption constant is equal to K_{oc} if $n = 1$ (the linear case).

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When $n > 1$ (n is always >1),[54] $K_{oc}^{f} = K_{oc}$ only when $C_w = 1$. At other concentrations

$$C_s = K_{oc}^{f} F_{oc} (C_w)^{1/n}; K_d = K_{oc}^{f} F_{oc} (C_w)^{(\frac{1}{n}-1)} \quad (19)$$

Correct units are very important here. Equation (19) will be correct only if the concentration units for C_w are the same as the units which were used in the regression used to estimate K_f. If a user enters values for the Freundlich constants K_f and $1/n$ then RZWQM assumes that the reference concentration is 1 mg liter^{-1}.

5.4 'Kinetic' adsorption/desorption

It is well known[51,61] that pesticide soil sorption may be reversible or irreversible and have rapid and slow stages. Ionic and neutral solutes are sorbed by soil organic matter and exhibit similar kinetics.[75] To allow for nonequilibrium effects, RZWQM uses a modification of the three-site model proposed by Boesten and others[51,76–78] in which a pesticide simultaneously undergoes (a) an essentially instantaneous reversible sorption (complete in seconds) onto 'class 1' soil sites; (b) a slower reversible sorption (complete in hours or days) onto 'class 2' soil sites, and (c) a still slower irreversible 'binding' process onto 'class 3' soil sites, which takes weeks to months. RZWQM assumes bound residues become a permanent, and biologically insignificant, component of the soil.

Allowing for a slower-than-instantaneous adsorption/desorption of part of the pesticide provides the potential for simulating many laboratory and field observations, including the slowness of desorption relative to adsorption,[78] some aspects of soil adsorption hysteresis,[79–81] column sorption kinetics,[82] and the often-observed retention of a band of pesticide near the soil surface at the same time that the classic chromatographic 'wave' of chemical leaching occurs.[83–86] The reversible, 'kinetic' process shown in Fig 3 may be represented by the first-order kinetic equation

$$\frac{dC_s^{abs}}{dt} = k_{abs} C_w - k_{des} C_s^{abs} \quad (20)$$

where C_s^{abs} is the concentration of pesticide in 'class 2' sites; we have left the charge superscript off C_w to indicate that it may be an ionic species that exhibits 'kinetic' behavior—Fig 2 shows the neutral species undergoing kinetic behavior, but pesticides which are predominantly ionic may also show fast/slow sorption. If neutral and ionic species are both present they are assumed to obey the same kinetics.

The typical K_d value reported for a pesticide is obtained in a 'batch' mixing experiment[87,88] in which pesticide is equilibrated between soil and water phases for several hours to a day of mixing. Following Boesten *et al*[51] we will assume that this period is long enough for the K_d measured to be simply a combination of the fast and slow reversible steps in Fig 2, but before irreversible binding has become significant. At such a quasi-equilibrium

$$\frac{C_s^{abs}(eq)}{C_w(eq)} = \frac{k_{abs}}{k_{des}} \quad K_d = \frac{C_s^{ads}(eq) + C_s^{abs}(eq)}{C_w(eq)} = K_{ads} + \frac{k_{abs}}{k_{des}} \quad (21)$$

where K_{ads} is the equilibrium for 'class 1' sites and $C_s^{ads}(eq)$ is the concentration of pesticide in class 2 sites at equilibrium. This model is invoked if the user supplies values for the soil sorption rate constant 'RK2' pesticides in class 2 sites and the fraction of kinetic (class 2) sites. This model has been shown to reasonably simulate some complex field data.[21,50,54]

5.5 Irreversible binding to soil

Formation of 'bound' or 'aged' residues of pesticide is described by a first-order kinetic formation constant K_{bind},

$$\frac{dC_s^{bound}}{dt} = k_{bind} C_w = \frac{\ln 2}{H_{bind}} C_w \quad (22)$$

where k_{bind} is the rate constant for irreversible binding, calculated from a half-life for binding H_{bind} if input by the user. It is calculated using a daily time step. This process has not yet been evaluated against laboratory or field data. If neutral and ionized pesticide species are both present in the soil, the binding rate constant applies to both.

6 PROCESSES WITHIN COMPARTMENTS: DISSIPATION, DEGRADATION AND TRANSFORMATION

6.1 Dissipation, degradation and transformation

Degradation, dissipation and transformation processes in the various compartments are listed in Table 2. Subscripts indicate the compartment: f = crop foliage, r = crop residue. Soil layers are $s1$ for the surface and $s(n)$ for subsurface layers.

We define dissipation to mean loss of a pesticide from the system by transport processes (see also Laskowski *et al*[89]). Volatilization, runoff, leaching below the bottom of the soil system, and uptake by plant foliage or roots are dissipation processes. Foliar washoff, and leaching downward or wicking upward within the soil profile are not dissipation processes, since the pesticide remains in the system. Transformation is any chemical change in the pesticide which results in the formation of another molecular species whose fate we will simultaneously simulate—a 'daughter' or 'granddaughter' species. Any of the degradation processes in Table 2 may be specified as a transformation process generating a daughter or a granddaughter product in the same compartment.

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Table 2. Pesticide parameters describing dissipation, degradation and transformation processes in RZWQM compartments, and the default and user options for parameters value selection. The 'code' in column 2 is used to select the process as a transformation process for production of daughter or granddaughter products — see text

Compartment	Code	Process	Parameters	Notes
Crop foliage	1	'Lumped' foliar dissipation/degradation	Rate constant k_f	Default k_f calculated from half-life H_f in database, or user-input half-life
	2	Photodegradation	Rate constant k_f^p	Calculated from user input of half-life H_f^p; default $k_f^p = 0$
	3	User-defined	Rate constant k_f^u	Calculated from user input of half-life H_f^a — use for hydrolysis, oxidation or other user-defined process; Default $k_f^{ab} = 0$
Plant residue	4	'Lumped' dissipation/degradation	Rate constant k_r	Default $k_r = 0$ (user may desire to set equal to foliar k_f)
	5	Photodegradation	Rate constant k_r^p	Default $k_r^p = 0$
	6	User-defined	Rate constant k_r^u	Default $k_r^u = 0$ (use for 'user-defined' process)
Top cm of soil	—	Runoff	Sorption constant K_d; Mixing exponential b	K_d calc from equation 6.14; default $b = 0.8$ (Ahuja[127])
	7	Aerobic biodegradation	Rate constant k_{s1}^{ae}	Default half-life H_{s1}^a is field value from database, or user input; varies with T, soil moisture, depth (dependence adjustable) — same as *sn* value
	—	Volatilization	Rate constant k_{s1}^v Henry's law constant K_{hl}, K_{oc}	Equation 6.53 or user input of half-life H_{s1}^v
	8	Photodegradation	Rate constant k_{s1}^p	Default $k_{s1}^p = 0$ or user input
	9	User-defined	Rate constant k_{s1}^u	Default $k_{s1}^u = 0$, or user input — same as *sn* value
Soil layer ***n***	10	Aerobic biodegradation	Rate constant k_{sn}^{ae}	Default half-life H_{s1}^a is field value from database, or user input; varies with depth, T, soil moisture (dependence adjustable)
	11	Anaerobic biodegradation	Rate constant k_{sn}^{an}	User input; activated by near-saturation soil moisture
	12	User-defined	Rate constant k_{sn}^u	User input; invariant with depth
	—	Soil binding	Rate constant k_{bind}	User input: invariant with depth

6.2 Persistence and the pseudo-first-order model

The RZWQM database provides 'lumped' half-lives for pesticides in the foliage and soil compartments, assuming that pesticide concentrations decrease exponentially in time. The exponential-decay model has a justification in the classical chemical kinetic theory[90] of pseudo-first-order reactions. However, In a given compartment several reactions typically occur simultaneously. Expressing the overall instantaneous degradation rate as dC_i/dt then the first-order model is (we use superscripts to signify processes and reserve subscripts for compartments)

$$\frac{dC_i}{dt} = -k_i^{a}C_i - k_i^{b}C_i - \cdots = -\left(\sum_j k_i^j\right) C_i \quad (23)$$

where C_i is the concentration and k_i^j are reaction rate constants for the processes which are occurring. Integrating between limits $t = 0$ and t, or between two times t_1 and t_2 gives[90]

$$\frac{C(t_2)}{C(t_1)} = e^{-(\Sigma k)(t_2 - t_1)} \quad \text{or} \quad \frac{C(t)}{C(t=0)} = e^{(\Sigma k)t} \quad (24)$$

respectively. The relationship to half-life is simple: if $C(t)/C(t=0) = 1/2$ or $C(t_2)/Ct_1 = 1/2$, then $e^{-\Sigma kt}$ or $e^{-\Sigma k(t_2 - t_1)} = 2$ and the 'lumped' half-life H_i^{Σ} resulting from combined first-order processes is

$$H_i^j = \frac{\ln 2}{k_i^j} \quad H_i^{\Sigma} = \ln \frac{2}{\sum_j k_i^j} = \frac{1}{\sum_j \left(\frac{1}{H_i^j}\right)} \quad (25)$$

where we use subscripts to indicate compartments and superscripts to indicate processes.

Many controlled laboratory studies such as 'aerobic soil flask' degradation rate experiments, and even some field experiments, obey, approximately, the first-order model.[17] In general, however, field experiments appear to indicate not a constant but an increasing 'half-life' with time.[91] The explanation for this is that pesticides in the field are not exposed to homogeneous conditions. There are three (at least) observable dissipation/degradation stages when a pesticide is applied in the field:[56,59,91–95] (a) losses due to initial rapid volatilization immediately after spraying/deposition (b) slower degradation/dissipation

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processes of exposed deposits on soil/plant surfaces such as photodecomposition, absorption and leaching; (c) still slower losses of residues in the soil interior, mediated by sorption and protection from light and air movement. A typical field dissipation experiment may only measure the second and third processes, because the first may be essentially complete before the first, 'time zero' sampling. This has led to a variety of more complex models for degradation.[56,73,92,96] Chapman[97] showed that five different models are distinguishable among the nine equations that have been used to fit persistence data, and that, given the scatter in field studies, no more than a two-parameter model is statistically justified in most cases.

Earlier versions of RZWQM allowed for a two-parameter model,[96] and the model was often a better description of field data than simple first-order decay.[98] However, many, if not most, of the processes that cause deviations from pseudo-first-order behavior are already accounted for in the RZWQM model—volatilization, photolysis, etc. While all possible processes are not known or accounted for, most known processes are. Thus, the use of an (empirical) two-parameter degradation model would appear to amount to double-accounting for the fast dissipation/degradation processes. Experience in use will determine whether this is so.

If a user wishes to input a field half-life value for a pesticide, it should probably be entered as the soil aerobic half-life. This value should also be approximately equal to that obtained by an 'aerobic soil flask' degradation rate measurement.[99] This procedure appears to be the best we can do with typical field persistence data, but a conventional procedure for doing this is needed.[100]

6.3 Dissipation/degradation on crop foliage

Pesticides deposited on crop foliage are exposed to direct sunlight, wind and rain. As a result, foliar residues generally have much shorter persistence than residues in the soil. Willis and McDowell.[26] have reviewed the literature on pesticide persistence on foliage. Most pesticides have half-lives on the order of a few days. Even DDT, an exceptionally persistent pesticide in the soil (typical half-life of 5 years[62]) has a foliar half-life of days to weeks.[26] Willis and McDowell indicated trends of greater persistence in cooler latitudes, and greater persistence of organochlorine and pyrethroid pesticides than other classes. The data are confounded by formulation, weather (especially rainfall), and uncertainties in the time elapsed between application and first sampling, when losses are most rapid. Many of these studies have been of 'dislodgable residues' (eg Ware *et al*[101]) and it is not always known what fraction of the total residue is being measured.

No provision is made for foliar uptake of pesticides except as a user-defined process. This is a high priority need for a future version of the model.

Default foliar half-lives in the database are obtained from the literature or, if values are not available, the following default values are used: 3 days for pesticides with vapor pressure >0; 7 days for pesticides with zero vapor pressure. These values are not likely to be in error more than a factor of three,[1] and will be at least a first-approximation improvement over assuming nothing about foliar degradation. There is no provision for the effects of temperature, humidity, solar radiation or other environmental variables on foliar half-life, except to allow for additional user-input half-lives. Such dependencies are likely, but there is little data. These effects should be considered in a future version of RZWQM. Also we recognize that there are probably no pesticides for which all or even two of these half-lives have been separated out experimentally. However, the structure of equation 25 at least provides the user with a way of classifying and ordering data, and points the way to some needed research.

6.4 Dissipation/degradation on plant residue

The default value for all rate constants on residue is zero. Although it might be reasonable to set pesticide half-lives in crop residue equal to those in foliage, and the user can do so, knowledge of the persistence of pesticides in plant residue is sparse, and the environmental conditions of such residues are likely to be milder than those for crop foliage: wind, temperature, and sunlight may all be less severe. A study by Baker *et al*[102] indicated that three herbicides appeared to have about the same short-term persistence on crop residue as when they were applied under the residues on the soil surface—which was shaded and protected from wind by the residues. For these reasons it seemed prudent not to assume anything about the fate of these residues, and the user will have to decide if it is likely that these residues exhibit breakdown. As with foliar half-life, there is no provision for the effect of variation in environmental variables, eg temperature, on the rates of processes in this compartment.

6.5 Degradation/dissipation in subsurface soil

When a pesticide reaches the root zone, either by incorporation or leaching, its typically longer persistence there generally determines its potential for future pollution.[103–105] There is considerable variability in soil half-lives. Racke *et al*[106,107] and Laskowski *et al*[93] indicate that half-lives can vary 10× to 80× in different soils even at the same moisture and temperature. This variation in half-life at depth is attributed to variability in soil microbial populations and their activity, which are in turn influenced by availability of organic substrates (quantity and quality), porosity and microaggregation, and the biodegradation process of the chemical itself (see Moorman[108]).

The RZWQM database contains a default soil half-life for each pesticide. Most of the half-life values are taken from Hornsby *et al*[62] and are based on field measurements: thus they are 'lumped' values. In the

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absence of input of more specific process information, and because aerobic microbial degradation is usually the most important degradative process in the field, the RZWQM database values are assumed to describe aerobic microbial degradation near the soil surface, at 25 °C and at field capacity. These values are used for aerobic degradation half-lives, $H_{\mathrm{ref}}^{\mathrm{ae}}$ for all soil layers. These assumptions may sensitively effect predictions and need to be validated.

6.5.1 *Temperature adjustment*

To adjust the reference half-life the recommendations of the FOCUS group[18] are adopted. The classical Arrhenius equation is used[109]

$$H_{sn}^{\mathrm{ae}} = H_{\mathrm{ref}}^{\mathrm{ae}} \exp_{\mathrm{e}}\left[\left(\frac{E_{\mathrm{a}}^{\mathrm{ae}}}{R}\right)\left(\frac{1}{T_{\mathrm{K}}} - \frac{1}{T_{\mathrm{K}}^{\mathrm{ref}}}\right)\right] \tag{26}$$

where $T_{\mathrm{K}}^{\mathrm{ref}}$ is assumed to be 298 K and T_{K} is the temperature (K) of the soil layer. $E_{\mathrm{a}}^{\mathrm{ae}}$ is the activation energy (kJ mol^{-1}) for aerobic degradation and R is the gas constant (8.314 J mol^{-1}K^{-1}). Walker *et al*[109] reviewed 148 determinations of activation energy for pesticide degradation in soils and reported an average E_{a} of 54 kJ mol^{-1}, with a range from 10 to 90 kJ mol^{-1} with a few outliers. They suggested that this average is a reasonable first approximation for temperature correction and it is the default value used in RZWQM. A limiting condition is also specified that when T_{k} is 273 K or less, $k_{\mathrm{sn}}^{\mathrm{ae}} = 0$, ie microbial degradation ceases when the soil layer freezes.

6.5.2 *Soil moisture adjustment*

To adjust the reference half-life for soil moisture the empirical equation of Walker[95,110,111] is used:

$$H_{sn}^{\mathrm{ae}} = H_{\mathrm{ref}}^{\mathrm{ae}}\left(\frac{\theta_{sn}}{\theta_{\mathrm{ref}}}\right)^{-\mathrm{B}} \tag{27}$$

where θ_{ref} is the reference moisture content, assumed to be field capacity for the half-lives in the database, and B is a constant. The FOCUS report,[18] citing the Doctoral thesis of B Gottesbüren, states that

"... Variation in measurements of B for individual pesticides are as great as variations between pesticides, indicating that little information would be added by measuring B values as opposed to estimating them..."

and recommended a value of 0.8; this is the default value used in RZWQM.

6.5.3 *Depth adjustment*

Degradation rates generally decline with depth for pesticides which are degraded primarily by biological processes. In agricultural soils this is primarily due to a decrease in the population, and reduced activity of the population, of those microbial organisms which are capable of degrading pesticides. For instance, Mueller *et al*[112] showed that microbial biomass declined in the top metre of a Dundee silt loam and the subsurface biomass was 70% less efficient than surface biomass in degrading fluometuron. Generally half-lives below 10 cm depth are 2 to 10 times greater than those near the surface.

In Fig 3 half-life data for atrazine,[113,114] alachlor,[113,115,116] fluometuron,[112] metribuzin[117,118] and chlorsulfuron[119] are plotted as a function of depth. Pesticides which are degraded by abiotic mechanisms, such as aldicarb, may not follow this pattern. Note that most of these data are from laboratory studies, in which soils from various depths were spiked with the pesticides at the same temperature and moisture content. Thus they do not double-account for the effects of temperature and moisture changes with depth. Fewer data are available for depths greater than 200 cm, and existing data do not allow generalizations for degradation rates across chemical classes and geologic settings. There are indications that half-lives of chemicals do not increase as rapidly with depth as they do nearer the surface as depicted in Fig 3, but reach some minimal level in the unsaturated vadose zone and may even increase in the aerobic groundwater near the surface.

RZWQM tracks detailed oxygen status, temperature, soil organic matter moisture, nutrient status, inorganic chemistry, pH and microbial activity in each soil layer. Thus it should be possible to develop a persistence model which relates to these variables. Unfortunately, the relationships are not well understood.[120] This is clearly a priority research need, but also an exceedingly difficult problem. It seems prudent at this time not to attempt to propose some complex empirical relationships. For this release, based on the data in Fig 3, the reference aerobic degradation half-life $H_{\mathrm{ref}}^{\mathrm{ae}}$ is assumed to hold from 0 to 25 cm depth; then a linear increase in half-life with depth occurs from 25 to 75 cm, after which the value at 100 cm is held constant for all deeper depths. These assumptions are likely to sensitively effect predictions and need to be validated.

There is considerable variation in Fig 3, but much of it appears to be due to variance in the *slope* of the half-life change from the neighborhood of 25 cm to 100 cm. Thus, we give the user the option of varying the maximum half-life factor, V_{mhf}, the maximum multiple of the near-surface half-life that the half-life reaches at 100 cm. Thus, half-life for each layer is calculated as a function of layer depth z_n as follows:

$$H_{sn}^{\mathrm{ae}} = H_{\mathrm{ref}}^{\mathrm{ae}} \quad z_n \le 25 \tag{28}$$

V_{mhf} is given a default value of 10, and the resulting depth function is shown in Fig 3.

$$H_{sn}^{\mathrm{ae}} = \left[1 + \left(\frac{V_{\mathrm{mhf}}}{75}\right)(z_n - 25)\right] H_{\mathrm{ref}}^{\mathrm{ae}} \qquad 25 \le z_n \le 100 \tag{29}$$

$$H_{sn}^{\mathrm{ae}} = V_{\mathrm{mhf}} H_{\mathrm{ref}}^{\mathrm{ae}} \qquad z_n \ge 100 \tag{30}$$

6.5.4 *Adjusting the aerobic model*

If the user has knowledge of the specific behavior of a pesticide in a given soil, eg from flask experiments,

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substitute values for the reference half-life, reference temperature and moisture content, activation energy, the maximum half-life depth factor in eqn (43), and the moisture adjustment exponent B in eqn (41) may be input. Setting V_{mhf} to zero, for instance, could be done in order to give a uniform half-life at all depths. Certainly, given the variability of half-life across soils, a specific reference half-life at a known temperature and soil moisture for a given soil/pesticide/site combination will greatly improve simulation performance for that scenario. Modifications of the default adjustments for temperature, depth and moisture are perhaps less significant: the defaults should provide reasonable first-approximation dependencies.

6.5.5 *Anaerobic degradation*

RZWQM allows the user to specify an anaerobic degradation half life H_{sn}^{an} which, if supplied, substitutes for the aerobic process under saturated conditions: the fraction of water-filled pore space (degree of saturation) is defined as

$$F_{\mathrm{wfps}} = \frac{\theta}{S} = \frac{\theta}{1 - (\rho_{\mathrm{b},sn}/\rho_{\mathrm{p}})} \tag{31}$$

where θ is the volumetric water content ($\mathrm{cm^3 cm^{-3}}$), S is the total volumetric porosity of the soil ($\mathrm{cm^3 cm^{-3}}$) and $\rho_{\mathrm{b},sn}$ and ρ_{p} are the soil bulk density and soil particle bulk density, all referring to soil layer n. Three conditions are invoked if the user specifies an anaerobic degradation half-life:

(1) If $z_n < 50\,\mathrm{cm}$, $k_{sn} = k_{sn}^{\mathrm{an}}$ where $k_{sn}^{\mathrm{an}} = \ln 2/H_{sn}^{\mathrm{an}}$ when F_{wfps} exceeds 90% for more than 3 days,
(2) If $z_n \geq 50\,\mathrm{cm}$, $k_{sn} = k_{sn}^{\mathrm{an}}$ when the $F_{\mathrm{wfps}} = 100\%$ for more than 6 days,
(3) At all depths, whenever F_{wfps} exceeds 60% the *aerobic* degradation rate constant is reduced by the empirical relationship[121]

$$k_{sn}^{\mathrm{ae}} = k_{\mathrm{ref}}^{\mathrm{ae}}(2.5)(1 - F_{\mathrm{wfps}}) \quad F_{\mathrm{wfps}} \geq 0.6 \tag{32}$$

The 3- and 6-day periods represent acclimation periods during which oxygen is consumed, nitrate is reduced (denitrified), and anaerobic processes begin. This corresponds to the lag period in pesticide degradation observed during the onset of anaerobic conditions.[122]

6.5.6 *Temperature adjustment*

The anaerobic half-life is adjusted for temperature using the same equation as for aerobic half-life, using an energy of activation for aerobic degradation $E_{\mathrm{a}}^{\mathrm{an}}$. It seems reasonable that general temperature effects on both populations of microbes would be approximately the same, so the same default activation energy is used for anaerobic degradation as for aerobic. The user may adjust $E_{\mathrm{a}}^{\mathrm{an}}$ if desired.

6.6 Degradation dissipation in surface soil

The soil at the interface with the atmosphere can undergo extremes of temperature and moisture because of its exposure to sun, wind and weather. The processes considered in the top cm of soil are listed in Table 2.

6.6.1 *Runoff*

Runoff is modeled in a way similar to other models by assuming that pesticides on or in a thin layer (a few mm to 1 or 2 cm) of soil at the surface are entrained in runoff water by the mixing of surface soil through raindrop impact.[4,10,123–126] The depth of this 'effective zone of interaction' has been measured to be a few millimeters but some interaction can extend as deep as 2 cm.[126] In such models the approach has been to use the pesticide soil sorption coefficient K_{d} (eqn (9)) as a measure of the proportionality between soil concentration and runoff concentration. However, for moderately and weakly adsorbed pesticides (ie pesticides which are mainly in the water phase of runoff), runoff concentrations are always only a small fraction of what eqn (14) would predict, even when simultaneous leaching of the pesticide out of the zone of interaction is accounted for. In fact, runoff concentrations are sensitive to rainfall intensity, age of residues, formulation, adsorption by soil clods and many other factors.[4,43]

RZWQM uses a simple version of the nonuniform mixing model of Ahuja[127] and of Heathman *et al.*[128] Starting at the time of runoff initiation, rainwater and surface soil undergo non-uniform but equilibrium mixing over small time steps within 1-mm depth increments in the top 2 cm of soil. The results are numerically integrated over this depth to obtain chemical transfer to runoff. Unlike the other dissipation processes in RZWQM which are calculated on a daily basis, and unlike previous runoff models, runoff is calculated in real time as hydrologic events occur. The degree of mixing β_{i} in each of the 1-mm layers is assumed to decrease exponentially with the depth of the layer below the surface:

$$\beta_i = \mathrm{e}^{-bz_i} \tag{33}$$

where z_i is the depth of layer i. The parameter b is sensitive to soil type, surface aggregation and other conditions[129] but values ranging from 0.6 to 1.3 fit rainfall simulator data.

Runoff concentrations are calculated as follows: if R is the rain intensity ($\mathrm{mm\,h^{-1}}$), when an increment of rainfall Rt occurs, each soil layer undergoes a solution concentration change due to the addition of the fraction of the rainfall $\beta_{\mathrm{i}} \cdot R\Delta t$. This change may be calculated from the mass balance expressions before (time t) and after (time $t + \Delta t$) the water addition:

$$C_{wi}(t)[M_{wi} + K_{\mathrm{d}}F_{\mathrm{ad}}M_{si}] = C_{wi}(t + \Delta t) \times [M_{wi} + \beta_i R\Delta t + K_{\mathrm{d}}F_{\mathrm{ad}}M_{si}] \tag{34}$$

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where M_{si} and M_{wi} are masses per unit area of soil and water in layer i. The concentration of pesticide in the runoff water is the average of the final concentrations in all layers weighted by the mixing fraction β_i:

$$C_{ro}(t+\Delta t) = \frac{\sum_{i=1}^{20} \beta_i C_{wi}(t+\Delta t) R\Delta t}{R\Delta t} = \sum_{i=1}^{20} \beta_i C_{wi}(t+\Delta t) \quad (35)$$

This model has been shown to calculate runoff concentrations accurately as a function of time during events.[127–129]

RZWQM uses equations similar to eqns (33)–(35) but applies an average degree of mixing to the top 1-cm layer, yielding an expression in the same functional form as eqn (33):

$$\beta_i^{av} = e^{-Bz_i} \quad (36)$$

where B is a new constant and z_i is the midpoint of the 1-cm depth increments. If b (eqn 33) is assumed equal to 1.0 the value of B is calculated to be 4.4 in both layers. This value is the default value in RZWQM.

6.6.2 *Volatilization*

In the presence of moisture at the soil surface, the driving mechanism for pesticide volatilization is volatilization from the soil moisture (since all but the driest soil will have a film of moisture present). This volatilization will depend on the rate of transport of pesticide to the soil surface (by diffusion or water transport), by the volatilization resistence of the overlying stagnant air layer, and by the soil/water/air pesticide concentration ratios which may be described using the Henry's law and soil sorption constants. Nash[130] (see also Laskowski *et al*[17]) developed a simple empirical equation for volatilization from moist soil surfaces:

$$k_{sl}^{v} = 3.07\left[\frac{K_{hl}}{K_{oc}(M^{mol})^{0.5}}\right]^{0.453} \quad (37)$$

where k_{s1}^{v} is the rate constant for volatilization K_{hl}, K_{oc} and M^{mol} are the pesticide's Henry's law constant, soil organic carbon sorption coefficient and molecular mass, respectively. Although developed for relatively volatile pesticides, it has been shown to work well with pesticides of lower volatility.[132] In the absence of user input, RZWQM will use eqn (37) plus aerobic degradation to calculate dissipation from the soil surface. No corrections to eqn (37) for temperature or moisture are made though, this would be desirable. This is a first-approximation designed to keep the user from neglecting this important loss pathway. This model has not been tested.

Values for the Henry's law constant in the database are all calculated[17,133] using the ratio of the vapor pressure and solubility values in the database, which are at (or near) 25 °C:

$$K_{hl}^{25} = \frac{0.0538 P_v M^{mol}}{S_w} \quad (38)$$

where P_v = pesticide vapor pressure (mm Hg) at 25 °C, M^{mol} = pesticide molecular mass (g mol^{-1}), and S_w = pesticide aqueous solubility (mg liter^{-1}) at 25 °C, and the 0.0538 constant converts P_v into air concentration units mg liter^{-1} (or g m^{-3}) at 25 °C. There are very few experimental measurements of K_{hl} for pesticides.[134,135] Fortunately eqn (38) is quite accurate for nonionic compounds with solubilities of a few g liter^{-1} or less.[136,137]

7 CONCLUSION AND RESEARCH NEEDS

In Table 3 all pesticide parameters are listed which are either input by the user or supplied by the model, or both. Except for the 'molecular' parameters, the parameters listed depend on the soil, weather and crop system in which the pesticide is used. Thus, the default values supplied by the database are unlikely to be accurate for any specific situation. The database will at least provide a parameter value which will be reasonable. Such values may be useful for general comparisons and environmental impact indexing.[61,138,139]

It seems likely that if RZWQM is ever to be used by a wider community of users it will have to be packaged with complete sets of data that provide a realistic working 'scenario' for some important (or interesting) combination of crops, soils, and weather. Putting together such a scenario requires a team of scientists with a wide range of expertise in hydrology, soil and plant science, but the resulting knowledge/prediction package will have significant potential usefulness for analyzing almost every aspect of crop production and its impact on the environment. RZWQM is one of the most comprehensive descriptions of pesticide fate and behavior in agricultural environments ever attempted. Thus it is also one of the most complicated, and it is still in the process of being both tested for code correctness and verified for predictions vs field observations. We invite the exploration of the features of this model: it may be downloaded from the URL: http://arsagsoftware.ars.usda.gov/. We welcome input—almost anyone who begins working with RZWQM to analyze their own field data will immediately discover ways in which it can be improved (not to mention debugged). Foliar washoff, chemigation, formulation effects, injection, the Freundlich isotherm, sorption of ionized species, volatilization and the aging of soil residues all need further exploration and validation. Since these are all important aspects of pesticide risk assessment, and may each impact exposure assessment dramatically, there is much work left to be done.

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Table 3. Pesticide parameters used by the model. Most may be replaced or adjusted by the user. Not all are required to run the model. Parameters which are in the current RZWQM database are indicated by bold face. All half-lives are in days

IDENTITY	CROP RESIDUE DEPOSIT PARAMETERS[c]
Name	Half-life (day)
Ancestry code	Washoff fraction (%)
Transformation process code	Washoff power term (mm^{-1})
Formation yield fraction	Photodegradation half-life (day)
	Abiotic or user-defined half-life (day)
MOLECULAR PARAMETERS	SOIL 'SURFACE' PARAMETERS
Molecular mass ($g\,mol^{-1}$)	Runoff mixing constant
Agueous solubility ($mg\,liter^{-1}$)	Volatilization half-life (day)
Aqueous diffusion coefficient (cm^2h^{-1})	Photodegradation half-life (day)
Vapor pressure (mm Hg)[a]	
Henry's law constant	
Octanol/water partition coefficient	SOIL MATRIX PARAMETERS[d]
Acid dissociation constant[a] ($mg\,liter^{-1}$)[b]	**Soil OC sorption constant**, (K_{oc}, $ml\,g^{-1}$)
Base dissociation constant[b] ($mg\,liter^{-1}$)[b]	**pH of source soil for K_{oc}** ($ml\,g^{-1}$)
	Freundlich soil K_{oc}($ml\,g^{-1}$)
APPLICATION PARAMETERS	Freundlich isotherm exponent
Application method	Anionic species K_{oc}($ml\,g^{-1}$)
Application rate ($kg\,ha^{-1}$)	Cationic species K_{oc}($ml\,g^{-1}$)
Application deposition efficiency (%)	Soil desorption half-life (day)
Controlled-release rate (day^{-1})	Soil binding half-life (day)
	Aerobic biodegradation half-life (H^{ae}, day)
FOLIAR DEPOSIT PARAMETERS	Reference moisture content for H^{ae} (v/v)
Half-life (day)	Reference temperature for H^{ae}(°C)
Washoff fraction (%)	Activation energy for H^{ae}($kJ\,mol^{-1}$ °C)
Washoff power term (mm^{-1})	Walker soil moisture constant
Photodegradation half-life (day)	Maximum H^{ae} change *w*/depth (factor)
Abiotic or user-defined half-life (day)	Anaerobic biodegradation half-life (H^{an}, day)
	Activation energy for H^{an}($kJ\,mol^{-1}$ °C)
	Abiotic or used-defined half-life (day)

[a] Calculated (eqn 38).
[b] Value given in database only if applicable.
[c] Few data available; typically user sets equal to foliar values.
[d] All soil matrix parameters except anaerobic half-life also apply to soil surface layer.

It is likely that RZWQM will continue to receive some degree of user support from ARS for the near future.[140] It has been selected as a test case for 'modularization' as part of the ARS Object Modeling System and it is currently being deconstructed into independent modules. This suggests that each module of the model, including the pesticide module, will acquire a life of its own. If past history is any guide, even as complicated a program as the RZWQM pesticide module may eventually become a useful and routine decision-support tool.

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