

COMPARISON OF PESTICIDE ROOT ZONE MODEL 3.12: LEACHING PREDICTIONS WITH FIELD DATA

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Abstract—As part of a process to improve confidence in the results of regulatory modeling, predictions of the pesticide root zone model (PRZM) 3.12 were compared with measured data collected in nine different field leaching studies. Reasonable estimates of leaching were obtained with PRZM 3.12 in homogeneous soils where preferential flow is not significant. The PRZM 3.12 usually did a good job of predicting movement of bromide in soil (soil and soil pore-water concentrations were generally within a factor of two of predicted values). For simulations based on the best choices for input parameters, predictions of soil pore-water concentrations for pesticides were usually within a factor of three and soil pore-water estimates within a factor of 11. When the model input parameters were calibrated to improve the simulation of hydrology, predicted pesticide concentrations in soil pore water were usually within a factor of two of measured concentrations. Because of the sensitivity of leaching to degradation rate, the most accurate predictions were obtained with pesticides with relatively slow degradation rates. When conservative assumptions were used to define input pesticide parameters, predictions of pesticide concentrations were usually a factor of two greater than when using the best estimate of input parameters without any built-in conservatism.

Keywords—Leaching Modeling Pesticides Pesticide root zone model

INTRODUCTION

In a previous paper [1], the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Environmental Model Validation Task Force compared PRZM 3.12 predictions of runoff with measured data collected in nine different field runoff studies. This paper compares the results of PRZM 3.12 predictions with measured data from nine different field leaching studies.

METHODOLOGY

Similar methodology was used in the leaching comparisons in this paper and the runoff comparisons described previously [1]. The portion of the methodology section in the runoff paper describing the types of comparisons, the model version, selection of input parameters, and guidance for performing calibration simulations also apply to the leaching comparisons and so will not be repeated in this paper.

Selection of experimental data sets

Data sets were selected using criteria for determining ideal and acceptable data sets based on the data requirements as identified in the guidance documents for selection input parameters for groundwater loading effects of agricultural management systems (GLEAMS) and PRZM as well as the consensus opinion of the task force scientists and advisers.

Ideal leaching data sets

Complete site-specific weather data covered the period of the study and included daily precipitation, daily temperature, and pan evaporation; edge-of-field runoff yield or temporal soil moisture with depth; data for a conservative tracer of water

flow; site-specific soil physicochemical properties and profile description; information on time, rate, and method of pesticide application; site-specific laboratory measurements of soil half-life and K_d or predictions from laboratory data on the basis of site-specific soil properties; output data including tracer concentrations and/or soil moisture measurements with depth and time; vadose zone measurements in replicate and at several depths providing pesticide and tracer concentrations in soil water and total soil residue concentrations; verifiable analytical methodology with adequate method sensitivity; documentation of sampling design and suction lysimeter placement; data sets with demonstrated pesticide detects in groundwater; and studies conducted and documented by a verifiable standard for quality assurance/quality control.

Acceptable leaching data sets

These data included spatially and temporally contemporaneous weather data available from a National Oceanic and Atmospheric Administration (NOAA) site; representative curve numbers obtained from a database using soil hydrologic group, soil texture, management practice, and crop; measured soil texture and organic carbon by horizon; number and thickness of soil horizons obtained from a database; a measured soil half-life and sorption coefficient; documented management practices and timings of critical events; estimated soil water content on the basis of weather and soil physicochemical properties; output data including total pesticide and tracer concentrations with depth and time determined via an acceptable method; and peer-reviewed data and interpretations.

Nine leaching data sets (summarized in Table 1) were chosen for comparisons of measured and predicted values. Data sets fitting the ideal criteria were used when available to the task force, but other data sets were also used to cover a wide range of geography and pesticide properties. The criteria re-

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Table 1. Details of the nine data sets used in the leaching simulations

Data set ^a	Soil type	Hydrologic group	Crop	Application rate (kg a.i./ha)	Half-life ^b (d)	K_d^b (ml/g)
CA1L	Loamy sand	B	Alfalfa	0.848	115	0.186
FL1L	Sand	A	Citrus	5.6	17.5	0.088
GA1L	Fine sandy loam	A	Sweet corn	12.6	8	0.176
GA2L	Mixture, ~loamy sand	B/C	Peanuts	2.49	20	0.42
				2.35	69	0.11
KS1L	Sandy loam	C	Wheat	0.074	21	0.50
NC1L	Loamy sand	A	Soybean	0.56	100	0.361
NC2L	Loamy sand	A	Soybean	0.14	47	0.425
NC3L	Loamy sand	A	Cotton	0.14	14	0.091
NC4L	Loamy sand	A	Soybean	0.56	365	0.35

^a Studies are identified by the state name, number of study, and the letter L, indicating a leaching study.

^b Site-specific half-life and sorption coefficient (K_d) values for surface horizons reflect the values provided by the registrants.

sulted in heavy emphasis on industry data sets conducted within the United States to fulfill registration needs, although data sets were also obtained from the literature and from nonindustry researchers. Studies conducted outside the United States were excluded from consideration due to the limitations of the standard operating procedure (SOP) for selection of input parameters. Column lysimeter studies and field dissipation studies with sampling less than 1 m were also excluded from consideration.

The nine leaching studies represented a range of hydrologic, edaphic, and agronomic conditions in agricultural settings located in California, Florida, Georgia, Kansas, and North Carolina, USA. The soil texture at these sites was predominantly hydrologic group A soils (typically sand or loamy sand, with a minimum infiltration rate of 8–11 mm/h). Two sites had less vulnerable loamy sand or sandy loam soils that were classified as hydrologic group B/C or C. A wide range of crops was grown on the test plots, including alfalfa, citrus, sweet corn, peanuts, wheat, soybeans, and cotton. The soil degradation half-life of the agricultural chemicals ranged from 8 to 365 d, and the sorption coefficient (K_d) varied from 0.088 to 0.50 ml/g for the surface horizon. Table 1 describes the main features of the leaching data sets.

Statistical analysis

For each level of modeling, the major output variables considered for model evaluation included hydrology parameters (precipitation, evapotranspiration, runoff, erosion, and recharge), pesticide fluxes and transformation rates (runoff, erosion, volatilization, plant uptake, foliar dissipation, degradation, and leaching), as well as concentrations of bromide and pesticide in soil and soil pore water over time. For regulatory purposes, the primary endpoints are the peak and annual average concentrations of pesticide in groundwater. The rate of travel (time of appearance) of peaks is generally of secondary importance. For a simple statistical evaluation of the model's performance, ratios of simulated and experimental values (simulated value/experimental value) were calculated for concentration values in soil and soil pore water over time. These ratios were calculated for both bromide and pesticide concentrations for depths and time points for which experimental data were reported.

One of the obstacles in comparing simulated and experimental leaching data arises from the fact that while modeling can provide both concentration data (mass per volume) and flux data (mass passing through a surface or plane over time), field studies typically provide only concentration data. In ad-

dition, annual average concentration values can readily be calculated from the daily values produced by modeling, but time-averaged values are less accurately determined from the monthly sampling events used in most groundwater studies.

To provide simple but meaningful comparisons between the simulated results and the experimental data, peak concentrations predicted by the model and observed in field monitoring were compared for four endpoints: bromide in soil, bromide in soil pore water, pesticide in soil, and pesticide in soil pore water. The absolute values of the log of the lowest and highest ratios from each study have been rank ordered and analyzed to provide an estimate of the median expected agreement.

To evaluate the impact of uncertainty, additional statistical analyses were performed on selected data sets. As an initial step to evaluate the impact of uncertainty, a sensitivity analysis was performed using an approach based on that of Plackett and Burman [2] to identify key model input parameters for runoff and leaching simulations. Monte Carlo analyses were then performed to evaluate the effect of uncertainty in the sensitive input parameters on the model predictions. The tools and results of the sensitivity and uncertainty analyses are presented in other papers in this series.

RESULTS

Overview of simulations

Site-specific simulations were performed for all nine data sets. Calibrated simulations or sensitivity analyses were performed for seven of the nine leaching studies. The leaching sites CA1L and GA2L did not undergo calibrated modeling or sensitivity assessment primarily because of either time and budgetary constraints or an expected low benefit from improving the fit obtained in site-specific modeling. A detailed description of the calibrated modeling analysis for each study is given elsewhere (R. Jones and M. Russell, 2001, unpublished report). Because of a combination of logistical problems in completing the cold modeling SOP as well as budgetary and time constraints, cold modeling was performed only for NC4L. This data set was selected because it contained the highest groundwater concentrations of the nine data sets being evaluated and thus provided the best opportunity to compare the results of progressively refining the accuracy of modeling through the three levels.

A summary of the mass balances obtained in each of the site-specific simulations for bromide is provided in Table 2. Because of a lack of degradation and volatility, the only two dissipation processes for bromide were plant uptake and leach-

Table 2. Summary of mass balances (expressed as a percentage of applied for the indicated data set) for bromide in leaching simulations

Dissipation mechanism	CA1L	FL1L	GA1L	GA2L	KS1L	NC1L	NC2L	NC3L	NC4L
Drift	1.00	1.00	1.00	1.00	1.00	ND ^a	1.00	1.00	1.00
Runoff	0.00	0.03	0.03	0.10	1.31	ND	0.00	0.00	0.00
Erosion	0.00	0.00	0.00	0.00	0.00	ND	0.00	0.00	0.00
Plant uptake	76.20	58.05	16.78	1.41	52.53	ND	2.78	48.07	6.76
Degradation in 1 m of soil	0.00	0.00	0.00	0.00	0.07	ND	0.00	0.03	0.05
Foliar dissipation	0.00	0.00	0.00	0.00	0.00	ND	0.00	0.00	0.00
Volatilization	0.00	0.00	0.00	0.00	0.00	ND	0.00	0.00	0.00
Leaching below 1 m	22.81	40.92	82.19	97.49	45.09	ND	96.22	50.91	92.19
Remaining in soil	0.00	0.00	0.00	0.00	0.00	ND	0.00	0.00	0.00

^a ND = not determined.

ing. For all the leaching simulations, the PRZM plant uptake parameter (UPTKF) was set at 1.0, the default value recommended in the PRZM manual, which implies that the chemical freely enters plant roots along with transpired water. The resulting plant uptake of bromide that was simulated varied dramatically, ranging from 2 to 7% in three settings to more than 50% in three settings. For compounds that do not sorb to soil, such as bromide, the primary factors that influence the plant uptake are the rooting depth and the recharge that occurs in the months immediately following application. Deeper-rooted crops, such as alfalfa and citrus, can abstract water and bromide from a greater depth than more shallowly rooted crops. In addition, more arid climates, such as California and Kansas, have lower rates of groundwater recharge following application that keep the bromide in the root zone for a longer period of time than in settings with more spring and summer recharge. Based on numerous published studies, typical uptake of bromide into agronomic crops can easily range up to 50% or more, supporting the results obtained in this exercise.

An overview of the comparisons for the peak bromide concentrations in soil and soil pore water are presented in Table 3. In general, site-specific modeling using PRZM 3.12 provides a very reasonable fit to both soil and soil pore-water data for bromide. The experimental soil data were typically obtained from the soil surface to a maximum depth of 120 cm. The simulated bromide concentrations in soil generally agree with the experimental data within a factor of three (i.e., the ratios of simulated to experimental data range from 0.33–3.0). Many

of the fits were within a factor of two. The only notably poor fit resulted at deeper soil depths in NC3L, where the experimental concentrations of bromide in soil declined rapidly to levels less than 0.05 ppm at depths of 90 to 120 cm. The simulated bromide concentrations also declined with depth but not as rapidly as the experimental data.

The simulated concentrations of bromide in soil pore water also showed excellent agreement with measured data with general agreement typically within a factor of three. The measured soil pore-water data were obtained from suction lysimeters installed at soil depths ranging from 90 to 360 cm, so these data corresponded to a longer time of travel than the soil data. The slightly different input values determined for NC4L in the cold and site-specific modeling produced slightly different simulated bromide concentrations with slightly better agreement in soil concentrations but slightly worse agreement in bromide soil pore water. Overall, the capability of PRZM 3.12 of simulating the fate and transport of bromide in the nine groundwater studies was very reasonable.

One of the values of using bromide in the groundwater studies is to obtain information on the rate of groundwater recharge. The simulated recharge rates for the nine studies varied from a low of 29% of applied rainfall and irrigation in California and Kansas to a high of 59% in North Carolina. The mean simulated recharge rate was 45% of applied water. These values agree well with expected recharge rates for shallow groundwater in vulnerable agronomic settings.

The simulated mass balances for the pesticides in the nine

Table 3. The ranges of bromide and pesticide soil and pore-water concentration ratios (simulated/experimental) for leaching simulations^a

Site	Modeling level	Bromide				Pesticide			
		Soil		Pore water		Soil		Pore water	
		Ratio	Depth (cm)	Ratio	Depth (cm)	Ratio	Depth (cm)	Ratio	Depth (cm)
CA1L	Site specific	0.19–0.74	0–60	0.01–0.12	90–360	0.56–1.21	0–60	0.01–0.10	90–360
FL1L	Site specific	0.12–3.05	0–300	—	—	0.05–0.17	30–300	—	—
GA1L	Site specific	0.47–1.11	0–120	0.74–1.26	90–360	1.09–85.6	0–120	0.03–1.7	180–360
	Calibrated	—	—	—	—	—	—	0.43–0.90	180–360
GA2L	Site specific	0.30–1.11	0–120	1.96–3.92	150–270	0.09–1.70	0–120	0.03–0.08	150–270
	Site specific	—	—	—	—	0.02–1.02	15–120	—	—
KS1L	Site specific	—	—	0.39–1.77	90–198	0.003–0.78	0–90	0.00	90–198
NC1L	Site specific	—	—	—	—	0.8–<3.39	0–220	0.76–1.36	90–270
NC2L	Site specific	—	—	0.77–1.82	90–360	0.09–0.76	0–120	0.28–1.68	90–360
NC3L	Site specific	0.4–73.71	0–120	0.33–1.66	90–360	0.45–<3.93	0–120	0.54–16.45	90–360
NC4L	Cold	0.47–3.24	0–120	1.38–3.11	90–210	0.49–12.04	0–120	3.53–4.01	90–210
	Site specific	0.40–2.71	0–120	1.59–3.36	90–210	0.47–7.08	0–120	1.99–2.22	90–210

^a The two lines for GA2L represent the results for the two pesticides in the same order as given in Table 1. Ratio is for peak concentrations (simulated/experimental); depth refers to the depth interval of the data. — indicates no measured data. The poor fit for pore-water concentrations in GA2L and KS1L indicates that the simulated degradation rate is faster than actually occurred under the experimental conditions.

Table 4. Summary of mass balances (expressed as a percentage of applied) for pesticide in leaching simulations

Dissipation mechanism	CA1L	FL1L	GA1L	GA2L ^a	KS1L	NC1L	NC2L	NC3L	NC4L
Drift	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Runoff	0.00	0.03	0.16	0.59	0.58	1.08	0.00	0.10	0.00
Erosion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Plant uptake	50.80	40.64	6.95	33.05	28.86	30.03	46.28	23.20	31.08
Degradation in 1 m of soil	36.61	55.02 ^b	50.67	62.65	68.87	67.89	36.11	71.77	64.31
Foliar dissipation	0.00	0.00	38.96	0.00	0.00	0.00	0.26	0.00	0.00
Volatilization	0.00	0.00	1.52	0.03	0.00	0.00	0.00	0.02	0.00
Leaching below 1 m	11.59	3.31 ^b	0.74	0.73	0.58	0.00	16.35	3.90	3.60
Remaining in soil	0.00	0.00	0.00	1.95	0.11	0.00	0.00	0.00	0.00

^a The two columns for GA2L represent the results for the two pesticides in the same order as given in Table 1.

^b In top 3.6 m of soil.

leaching studies are summarized in Table 4. Based on this summary, the major dissipation mechanisms for the various pesticides were degradation and plant uptake with these two mechanisms totaling 58 to 98% of all dissipation (average of 88%). Similar to the plant uptake of bromide, the uptake of pesticides was also significant, ranging from 7 to 51% of the applied chemical. Plant uptake is expected to be highest for pesticides with moderate to long half-life values that are weakly sorbed to soil, a description that fits most of the test chemicals in the cited leaching studies. However, this uptake is higher than would be expected on the existing limited data, probably because of the simplicity of the uptake model used in PRZM. Foliar dissipation of the pesticide was significant for only one study, which involved a series of 25 applications of an insecticide to a developing sweet corn crop (GA1L). For this case, the extent of simulated foliar dissipation was appropriate.

The simulated runoff and erosion losses were minimal for the leaching studies, which agrees well with the fact that these studies were typically sited on flat sites on highly permeable hydrologic group A soils. The two sites with runoff of approximately 0.6% were conducted on hydrologic group B or C soils.

The fraction of applied pesticide that was simulated to leach below a depth of 1 m varied between 0% (KS1L) and 36% (NC4L) with a mean value of 8%. The studies with the highest leaching percentages (CA1L, NC1L, and NC4L) all had application rates of more than 0.5 kg a.i./ha, sorption coefficients of 0.36 g/ml or less, and soil half-lives of 100 d or more. The screening model SCI-GROW (M.R. Barrett, 1997, The Screening Concentration in Ground Water, U.S. Environmental Protection Agency, Office of Pesticide Programs, Washington, DC) suggests that the groundwater detections resulting from these combinations of use rate, sorption, and half-lives would be expected to result in groundwater detections of 3 µg/L or more, which agrees with the results obtained from the deepest lysimeters in these studies.

A summary of the ratios of simulated to experimental results for peak pesticide concentrations in soil is presented in Table 3. The simulated soil concentrations of pesticide varied between extreme underprediction (e.g., ratio near 0) to up to 86× overprediction. To provide an estimate of the median expected agreement, the absolute value of the logarithms of the best and worst ratios from each study were rank ordered and analyzed. This procedure shows that the simulated values of pesticide concentrations in soil are expected to be within a factor of three of experimental values up to 50% of the time; 80% of the time the values are expected to be within a factor

of 10 to 11; and less than 10% of the time the simulated results are expected to be relatively poor with ratios of 100 or more.

The simulated concentrations of pesticide in soil pore water also varied widely, with a clear bias toward underprediction (Table 3). The highest overprediction was a factor of 16 for NC3L, while four studies had significant underprediction of pesticide residues in soil pore water.

To estimate the decline in degradation rate with depth in the soil profile, the site-specific SOP specified that the soil profile be divided in thirds with degradation half-lives of 1×, 2×, and 3×, respectively, with depth. This approximation reflects the general recognition that the rate of degradation declines with depth and uses a simple approach to estimate this effect. In several of the groundwater studies, this simulation approach generated more degradation than was experimentally observed and resulted in underprediction. For compounds with significant leaching concerns, it may be necessary to obtain one or more experimental measurements of degradation rate in subsoils to ensure reasonable accuracy in simulating the leaching of trace concentrations of pesticides from the root zone. In the absence of experimental rate data, a more rapid rate of decline in degradation rate with depth would help eliminate the underprediction problem.

Rank ordering the absolute value of the logarithms of the best and worst ratios from the ratios for pore-water concentrations gave a median expected accuracy of approximately 11× for simulating pesticide concentrations in soil pore water following the site-specific SOP. The simulation was within a factor of 100 up to 80% of the time.

The prediction of trace-level residues in soil pore water or groundwater is a technically difficult challenge, especially for multiple applications of pesticides at relatively high use rates. However, the results obtained in this modeling exercise indicate that reasonably accurate values can be obtained in many cases. A number of studies have resulted in concentration ratios of approximately 2×, which is excellent agreement for a model such as PRZM 3.12. For NC4L, both cold and site-specific modeling were performed. The cold modeling agreed with the experimental data within approximately 4×, while the site-specific modeling improved this agreement to within a factor of two. This good agreement in this case resulted from the fact that the pesticide degraded rather slowly in the soil profile and the adjustment of the half-life with depth did not significantly affect the predicted concentrations.

The overall agreement between the simulations and the experimental data has been summarized in Table 5. Following the SOP for site-specific modeling, bromide concentrations in soil and soil pore water can typically be simulated within a

Table 5. Summary of median ratios of simulated/experimental values for bromide and pesticide from leaching simulations

Parameter	Depth intervals (cm)	Median ratio (typical expected accuracy)		
		Cold	Site specific	Calibrated
Bromide concentration				
Soil	0–120	3 ×	2–3 ×	ND ^a
Soil pore water	100–300	3 ×	2 ×	ND
Pesticide concentration				
Soil	0–120	4 ×	3 ×	ND
Soil pore water	100–300	Typically >11 ×	11 ×	2–3 ×

^a ND = not determined.

factor of two to three of experimental results. Pesticide concentrations can be simulated within a factor of three in soil in the top 120 cm of the soil profile. Pesticide soil pore-water concentrations can typically be simulated within a factor of 11 to depths up to 360 cm.

Sensitivity analysis

A detailed sensitivity analysis was also performed for three runoff data sets (NC1L, NC2L, and NC3L) using the Plackett–Burman approach. The PB analyses indicated that total application rate, soil bulk density (an indicator of available water-holding capacity), the soil partition coefficient, and pesticide degradation rates were commonly the most sensitive inputs (Table 6).

Uncertainty analysis

Monte Carlo simulations were also performed with GA1L and NC4L to evaluate the effect of uncertainty in the input parameters on the model predictions (Carbone et al., this issue). For GA1L, the predicted soil concentrations seemed to be in good agreement with the measured values. The estimated spatial and temporal profile of pore-water bromide movement through the soil core was highly correlated to the measured data from the soil suction lysimeters, but the model predictions of the magnitude of the bromide pore-water concentration were not accurate. Similar results were obtained for NC4L except that the predicted soil concentrations were not as close to the measured values.

CONCLUSIONS

The initial work conducted by different contractors showed the importance of having a SOP that completely defines the selection of all model input parameters. The most satisfactory way to implement regulatory modeling is through the development of a shell that provides all input parameters related to the scenario, with the user providing only the parameters related to the specific pesticide being assessed.

Simulations with PRZM 3.12 show that reasonable estimates of leaching were obtained in homogeneous soils where preferential flow is not significant. The PRZM 3.12 usually did a good job of predicting movement of bromide in soil (soil and soil pore-water concentrations were generally within a factor of two of predicted values). For simulations based on the best choices for input parameters (no built-in conservatism), predictions of soil pore-water concentrations for pesticides were usually within a factor of three, and soil pore-water estimates were within a factor of 11. When the model input parameters were calibrated to improve the hydrology, predicted pesticide concentrations in soil pore water were usually within a factor of two of measured concentrations. Because of the sensitivity of leaching to degradation rate, the best predictions were obtained with pesticides with relatively slow degradation rates. When conservative assumptions were used to define input pesticide parameters, predictions of pesticide concentrations were usually a factor of two greater than when using the best estimate of input parameters without any built-in conservatism.

Table 6. Results of Plackett–Burman analyses for leaching in three data sets expressed as relative importance of sensitive components

Variable	NC1L		NC2L			NC3L		
	Total	Dissolved	Total	Dissolved	Flux	Total	Dissolved	Flux
Bulk density (AWHC) ^a	22	16	51	77	15	20	14	13
Total applied	26	23				20	19	12
Maximum rooting depth	7	6	3	1	6	8	8	16
Decay rate (layer 1)	20	16	34			7	7	6
Decay rate (layer 2)						4	4	11
Decay rate (layer 3)								2
K _d (layer 1)	4	17		4	60	5	5	
K _d (layer 2)						3	9	6
Runoff curve number 1			4	2	5			4
Runoff curve number 2	3	2	5	4	10			
Pan factor		2	4		2	4	3	8

^a AWHC = available water-holding capacity.

The Rawls and Brakensiek regression equations provided in the PRZM3 manual provided appropriate soil characteristics, at least for the sandy, highly transmissive soils present in all study sites. Soil hydraulic properties from the Rawls and Brakensiek equation [3] are preferred over measurements made on disturbed samples. However, information from undisturbed cores should be used when available.

Based on the results obtained from bromide simulations, PRZM 3.12 is capable of simulating groundwater recharge reasonably well in highly vulnerable agronomic settings when the soil characteristics are appropriately represented. Annual recharge rates of 29 to 59% of precipitation plus irrigation were simulated for the study sites.

The plant uptake of bromide and pesticide was simulated to be a significant dissipation mechanism for highly mobile chemicals with moderate to long soil half-life values. The simulated uptake of pesticides is somewhat higher than would be expected based on the limited data available.

Two of the most sensitive parameters affecting the simulated concentrations of pesticide in soil and soil pore-water were the sorption coefficient and the degradation rate. Appropriate values of these properties must be used in order to obtain reasonable estimates of leaching under field conditions. Moving from cold modeling using worst-case physical properties to site-specific modeling using typical or best-estimate values resulted in significant improvement in agreement with actual field data. For NC4L, the agreement for pesticide concentration in soil pore water changed from a factor of four for cold simulations to a factor of two for site-specific simulations.

For foliarly applied compounds, the extent of canopy interception, degradation on the plant canopy, and foliar wash-off are critical in determining the soil loading. Reasonable estimates of these values for foliarly applied chemicals must be provided for accurate predictions.

The PRZM 3.12 was unable to simulate early detections of pesticide that were attributed to a preferential flow mechanism. Some experimentally observed concentrations were relatively low (less than 1 $\mu\text{g/L}$) and did not result in repeated detections in shallow groundwater. The model was generally unable to simulate this behavior.

RECOMMENDATIONS

A standardized operating procedure should be developed to guide the parameterization of model simulations used in

regulatory assessments. The SOP should provide guidance on selecting appropriate chemical, soil, agronomic, and climatic data to ensure consistent and technically sound modeling results that are acceptable for regulatory purposes.

Because of known deficiencies in the Thornwaite evapotranspiration routine used in PRZM3, daily evapotranspiration was calculated for each site using a modified Penman equation. The evapotranspiration routine in PRZM3 should be upgraded to a more reliable algorithm.

For purposes of model evaluation, hydrodynamic dispersion was set to zero at all depths, and fixed compartment sizes were used at various depths in the soil profile as specified in the SOP. This approach created some degree of numerical dispersion that resulted in band broadening of the concentration profile with depth. To improve the simulation of the movement of pesticides, recommendations for appropriate levels of hydrodynamic dispersion should be developed through use of parallel modeling using a Richards equation-based model coupled with the convection-dispersion equation.

The accuracy of simulating pesticide concentrations at soil depths deeper than 1 m could be improved with additional experimental data on the rate of degradation in subsoils. For some pesticides, more sophisticated degradation kinetics may be needed to accurately simulate movement of trace-level residues to deeper soil depths.

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