

MODELING PESTICIDE FATE AND NONIDEAL TRANSPORT FROM SEEDS TREATED WITH A SLOW-RELEASE PESTICIDE IN A LABORATORY SOIL COLUMN

G. J. Sabbagh, G. A. Fox, L. Ma, R. W. Malone, E. L. Arthur, D. G. Dyer

ABSTRACT. *This research evaluated the predictive ability of a pesticide fate and transport model to simulate the potential for pesticide leaching from slow-release insecticide-treated corn seeds. No studies in the literature report model evaluation for pesticide-treated seeds. The column studies consisted of ten 60 cm soil columns of silt loam soil, each planted with one corn seed treated with the active ingredient of an experimental pesticide. The columns were modeled using the Root Zone Water Quality Model (RZWQM), which is capable of simulating slow-release, instantaneous equilibrium (IE) and equilibrium kinetic (EK) sorption, and irreversible binding. The model was calibrated for hydrology (i.e., leachate from the bottom of the soil columns), crop growth, and total pesticide in the soil profile. Measured concentrations were compared to model predictions for IE and EK sorption scenarios across a range of sorption parameters derived from batch and time-dependent sorption studies. Modeling scenarios failed to predict the observed pesticide confinement (70% of applied pesticide) to primarily the upper 15 cm of the soil profile, with 1% to 20% of applied in the upper 15 cm for IE sorption and 3% to 18% of applied for EK sorption at the end of the simulation period. Both IE and EK sorption scenarios failed to predict pesticide in leachate (observed cumulative of 0.12% of applied) unless using minimum IE and EK sorption parameters. Model deviations from observations were hypothesized to be due to the model representing a theoretical two-dimensional process in one-dimension and the potential for preferential flow paths formed by root formation. Long-term (i.e., 20-year) simulations suggested that significant differences (i.e., average of 8% compared to less than 1% cumulative leaching) arise between IE and EK sorption after several plantings of the pesticide-treated seed. The error in assuming IE sorption for an EK sorption process is negligible over the short term but increases with subsequent chemical applications over the long term.*

Keywords. *Kinetic sorption, Leaching, Pesticide-treated seed, Root Zone Water Quality Model, RZWQM, Seed treatment.*

Numerous one-dimensional models are currently being evaluated for use in screening pesticide applications for environmental exposure assessments in groundwater (Fox et al., 2006; EMWG, 2004, 2005). These models include simple “tipping bucket” hydrology models, such as Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) and Pesticide Root Zone Model (PRZM), and more complex models based on solution of Richard’s equation for vadose zone flow,

such as the Root Zone Water Quality Model (RZWQM) and Leaching Estimation and Chemistry Model-Pesticide (LEACHP). Each model possesses different levels of sophistication in regard to hydrology, crop growth, agricultural management practices, and pesticide fate and transport. Research has reported successful application of all of these models for predicting surface broadcast or incorporated broadcast pesticides. However, none of these models has been evaluated regarding the fate and transport of pesticide from pesticide-treated seeds. This research aims to identify research gaps in current models in regard to seed treatment, pesticide slow-release from seeds, and plant uptake of pesticides. Identifying such gaps has been suggested as the main benefit of natural resource models (Oreskes et al., 1994).

Pesticide-treated seeds are increasingly being formulated as a chemical application method for reducing environmental exposure (Agarwal and Sinclair, 1997; Maloy, 1993; Dawson, 1987; Bateman et al., 1986), but early studies only considered atmospheric movement, personal exposure during handling, or dissipation in the soil profile (Börjesson et al., 2003; Waite et al., 2001; Gray et al., 1983). Poag et al. (2005) recently demonstrated the economic feasibility of fungicide seed treatment, suggesting that the insignificant input for seed treatment results in significant enhanced profitability. Even the expected small concentrations of pesticide leaching to groundwater from seed treatment may negatively impact water quality. Maximum concentration limits for many pesticides are on the order of magnitude of $\mu\text{g L}^{-1}$ or part per bil-

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lion (ppb) concentrations. Therefore, the ability to predict low concentrations of pesticides leaching to groundwater is important over both short-term and long-term temporal scales. Can a one-dimensional model that assumes a uniform pesticide application over a cross-sectional area adequately simulate the fate and transport of pesticide from a pesticide-treated seed?

Many of the pesticides being used for seed treatment exhibit time-dependent sorption (Börjesson et al., 2003). According to Brusseau (1998), the importance of nonlinear sorption is dependent on the degree of spreading, and rate-limited sorption is dependent on the magnitude of characteristic reaction time to contaminant residence time. For a slow-release pesticide-treated seed, the degree of pesticide spreading may be inhibited by localized release. Furthermore, it is difficult to assess the time-dependent relationship between characteristic reaction time to contaminant residence time for such pesticides.

By using data from a uniformly packed, greenhouse soil column, the research presented in this article was able to separate nonequilibrium or nonideal transport due to nonlinear and rate-limited sorption from physical nonequilibrium and field-scale heterogeneity (Ma and Selim, 2005; Ma et al., 2004a; Ma et al., 2004b; Saffih-Hdadi et al., 2003; Guo et al., 1999; Brusseau, 1994, 1998; Brusseau et al., 1997; Brusseau and Rao, 1989; Crittenden et al., 1986). This information will assist in identifying the most suitable approach for simulating the movement of pesticides from slow-release pesticide-treated seeds.

In addition, parallel laboratory experiments to derive instantaneous equilibrium and kinetic sorption parameters were unavailable for the specific soil type (Marshall silt loam) used in this packed soil column study, but were derived for other soils. This research will assess the transferability of using these laboratory-derived sorption parameters from varying soil and environmental conditions observed in the column leaching study. Previous modeling studies in the literature reported the need to calibrate models for kinetic sorption parameters (Ma and Selim, 2005; Ma et al., 2004a; Ma et al., 2004b; Saffih-Hdadi et al., 2003; Guo et al., 1999; Ma et al., 1996). It should also be noted that these parameters were not derived specifically for treated seeds. The modeling assumed that mobility and transformation occur after release from the seed.

MATERIALS AND METHODS

PESTICIDE FATE AND TRANSPORT MODEL

A model capable of simulating slow release, IE and EK sorption, and irreversible binding is the RZWQM (Wauchope et al., 2000; Ahuja et al., 2000). The RZWQM is a one-dimensional (vertical) model that simulates physical, chemical, and biological processes of a unit area of an agricultural crop production system (Ahuja et al., 2000). This model is currently being considered by the Office of Pesticide Programs of the U.S. Environmental Protection Agency (U.S. EPA) for adoption as a more refined exposure assessment model for groundwater sources of drinking water (Fox et al., 2006). The RZWQM can simultaneously simulate pesticide and metabolite fate and transport, macropore flow, and artificial subsurface drainage (Ahuja et al., 2000; Fox et al., 2004).

The model divides water flow processes into two phases: (1) infiltration into the soil matrix and macropores with macropore-matrix interaction, and (2) redistribution of moisture in the soil matrix modeled using a mass conservative numerical solution of Richard's equation, which includes plant uptake, surface evaporation, fluctuating water table, and tile flow (Ahuja et al., 2000). The infiltration of water through a layered soil profile is modeled using a modified Green-Ampt approach. The model routes precipitation that exceeds the infiltration rate into macropores based on a flow capacity limit determined by Poiseuille's law (Malone et al., 2001; Malone et al., 2004). The model then evenly distributes water entering into macropores among the number of effective macropores per unit area. The RZWQM models potential evaporation and transpiration using a modified form of the Shuttleworth and Wallace (1985) double-layer model (Farahani and DeCoursey, 2000).

The RZWQM simulates microencapsulated (slow-release) pesticide formulations with the pesticide incorporated into the soil profile. The term "microencapsulated" is a misnomer, and the RZWQM more appropriately models a "controlled" release formulation (Wauchope et al., 2000). The controlled release allows the specification of a linear release rate whereby active ingredient is released into the soil moisture at the start of each computational day.

The RZWQM uses a non-uniform mixing approach to model chemical transfer to overland flow (Ahuja et al., 2000). Chemical transport in the matrix is modeled using a sequential partial-displacement and mixing approach in 1 cm increments. The soil matrix is subdivided into micropore (immobile) and mesopore (mobile) zones. The soil matrix porosity is divided into micropores and mesopores based on partitioning the soil water retention curve at 2000 cm pressure. During infiltration, miscible displacement only occurs in the mesopores. The model allows diffusion between the mesopores and micropores based on an apparent diffusion coefficient or diffusion distance factor supplied by the user or defined by a default database in the model. The pesticide sub-model within RZWQM assumes dissipation processes in crop foliage, crop residues, soil surface, and soil subsurface (Wauchope et al., 2000). The model also estimates plant uptake of pesticide based on a transpiration stream concentration factor (K_{tscf}), which Briggs et al. (1982) estimated to be a function of the octanol-water partition coefficient (K_{ow}):

$$K_{tscf} = 0.784 \exp \left[- \frac{(\log(K_{ow}) - 1.78)^2}{2.44} \right] \quad (1)$$

However, this plant uptake function has not yet been thoroughly evaluated.

The RZWQM uses a three-site model for kinetic sorption (fig. 1): (1) instantaneous reversible sorption onto equilibrium sorption sites, (2) slow reversible sorption (Boesten and van der Pas, 1988; Kan et al., 1994) onto kinetic sorbed sites, and (3) slow formation of bound residues that become unavailable for leaching or degradation (Wauchope et al., 2000). This kinetic sorption model is a modification of the three-site model of Boesten and van der Pas (1988) and Boesten et al. (1989). The relationship between dissolved and equilibrium sorbed phase is characterized by a linear instantaneous equilibrium between concentrations in both phases:

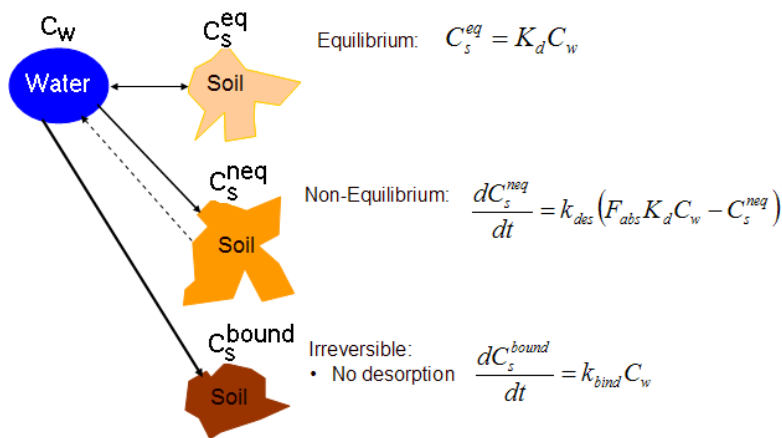


Figure 1. Three-site kinetic sorption model used by the RZWQM, which divides adsorption sites into instantaneous reversible sorption sites, slower reversible sorption sites, and irreversible binding sites (C_w = concentration of pesticide in water phase; C_s^{eq} , C_s^{neq} , and C_s^{bound} = concentration of pesticide on instantaneous reversible sorption sites, non-equilibrium, and irreversible sorption sites, respectively).

$$C_s^{eq} = K_d C_w \quad (2)$$

where C_s^{eq} is the concentration in the equilibrium sorbed phase (mass of compound per mass of dry soil, mg kg^{-1}), K_d is the distribution coefficient (L kg^{-1}), and C_w is the concentration in the dissolved phase (mass of compound per volume of water, mg L^{-1}). The concentration in the kinetic sorption sites (C_s^{neq}) is defined as the non-equilibrium sorbed phase (mass of compound per mass of dry soil, mg kg^{-1}). A first-order kinetic equation is assumed for the relationship between C_s^{neq} and C_s^{eq} :

$$\frac{dC_s^{neq}}{dt} = k_{des} (F_{abs} K_d C_w - C_s^{neq}) \quad (3)$$

where k_{des} is the desorption rate constant (d^{-1}) and F_{abs} is the fraction of kinetic sorption sites. Formation of bound or irreversible pesticide residues (C_s^{bound}) occurs through specification of a rate constant for irreversible binding, k_{bind} (d^{-1}):

$$\frac{dC_s^{bound}}{dt} = k_{bind} C_w \quad (4)$$

The model does not currently simulate kinetic sorption based on Freundlich sorption coefficients. In addition, the model assumes degradation within the profile only within the dissolved aqueous phase and not on the equilibrium or kinetic sorbed phase (Wauchope et al., 2000). The model assumes that microbiological degradation of pesticide is minimal on the sorbed phase because the pesticide is unavailable for adsorption by microorganisms (Novak et al., 1995).

COLUMN LEACHING EXPERIMENTS

Ten soil columns of 25.4 cm diameter contained 60 cm of silt loam surface (0-15 cm) soil (Marshall silt loam, fine-silty, mixed, superactive, mesic Typic Hapludolls) (table 1). Surface soil was collected from a field near Springfield, Nebraska, to represent a typical growing region for corn in the U.S. Disturbed soil samples were sieved with a 4 mm sieve as they were placed in the column. The chemical application method in this study was seed treatment. Corn

seeds were treated with an active ingredient (i.e., undisclosed experimental pesticide), radiolabeled (^{14}C), and aged for four days at room temperature (23°C to 25°C).

The experimental compound was classified as persistent and mobile (soil half-life in the laboratory greater than 80 days), stable to hydrolysis, soluble (i.e., solubility greater than 0.25 g L^{-1}), and does not volatilize (vapor pressure less than 10^{-10} Pa) especially considering the chemical application method (i.e., seed treatment). Laboratory batch equilibrium studies on three soil types ranging from sandy loam to clay loam suggested organic carbon sorption coefficients (K_{oc}) ranging from 98 to 283 L kg^{-1} . Time-dependent sorption studies (99-day duration) on two soil types ranging from sandy loam to silt loam suggested k_{des} of 0.03 d^{-1} and a range of F_{abs} of 0.05 to 0.15. These parameters are similar in value to those reported by Boesten et al. (1989) and Boesten and Gottesburen (2000) for similar pesticides. Soil was tilled to 15 cm, and fertilizer was incorporated into the top 15 cm of the soil. Soil columns were saturated and allowed to drain by gravity for 24 h prior to planting one seed at a depth of approximately 5 cm (normal agronomic practice) in the center of each column on 23 July 2004 (Shepherd et al., 2006). While the planting date was slightly later than would be expected in a normal corn growing season, the study was carried out in a greenhouse where the conditions were maintained to mimic the appropriate light-dark intervals and temperatures of a normal growing season.

Temperature and relative humidity were recorded in the greenhouse. During the study period, the mean weekly temperatures ranged between 19°C and 30°C . The mean weekly relative humidity ranged between 24% and 38%. Daily solar radiation data were not measured but were available for the nearby Kansas City, Missouri, airport. Columns were

Table 1. Physical and chemical soil characteristics for Marshall silt loam soil used in the greenhouse column studies.

Characteristic	Value
Sand (%)	24
Silt (%)	53
Clay (%)	23
Moisture at 1/3 bar (%)	28.3
Organic matter (%)	3.1
pH (1:1, soil:water)	6.2
Cation exchange capacity (meq/100 g)	22.7

suspended on a rack by chains, and the lower portion of each column was enclosed in black plastic to prevent sunlight from reaching the leachate collected below the columns. A week after planting the seeds, three fans were used in the greenhouse that resulted in average wind speeds of 400 km d⁻¹.

Two columns were removed at four intervals (2, 4, 8, and 16 weeks post-emergence) with two columns maintained as backup. Water was applied to maintain the crop. Leaching events were simulated by the addition of excess water over several days to produce leachate from the bottom of the columns as required by regulatory agencies. Water application rates were adjusted during a leaching event so that no ponding of water occurred on the soil surface. These events are referred to as “leaching events” and required near-saturation of the soil column over several days to produce leachate. Thus, the conditions of the column experiments were a hydrologically worst-case situation for leaching as compared to normal growing conditions for corn, as the total irrigation was approximately five to six times the cumulative 30-year average precipitation.

Leachate was analyzed daily for the active ingredient for one week after first breakthrough and then weekly thereafter. At sampling, the plants above the soil surface were cut off, bagged, weighed, and frozen. The plant matrix and roots were analyzed separately for total radioactive residues. Soil columns were frozen, sliced into 15 cm sections, and the individual layers were homogenized. A portion of the soil was extracted, and the extracts were analyzed by high-performance liquid chromatography (HPLC). Nonextractable radioactivity was determined by combustion analysis of the extracted soil (Shepherd et al., 2006). The pesticide on the seed coat was separated from the soil in determining soil concentrations in the 0-15 cm soil layer; therefore, residues reported in the soil do not include the residues in the seed.

MODELING THE COLUMN LEACHING EXPERIMENTS

RZWQM calibration was based on predicted versus observed crop height and leachate from the columns. The modeling followed a two-step hierarchical approach of data complexity from a “cold” or uncalibrated simulation with default soil and crop parameters to more sophisticated model calibration. The simulation period was from 1 July 2004 to 31 December 2004. The RZWQM cold simulation was based on particle size distribution and percent organic matter measured from in situ soil samples for the silt loam soil (table 1). The RZWQM possessed the ability to derive hydraulic properties (i.e., soil bulk density, saturated hydraulic conductivity, water retention, and entry pressure head) for the soil based on this minimum input. Daily maximum and minimum temperature and relative humidity as measured in the greenhouse during the study period were used in this “cold” simulation. Daily solar radiation values were obtained from the Kansas City, Missouri, airport. Wind speeds of approximately 400 km d⁻¹ were input into RZWQM. Daily potential evapotranspiration (PET) was simulated by the model. Irrigation was input into the model based on the amounts applied to each column and assuming a uniform distribution across a typical 6 h duration to minimize runoff predicted by the model. The default RZWQM plant parameters for corn were used in the “cold” simulations with a planting date of 23 July 2004 at 1 seed per 507 cm².

For model calibration, soil parameters and daily PET were adjusted to simulate appropriate leaching from the columns.

Soil bulk density and hydraulic conductivity were adjusted because the soil columns were not repacked to field bulk densities. Daily PET values were adjusted during the growth stage between four leaves on the plant to maximum vegetation and for the growth stage between full vegetation and reproduction. The daily PET values were adjusted due to the significant underprediction of PET that occurred by attempting to model plant growth in a greenhouse. In addition, plant leaves extended beyond the physical dimensions of the column and therefore provided a greater area of transpiration relative to available soil area than would have been expected in the field. PET adjustments for leaves extending beyond lysimeter/column dimensions, termed the “effective area of transpiring vegetation” by Allen and Fischer (1990), have been used in lysimeter experiments (Allen et al., 1991).

The pesticide was simulated in the model with a microencapsulated slow-release rate governed by pesticide seed concentrations measured during the laboratory experiments at 2, 4, 8 and 16 weeks after application starting on 23 July 2004. The model assumes that the pesticide is mixed uniformly within the secondary tillage zone, where this depth is assumed by the model to be the depth of the first horizon (i.e., 5 cm in this case). The application rate was calculated based on the rate of mass of pesticide applied per seed and a column area of 507 cm². The release rate was assumed uniform between the dates of measured seed concentrations (23 July, 7 August, and 21 August). The pesticide was simulated assuming IE and EK sorption. Laboratory data on batch equilibrium experiments on three different soils ranging from sandy loam to clay loam were used to derive K_d . Since the concentration in the pore water was significantly less than 10⁻⁵ M or 1.0 to 3.0 mg L⁻¹, linear isotherms were appropriate (Green and Karickhoff, 1990; Karickhoff, 1981). Because none of the soils in the batch experiments matched the soils used in the greenhouse soil column, a probabilistic approach was used in the modeling. Three values of K_d were derived: average K_d and the upper and lower K_d from all three soils. Time-dependent sorption data from an unpublished report on two different soils (silt loam and sandy loam) were used to derive linear kinetic sorption parameters for the three-site model (i.e., k_{des} , F_{abs}) for each K_d value. Therefore, three sets of values for k_{des} and F_{abs} were derived.

For IE sorption, the soil aerobic half-life was calibrated in the model by matching the total pesticide in the soil profile. This was appropriate, since the total pesticide leached from the soil column was approximately 0.12%. The laboratory greenhouse studies estimated that approximately 7% to 8% of the applied pesticide was uptake by the corn plant. Therefore, the K_{ow} was calibrated to match this plant uptake. For EK sorption, the same soil aerobic half-life as in the IE scenario was used; however, additional adjustments were necessary to match observed and model-predicted total pesticide concentrations in the soil profile. This adjustment was necessary because degradation is assumed only to occur within the aqueous phase. Therefore, pesticide in kinetic sorption sites during EK sorption, which cannot instantaneously desorb into the water phase, will not degrade at the same rate as in the IE sorption scenario. The adjustment required specifying a half-life for binding that invokes the model to simulate irreversible binding (i.e., formation of bound or aged residues). The plant uptake was also matched to the observed 7% to 8% of applied by adjusting the K_{ow} .

Following the simulations for the specific time period of the greenhouse column study, a long-term simulation was performed to investigate long-term leaching potential from the pesticide-treated seed and quantify differences between IE and EK sorption. A representative weather station with 20 years (1961-1980) of hourly weather data in the midwestern U.S. (Indianapolis, Ind.) was selected for the long-term simulation. Soil and pesticide properties were maintained consistent between the greenhouse column study and the long-term simulation. The cumulative mass loss of pesticide as percent of applied was quantified for each of the 20 years.

RESULTS AND DISCUSSION

COLUMN HYDROLOGY AND PLANT GROWTH

The RZWQM “cold” simulation using default silt loam soil properties overpredicted observed leaching from the bottom of the soil column and failed to match observed plant growth. The default RZWQM soil parameters for bulk density (ρ_b), porosity (ϕ), saturated hydraulic conductivity (K_{sat}), and field capacity water content (θ_{fc}) were 1.3 g cm^{-3} , $0.50 \text{ cm}^3 \text{ cm}^{-3}$, 0.68 cm h^{-1} , and $0.29 \text{ cm}^3 \text{ cm}^{-3}$, respectively, for the silt loam soil. The RZWQM “cold” simulations consistently overpredicted observed leaching during maximum growth stages of the corn plant, hypothesized to be due to a considerable underprediction of evapotranspiration. Simulated PET was equivalent to PET values expected in field sites. A potential difficulty in using default crop growth parameters in soil columns is that a plant grown within a soil column has the potential to occupy a much greater ratio between the leaf area and the underlying soil area because plant leaves can extend beyond the diameter of the soil column. Therefore, using the default maximum leaf area index underpredicted the evapotranspiration of the corn plant relative to the soil column area. Also noted was a lack of predicted leaching at the beginning of the simulation period. Several significant leaching events were observed between day 208 and 217, but not predicted when using default RZWQM soil parameters for silt loam soil. Predicted leaching events at the end of the simulation period matched observed leaching from

the soil columns. The model was capable of matching both the timing (day 301-302 and day 315) and magnitude of leached water depth (1.9 cm and 0.7 cm) at the end of the simulation period.

The default RZWQM soil and plant growth parameters were then adjusted based on the expected lower bulk density ($\rho_b = 1.1 \text{ g cm}^{-3}$), lower θ_{fc} ($0.10 \text{ cm}^3 \text{ cm}^{-3}$), and higher hydraulic conductivity ($K_s = 20 \text{ cm h}^{-1}$) of the soil column. These values were reasonable, based on observations of infiltration capacity during irrigation. To simulate the magnitude of evapotranspiration, daily PET values were adjusted by a factor representing the difference between irrigation and leaching. The adjustment of the RZWQM default soil parameters allowed the model to respond to leaching events at the beginning of the simulation period. When the soil parameters were adjusted without changing daily PET, differences in predicted leaching were minimal except between days 208 and 217 of the simulation period. Adjusting the PET reasonably predicted leaching based on a normalized objective function (NOF) criterion (Fox et al., 2006), where the NOF between measured and observed data was 6.4, suggesting that the model was suitable for screening applications (fig. 2). In the case that similar column experiments are to be used for determining the mobility of an experimental compound as a seed treatment (Shepherd et al., 2006), care must be taken to obtain accurate measurements of the PET.

PESTICIDE TRANSPORT FROM SLOW-RELEASE PESTICIDE-TREATED SEED

Laboratory batch equilibrium studies on three sandy loam to clay loam soils suggested Freundlich isotherms (Clark, 1996) throughout a range of aqueous concentrations up to 3 mg L^{-1} . However, at aqueous concentrations observed for this laboratory column study, a linear isotherm could be fit to the early portion of the sorbed versus dissolved phase concentrations to derive average, upper, and lower K_d values (table 2). Since the soil used in this column contained a 1.8% fraction of organic carbon (f_{oc}), average, lower, and upper K_d values correlated to K_{oc} values of 198, 98, and 283 L kg^{-1} , respectively. If dissolved-phase aqueous concentrations had

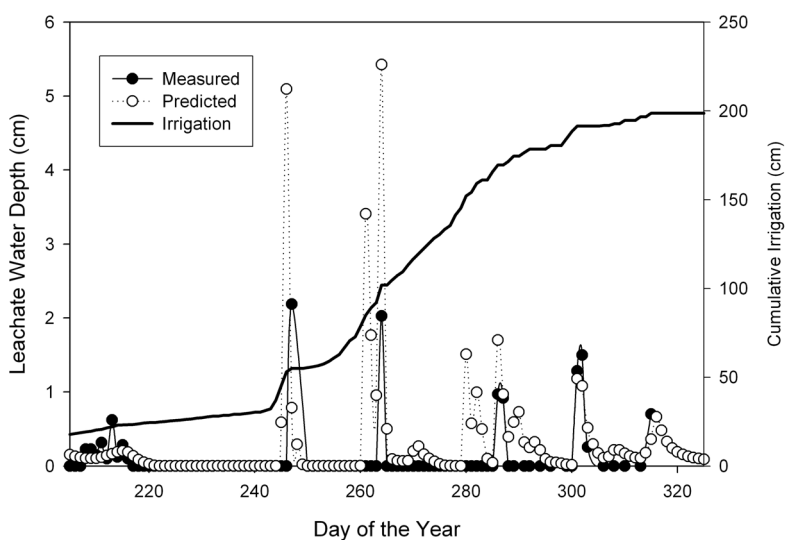


Figure 2. RZWQM-predicted versus observed leaching from the greenhouse column after calibration of soil hydraulic parameters.

Table 2. Pesticide fate and transport properties used in the RZWQM instantaneous equilibrium (IE) and equilibrium (EK) scenarios of the greenhouse column studies.

Parameter	Value
Organic carbon sorption coefficient (K_{oc} , L kg ⁻¹) ^[a]	Average 198 (Lower, Upper) (98, 283)
Desorption rate constant (k_{des}) ^[b]	Average 0.03 (Lower, Upper) (0.03, 0.03)
Fraction of kinetic sites (F_{abs}) ^[b]	Average 0.10 (Lower, Upper) (0.05, 0.15)
Soil aerobic half-life ($t_{1/2}$, days) ^[c]	IE/EK sorption 540/540
Irreversible half-life (k_{bind} , days) ^[c]	EK sorption 250
Octanol-water partition coefficient (log K_{ow}) ^[c]	IE/EK sorption 0.2/0.3

- [a] Derived from laboratory batch equilibrium studies on three soil types ranging from sandy loam to clay loam.
 [b] Derived from time dependent sorption studies on two soil types ranging from sandy loam to silt loam.
 [c] Calibrated with the RZWQM to match total pesticide in the soil profile.

ranged above approximately 1.0 to 3.0 mg L⁻¹, then a Freundlich isotherm would have been necessary for adequately modeling instantaneous equilibrium. Data from the two time-dependent sorption laboratory studies were used to derive k_{des} and F_{abs} based on matching the time derivative of kinetic site sorbed concentration in equation 2, based on measured dissolved aqueous concentrations and the kinetic site sorbed concentration. Average, lower, and upper k_{des} and F_{abs} values based on the linear kinetic sorption are also given in table 2, which suggested that 5% to 15% of soil sites were kinetic as opposed to instantaneous sorption sites.

Using the values given in table 2 with IE sorption, a 540-day soil aerobic half-life was required for the model to match the total pesticide in the soil profile (fig. 3). For EK sorption, the equivalent soil aerobic half-life was used in combination with a half-life for binding of 250 days to invoke irreversible binding in the model (table 2). Irreversible bind-

ing was necessary because the model only allowed degradation in the dissolved aqueous phase. Therefore, pesticide on nonequilibrium kinetic sites was not subject to degradation. The EK sorption scenario also required a slightly higher K_{ow} value to match the observed 7% to 8% plant uptake of pesticide, since the model assumes that uptake is through the dissolved aqueous phase. The calibrated K_{ow} (1.5 to 2.0 L kg⁻¹) for matching plant uptake failed to match the laboratory-estimated range of possible K_{ow} based on empirical regression equations relating K_{ow} and K_{oc} (Karickhoff, 1981). Therefore, more adequate plant uptake functions are necessary.

A comparison of observed and IE and EK model-predicted leaching from the greenhouse column study indicated that the model was only able to predict significant leaching with the lower bound sorption parameters (K_{oc} , k_{des} , F_{abs}) (fig. 4). Both IE and EK sorption with the lower bound parameter values matched the timing of the last four observed pesticide concentrations in the leachate, but in general tended to over-predict leaching. Observed pesticide leaching was 0.12% of applied compared to predicted pesticide leaching of 0.80%, 0.004%, and <0.001% of applied for IE sorption for the lower, average, and upper bound sorption parameters. Model-predicted pesticide leaching was 0.72%, 0.003%, and <0.001% of applied for EK sorption for the lower, average, and upper bound sorption parameters. However, it remains unknown whether the lower bound sorption parameters more appropriately match the actual time-dependent sorption parameters for this specific greenhouse soil, primarily because of the correlation between the observed pesticide in the leachate and the observed pesticide in the soil profile (figs. 5 through 7).

Modeling scenarios failed to predict the observed pesticide confinement (observed 70% of applied pesticide) to primarily the upper 15 cm of the soil profile (figs. 5 through 7). For example, on day 317, IE sorption scenarios predicted between 1% and 20% of applied in the upper 15 cm, with peaks at 34, 27, and 17 cm below ground surface for the lower, average, and upper bound sorption parameters, respectively (fig. 7). EK sorption scenarios predicted between 3% and 18% of applied in the upper 15 cm, with peaks at 31, 25, and 17 cm below ground surface for the lower, average, and upper

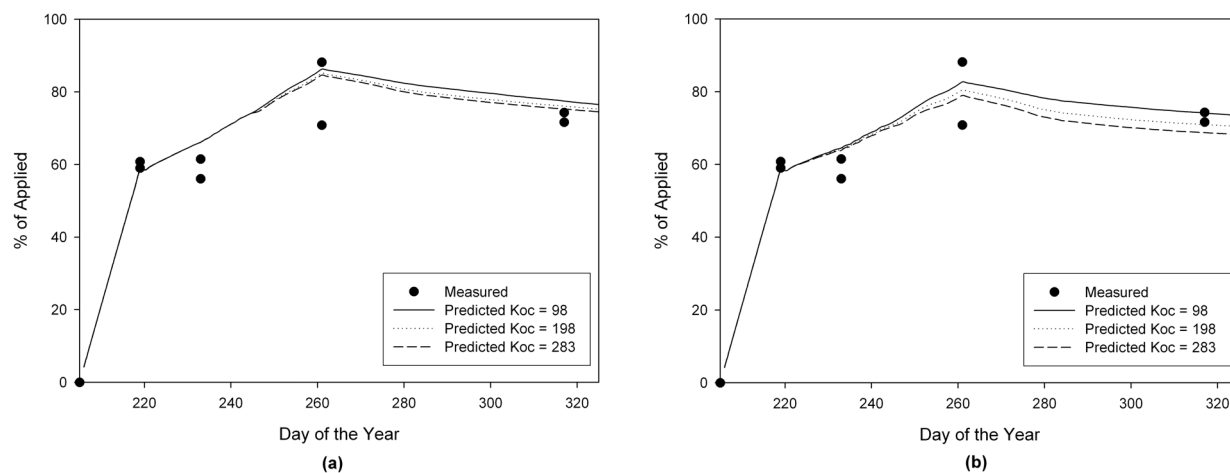


Figure 3. Observed and model-predicted total pesticide concentration in the soil profile for (a) instantaneous equilibrium (IE) and (b) equilibrium kinetic (EK) sorption. Equivalent soil aerobic half-lives were used in both scenarios; however, the EK scenario required irreversible binding. Plant uptake was simulated in each scenario to match the observed 7% to 8% uptake.

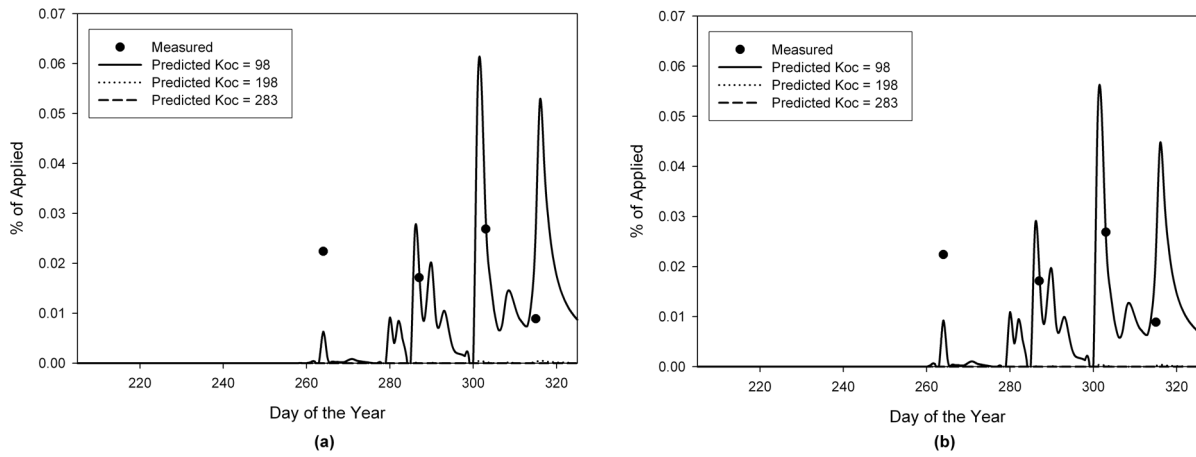


Figure 4. Observed and model-predicted pesticide in the leachate for (a) instantaneous equilibrium (IE) and (b) equilibrium-kinetic (EK) sorption with three modeling scenarios (i.e., average, lower, and upper K_{oc} , k_{des} , F_{abs} datasets).

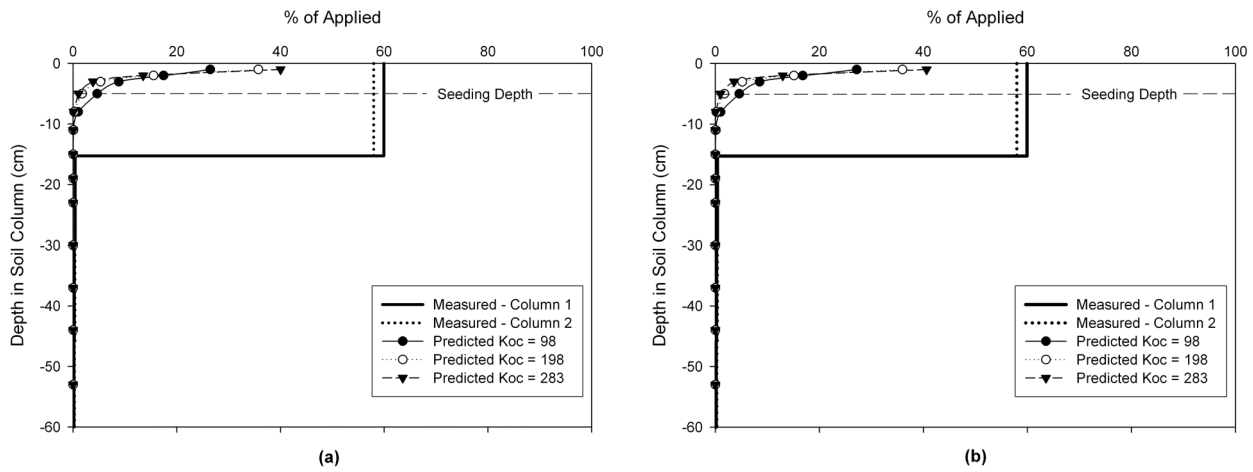


Figure 5. Observed and model-predicted pesticide in the soil profile at Julian day 219 expressed as percent of applied pesticide for (a) instantaneous equilibrium (IE) and (b) equilibrium-kinetic (EK) sorption with three modeling scenarios (i.e., average, lower, and upper K_{oc} , k_{des} , F_{abs} datasets).

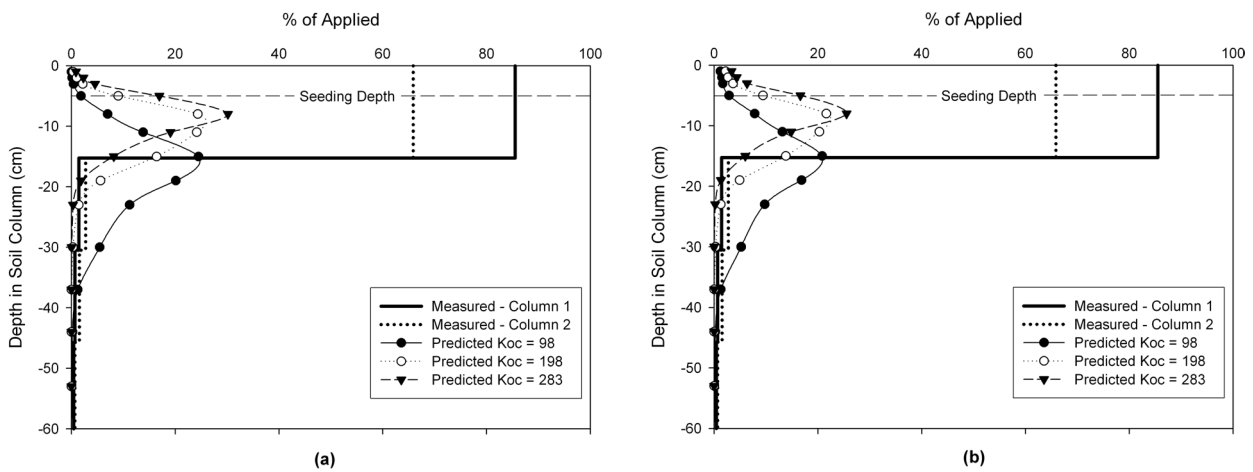


Figure 6. Observed and model-predicted pesticide in the soil profile at Julian day 261 expressed as percent of applied pesticide for (a) instantaneous equilibrium (IE) and (b) equilibrium-kinetic (EK) sorption with three modeling scenarios (i.e., average, lower, and upper K_{oc} , k_{des} , F_{abs} datasets).

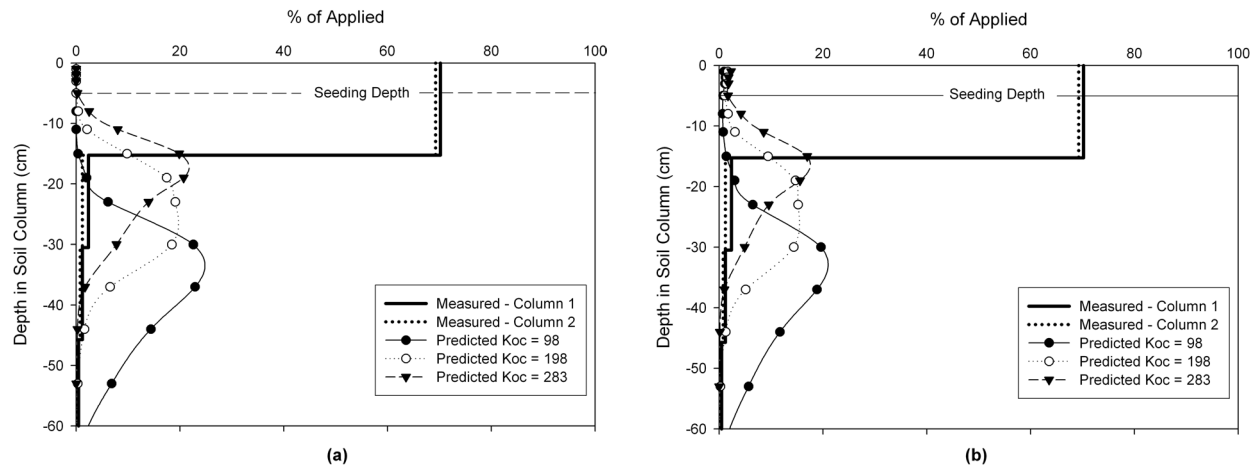


Figure 7. Observed and model-predicted pesticide in the soil profile at Julian day 317 expressed as percent of applied pesticide for (a) instantaneous equilibrium (IE) and (b) equilibrium-kinetic (EK) sorption with three modeling scenarios (i.e., average, lower, and upper K_{oc} , k_{des} , F_{abs} datasets).

bound sorption parameters. Differences in IE and EK sorption appeared more prevalent for the lower bound sorption parameters as compared to the average or upper bound parameters.

An interesting observation arises when one notices the date of occurrence of the first peak in pesticide leachate from the soil column (i.e., Julian day 245). The RZWQM model fails to predict this peak for the average, upper, or lower parameters sets for either IE or EK sorption. If one observes the measured pesticide concentrations (expressed as percent of applied) in figure 6 (Julian day 261), it is apparent that no pesticide was measured at depths below 45 cm in the greenhouse soil column, which suggests that pesticide in the leachate may be due to localized fingering that cannot be predicted by one-dimensional pesticide fate and transport models. In fact, the majority (70% to 80% of applied) of the pesticide remained in the upper 15 cm of the soil column. Columns were divided into 15 cm increments and the soil was homogenized before quantification of the pesticide concentration in the soil. Therefore, localized pesticide concentrations in fingers deeper in the soil profile may have been diluted.

This hypothesized fingering may be due to two phenomena. First, the application of pesticide is localized at the location of root formation. The formation of roots may have developed preferential pathways for the migration of the pesticide in the soil profile. More research is needed on the development of possible preferential flow pathways by roots, especially if use of pesticide-treated seeds becomes widespread. Second, the localized release of pesticide from a theoretical sphere leads to saturation of soil equilibrium and nonequilibrium sorption sites within the zone of soil directly below the seed. A slow-release pesticide-treated seed does not uniformly release pesticide across the entire soil profile area. A one-dimensional model such as RZWQM that treats a unit area as a point will tend to distribute this pesticide mass across the entire soil area. However, the pesticide release occurs within a concentrated location within the soil profile, which is then subject to large concentration gradients in the vertical direction near the seed. In addition, only a portion of the infiltrating water will actually contact the released pesticide. One-dimensional models such as RZWQM allow all infiltrating water to interact with the slow-release pesticide,

increasing the predicted transport in the soil profile. In reality, only that portion of water infiltrating directly above the release would be available to transport the pesticide. In the field, the use of one-dimensional models may be appropriate as compared to model use for column studies where only one seed is planted, but more research is needed to confirm this statement.

One-dimensional models appear to underpredict pesticide leaching from seed treatments in soil columns. If regulators and scientists are to use one-dimensional models to simulate potential environmental exposure from pesticide-treated seeds, then adjustments may be necessary to account for this localized release. Possible adjustments could include changing the soil contributing area by modifying the pesticide release rate. More sophisticated two- and three-dimensional models may be necessary to adequately capture the combined processes of sorption, dissipation, and plant uptake of pesticide near the localized release point.

Long-term simulations using Indianapolis weather data indicated that differences between IE and EK sorption arose after multiple plantings of the pesticide-treated seed (fig. 8). Differences in IE versus EK predicted percent loss of pesticide by leaching were not observed until the third year after planting, which corresponded to the first year where significant (i.e., greater than 0.1% loss) pesticide concentrations in leachate were observed. This observation was hypothesized to be due to the fact that kinetic sorption effects require a significant mass of compound to be present in the soil and time for that mass to adsorb to instantaneous, kinetic, and irreversibly bound sorption sites. Leaching simulations with IE and EK sorption generally predicted an average percent mass loss of 8.5% (standard deviation of 4.2%) and 0.6% (standard deviation of 0.3%), respectively. Short-term simulations (i.e., 120 days) showed minimal differences between IE and EK sorption, while differences increased over long-term simulations when concentrations in the soil increased. Over the short-term, IE simulations will adequately mimic data from the column even though the appropriate model for sorption is kinetic. However, the use of IE sorption models for EK sorption processes is not appropriate for long-term simulations.

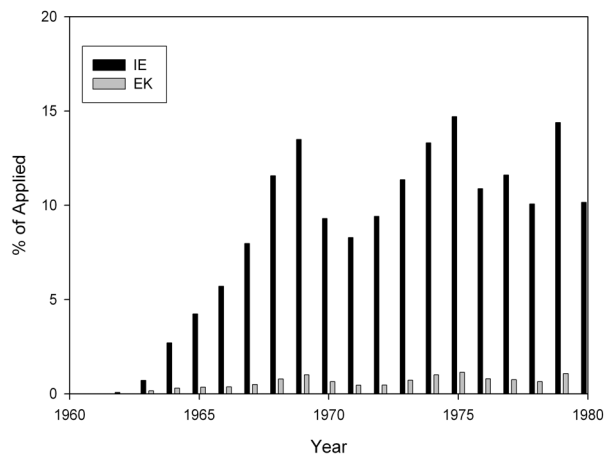


Figure 8. Cumulative predicted mass loss as percent of applied (%) for RZWQM simulations with instantaneous equilibrium (IE) and equilibrium kinetic (EK) sorption for long-term (20-year) simulations.

SUMMARY AND CONCLUSIONS

Leaching and soil profile concentrations of an experimental compound reported from greenhouse soil column studies were used to evaluate the ability of a one-dimensional pesticide fate and transport model (RZWQM). Models have not been evaluated in the literature for pesticide-treated seed. The RZWQM was used to simulate this slow-release pesticide and investigate the importance of considering EK sorption as opposed to a simple IE sorption model. Pesticide fate and transport properties were derived from batch equilibrium and time-dependent sorption laboratory studies on soils unique from the soil utilized in the greenhouse column study. Therefore, three sets of parameters were derived for the distribution coefficient and kinetic sorption parameters (i.e., rate of desorption, fraction of kinetic sites, and irreversible half-life): average, upper, and lower parameter values. Only the lower bound on pesticide parameters (distribution coefficient, rate of desorption, and fraction of kinetic sites) predicted significant pesticide concentrations in the leachate. However, pesticide concentrations in the leachate occurred on days when observed pesticide concentrations in the soil profile were restricted to the upper 45 cm of the 60 cm soil column. Such results suggest that transport from the pesticide-treated seed was influenced significantly by localized fingering, oversaturation of soil sorption sites beneath the seed, and preferential flow paths created by roots. These results suggest that more sophisticated modeling techniques may be required for conducting environmental exposure assessments for groundwater sources of drinking water when seed treatment use becomes more widespread. This research also identified research gaps in current models in regard to plant uptake of pesticides. Empirical functions commonly used to estimate plant uptake by pesticide were not adequate to predict plant uptake from pesticide-treated seeds.

For the greenhouse column study, model simulations suggested minimal differences between IE and EK sorption in terms of pesticide leachate concentrations and concentration of pesticide in the soil profile. It was hypothesized that the lack of variation between IE and EK sorption was primarily due to the small mass of pesticide (i.e., on the order of mg) and the small simulation period (180 days). By conducting long-term (20-year) simulations with annual plantings of the

pesticide-treated seed, a significant difference was observed in average percent loss as a function of mass applied (i.e., 8% compared to less than 1% for IE versus EK sorption, respectively). For the first two years of the simulation, no difference was observed between IE and EK sorption. However, variations in the two sorption assumptions were observed in subsequent years where significant (i.e., greater than 0.1% loss) leaching of the pesticide occurred. These results demonstrate that EK sorption is of vital importance when conducting environmental exposure assessments for pesticide leaching to groundwater for pesticides that demonstrate time-dependent sorption. However, more research is needed on degradation mechanisms for pesticides with time-dependent sorption. More specifically, research is needed on whether or not degradation of pesticide only occurs within the dissolved aqueous phase or also on equilibrium and kinetic sorption sites.

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