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Pesticide Root Zone Model

REVIEW OF THE VALIDATION OF MODELS USED IN FEDERAL INSECTICIDE, FUNGICIDE, AND RODENTICIDE ACT ENVIRONMENTAL EXPOSURE ASSESSMENTS

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Abstract—The first activity of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Environmental Model Validation Task Force, established to increase confidence in the use of environmental models used in regulatory assessments, was to review the literature information on validation of the pesticide root zone model (PRZM) and the groundwater loading effects of agricultural management systems (GLEAMS). This literature information indicates that these models generally predict the same or greater leaching than observed in actual field measurements, suggesting that these models are suitable for use in regulatory assessments. However, additional validation research conducted using the newest versions of the models would help improve confidence in runoff and leaching predictions because significant revisions have been made in models over the years, few of the literature studies focused on runoff losses, the number of studies having quantitative validation results is minimal, and modelers were aware of the field results in most of the literature studies. Areas for special consideration in conducting model validation research include improving the process for selecting input parameters, developing recommendations for performing calibration simulations, devising appropriate procedures for keeping results of field studies from modelers performing simulations to validate model predictions while providing access for calibration simulations, and developing quantitative statistical procedures for comparing model predictions with experimental results.

Keywords—Runoff Leaching Pesticides Pesticide root zone model

INTRODUCTION

Environmental fate models have been used to describe the behavior of crop protection products in the environment since the early 1980s. The pesticide analytical solution model (PESTAN) [1] and early versions PRZM [2] were used by the U.S. Environmental Protection Agency (U.S. EPA) and industry to evaluate potential movement to groundwater. Both GLEAMS [3] and PRZM were linked to the exposure analysis modeling system (EXAMS) [4] to provide estimates of concentrations of crop protection products in surface water resulting from runoff and later spray drift. The use of models was not restricted just to the United States; the earliest version of the pesticide leaching model (PELMO) [5] was released in 1988 for evaluating potential movement of crop protection products to groundwater as part of the registration process in Germany and began to be used routinely.

By 1990, the use of models to predict potential concentrations of crop protection products in the environment had been firmly established. In the United States, both the U.S. EPA and industry routinely used models to estimate potential concentrations in surface water. Although the U.S. EPA currently does not use mechanistic models for assessing risk to groundwater in registration decisions, industry has made extensive use of models to better understand and steward its products. At this time, German regulatory agencies also began to use the results of PELMO simulations as a trigger for conducting lysimeter studies.

In recent years, the importance of modeling for evaluating environmental exposure has continued to increase. In 1992 the U.S. EPA established a new paradigm for the evaluation of ecological risk that recommended computer modeling as a cost-effective exposure assessment tool that could help speed up regulatory decision making (L.J. Fisher, 1992, Decisions on the Ecological, Fate, and Effects Task Force, Memorandum to D. Campt, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, DC). Modeling was also incorporated into the European Union registration process for estimating potential concentrations of crop protection products and their metabolites in surface soil, surface water, and groundwater as well as a trigger for lysimeter or field leaching studies. A database containing cropping information, climatological data, and soil properties—the spatial environmental information system for modeling the impact of chemicals (SEISMIC)—was developed for use in modeling assessments of environmental risk in the United Kingdom [6] during the registration process.

As a result of the increased regulatory use of environmental models, several work groups consisting of regulators, industry, and research institutes/environmental consulting firms have been established to develop procedures for the use of these models in estimating environmental concentrations for regulatory risk assessment. Two of the most active are the FIFRA Exposure Modeling Work Group in the United States and the Forum for International Coordination of Pesticide Fate Models and Their Use (FOCUS) in Europe. Issues that these two groups have faced include establishment of good modeling practices, tiered assessment procedures, standardization of models and procedures used in regulatory modeling, limitations of existing models, and accuracy and precision of existing models used to predict environmental concentrations of crop protection products. The topic of model validation also has been extensively discussed in both groups. In addition, the

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Table 1. A partial listing of model validation or calibration studies conducted with GLEAMS and PRZM

Reference	Models	Locations	Compounds	Soil types
Barrett [19]	PRZM	Kansas, USA	Triasulfuron	Las Animas loamy sand
Cai et al. [20]	PRZM	Jiangsu province, China	Aldicarb	Sandy loam
Carsel et al. [2]	PRZM	New York, USA	Aldicarb	Haven sandy loam
Carsel et al. [21]	PRZM	Florida, USA	Metalaxyl	Blanton fine sand
		Maryland, USA		Marton fine sandy loam
Dibbern and Pestemer [22]	GLEAMS, PRZM, CALF, LEACHM, SESOIL, EQUI	Germany	Terbuthylazine	Loess soil
Dowd et al. [23]	PRZM	Georgia, USA	Lindane	Cecil (clayey thermic, typic kanhapludult)
Flori et al. [24]	PRZM	Po Valley, Italy	Metamitron, chloridazon, ethofumesate, lenacil	Field capacity and wilting point of 33 and 10 vol %
Hegg et al. [25]	PRZM	South Carolina, USA	Aldicarb	Dothan loamy sand
Jones et al. [26]	PRZM	Florida, USA	Aldicarb	Sand and fine sands
Jones et al. [27]	PRZM	Arizona, USA	Aldicarb, aldoxycarb	Sandy loam
		California, USA	Aldicarb	Loamy sand and sandy loam
		Florida, USA	Aldicarb, aldoxycarb	Sand and fine sands
		Indiana, USA	Aldicarb	Silty clay loam
		Maine, USA	Aldicarb	Loam
		Michigan, USA	Aldicarb	Sandy loam
		Nebraska, USA	Aldicarb	Loamy sand
		New York, USA	Aldicarb	Sandy loam
		North Carolina, USA	Aldicarb, aldoxycarb	Sandy loam
		South Carolina, USA	Aldicarb	Dothan loamy sand
		Virginia, USA	Aldicarb, aldoxycarb	Clay loam
		Washington, USA	Aldicarb	Sandy loam
		Wisconsin, USA	Aldicarb, aldoxycarb	Sand, loamy sand, and sandy loam
Jones et al. [28]	PRZM	Nebraska, USA	Aldicarb	Loamy sand
Khan and Green [29]	PRZM	Hawaii, USA	DBCP	Pauwela clay and Hamakuapoko silty clay
Leonard et al. [30]	GLEAMS	Georgia, USA	Fenamiphos	Cowarts loamy sand
Loague [31]	PRZM	Hawaii, USA	EDB	Leilehua (humoxic tropohumults)
Loague et al. [32]	PRZM	Hawaii, USA	EDB	Leilehua (humoxic tropohumults), Wahiawa (tropeptic eutrustox)
Loague et al. [33]	PRZM	Hawaii, USA	DBCP, EDB, TCP	Leilehua (humoxic tropohumults)
Loague et al. [15]	PRZM	Hawaii, USA	Bromide, chlorpyrifos, fenamiphos	Kawaihapai and Wahiawa volcanic soils
Lorber and Offutt [34]	PRZM	North Carolina, USA	Aldicarb	Sandy loam
		Wisconsin, USA		Loamy sand and sandy loam
Mueller [35]	PRZM	Sweden (lysimeter)	Dichlorprop, bentazon	Lanna clay and Mellby sand
Mueller et al. [36]	GLEAMS, PRZM	Georgia, USA	Alachlor, metribuzin, norflurazon	Dothan loamy sand and Appling sandy loam
Nicholls [37]	PRZM, CALF	Sweden (lysimeter)	Bentazon	Nantuna sand
Parrish et al. [38]	PRZM, AGGR	Georgia, USA	Aldicarb, metolachlor, bromide	Loamy sand to sandy loam
Pennell et al. [39]	GLEAMS, PRZM, CLMS, MOUSE, LEACHMP	Florida, USA	Aldicarb, bromide	Astatula sand
Perry [40]	PRZM	Kansas, USA	Atrazine, alachlor, metolachlor, trifluralin, 2,4-D	Eudora silty loam, Eudora sandy loam, and Eudora-Kimo clay
Sadeghi et al. [41]	PRZM	Maryland, USA	Atrazine	Iuka and Hatboro silt loam
Sauer et al. [42]	PRZM	Wisconsin, USA	Atrazine, metolachlor, carbofuran, chlorpyrifos	Plainfield sand
Shirmohammadi and Knisel [43]	GLEAMS	Sweden (lysimeter)	Dichlorprop, bentazon	Mellby sand
Shirmohammadi et al. [44]	GLEAMS	Maryland, USA	Atrazine, carbofuran, cyanazine, dicamba, metolachlor, simazine	Matapeake silt loam
Sichani et al. [45]	GLEAMS	Indiana, USA	Alachlor, atrazine, cyanazine, carbofuran, chlorpyrifos	Clermont silt loam
Smith et al. [46]	GLEAMS, PRZM	Georgia, USA	Atrazine, alachlor, bromide	Lakeland sand
Smith et al. [47]	PRZM, LEACHMP	Laboratory experiments with intact soil cores	Atrazine	Sandy loam
Trevisan et al. [48]	PRZM, BAM, LEACHM	Italy	Atrazine, metolachlor	Loam

Table 1. Continued

Reference	Models	Locations	Compounds	Soil types
Walker et al. [7]	GLEAMS (runoff only), PRZM2, LEACHP, VARLEACH (leaching only)	United Kingdom (six locations), Germany (10 locations), France (six locations), Italy (four locations)	Specific compounds not specified but including alachlor, chloridazon, metribuzin, metsulfuron-methyl, terbuthylazine, runoff simulations only with alachlor	Various soils, runoff simulations with sandy loam and clay loam
Walker et al. [49]	PRZM, VARLEACH, LEACHP	United Kingdom	Alachlor, atrazine, metribuzin	Packed columns of sieved surface soil (75% sand, 10% silt, 15% clay, and 1.91% organic matter)
Zacharias and Heatwole [50]	GLEAMS, PRZM	Virginia coastal plain, USA	Bromide, atrazine, metolachlor	Suffolk sandy loam

European Union has funded a research program on environmental models [7], and a special section of the European-sponsored COST 66 program is devoted to validation of environmental models.

Concern over the validation status and a general lack of confidence in present-day models have limited their use. In the United States, both groundwater and surface water sections within the Environmental Fate and Effects Division of the Office of Pesticide Programs, U.S. EPA, have indicated that validation would improve their confidence in the use of models and that the current models will be used only reluctantly until this level of confidence can be increased. In addition, recent reports from the Aquatic Risk Assessment and Mitigation Dialogue Group [8] and the U.S. EPA Science Advisory Panel (SAP) that it spawned (R.B. Jaeger, 1995, Transmittal of the Final Report of the Joint Science Advisory Board [SAB] and the FIFRA Scientific Advisory Panel on the Aquatic Dialogue Group Report: Pesticide Risk Assessment & Mitigation; meeting held July 17, 1995, memorandum to D.M. Barolo, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, DC) have pointed out the critical importance of having confidence in the results of computer models in the following statements: ''The Office of Pesticide Programs views all modeling, regardless of the level of sophistication, as a screening mechanism. When the models are run conservatively, they can indicate which chemicals are unlikely to pose a hazard to nontarget organisms. However, they cannot be used to determine if a chemical actually poses significant risks to aquatic nontarget organisms. With what level of confidence can these models estimate the range of risk?'' The following questions were also raised:

Are the proposed primary and secondary models adequate for aquatic risk assessments?

Which models are most appropriate, and should additional models be considered?

What is the best approach for model validation?

Therefore, the FIFRA Exposure Modeling Work Group initiated a model validation project in 1995 aimed at justifying the use of modeling tools that are needed for risk refinement under U.S. EPA's new paradigm and to address the issues raised by the SAP. This model validation project was funded and conducted by an industry task force (the FIFRA Environmental Model Validation Task Force) in collaboration with scientists from regulatory agencies, other government agencies, and universities. This project was to be conducted in three phases: a literature review, model validation studies, and final phase (if needed) to address model or data deficiencies. The last two phases were combined.

The scope of this validation effort had to be carefully defined to make the task achievable. Both PRZM and GLEAMS were chosen as the initial models to be tested because these two models are currently used within the U.S. EPA and industry for regulatory exposure assessments (GLEAMS was later dropped since this model was no longer being supported by its developers). Exposure assessments were limited initially to movement in the unsaturated zone for leaching assessments and edge-of-field concentrations for runoff assessments.

The first phase of the model validation project was to review the existing information on model validation of PRZM and GLEAMS. The primary purpose of this literature review was to assess the quality and quantity of existing information on the validation of PRZM and GLEAMS to determine whether the additional model validation studies are needed. A second purpose of the literature review was to collect information that would be useful in planning future model validation studies. This report summarizes both aspects of this literature review and presents the reasons why the FIFRA Exposure Modeling Work Group concluded that more validation research would be useful in improving confidence in models used in regulatory assessments. Other papers in this series describe the results of the leaching and runoff comparison and the statistics used in making these comparisons.

LITERATURE AND VALIDATION OF PRZM AND GLEAMS

A literature search identified 35 articles involving the calibration/validation of model simulations with PRZM and/or GLEAMS with measured data. These calibration/validation studies, summarized in Table 1, use data from seven countries on three continents as well as a number of different compounds.

Because of the varied nature of the papers and the lack of details for both model predictions and measured results, a detailed systematic comparison of model predictions is not possible. In order to provide qualitative information on model performance, the results of each paper are summarized in an appendix to this paper. The majority of the papers indicated good agreement between model predictions and measurements or that the models generally predicted more movement than actually occurred. These results over the wide range of conditions reported in the papers lend general support to the use of PRZM and GLEAMS in the regulatory process, especially for predicting leaching.

Some of the deficiencies in the PRZM and GLEAMS models noted in the 35 papers are summarized in Table 2. Authors' comments on deficiencies were included whether or not such deficiencies were actually reflected in the comparison of predictions with measured data. The larger number of deficiencies listed for the PRZM model is a reflection of the greater use of PRZM in the 35 papers rather than an indication that GLEAMS has fewer deficiencies. In fact, most of the deficiencies noted in the table are common to both models. Similarly, the lack of comments related to runoff is the result of most of the comparisons reported in the papers being for downward movement in the soil profile.

Table 2. A summary of selected deficiencies noted by papers summarized in Table 1

Deficiency	References
PRZM	
Does not consider preferential flow (including residues in lower layers underpredicted due to preferential flow)	Barrett [19], Dowd et al. [23], Loague et al. [15,33], Nicholls [37], Parrish et al. [38], Perry [40], Sadeghi et al. [41], Smith et al. [46], Smith et al. [47], Zacharias and Heatwole [50]
Overestimates downward movement through soils, especially at later sampling intervals	Carsel et al. [2], Hegg et al. [25], Jones et al. [27,28], Loague et al. [15,32,33], Mueller et al. [36], Parrish et al. [38], Pennell et al. [39], Sauer et al. [42], Trevisan et al. [48], Walker et al. [7]
Soil concentration profiles not predicted accurately	Dibbern and Pestemer [22], Jones et al. [27], Loague et al. [32], Parrish et al. [38], Zacharias and Heatwole [50]
Difficulties with estimating dispersion accurately (including effect on peak concentrations and the effect of thickness of soil horizon on simulation results)	Barrett [19], Flori et al. [24], Jones et al. [26], Parrish et al. [38], Walker et al. [7]
Underpredicts persistence in surface soils	Cai et al. [20], Jones et al. [27], Loague et al. [15], Lorber and Offutt [34], Pennell et al. [39]
Does not consider upward movement due to capillary transport	Loague et al. [15], Walker et al. [7]
Estimation routines for evaporation are too simple and inaccurate	Walker et al. [7], Zacharias and Heatwole [50]
Simplicity of degradation description (including degradation rate independent of soil moisture and temperature)	Loague et al. [15], Mueller et al. [36], Walker et al. [7]
Soil hydraulics are too simplistic for vadose zone applications or for less porous soils	Smith et al. [46]
Poor results for uncalibrated simulations of deep leaching (about 20 m)	Loague [31]
GLEAMS	
Does not consider preferential flow (including residues in lower layers underpredicted due to preferential flow)	Shirmohammadi and Knisel [43], Sichani et al. [45], Smith et al. [46], Zacharias and Heatwole [50]
Overestimates downward movement through soils, especially at later sampling intervals	Mueller et al. [36], Pennell et al. [39], Shirmohammadi et al. [44]
Soil concentration profiles not predicted accurately	Dibbern and Pestemer [22], Zacharias and Heatwole [50]
Degradation rate is independent of soil moisture	Mueller et al. [36]
Underestimates surface runoff	Shirmohammadi et al. [44]
Model cannot handle partially frozen soil	Shirmohammadi and Knisel [43]
Runoff parameters are hard to obtain for soils located outside the United States	Walker et al. [7]

EVALUATION OF PRZM AND GLEAMS VALIDATION STUDIES

After review of the papers listed in Table 1, the FIFRA Exposure Modeling Work Group decided that additional comparisons of field data and model predictions would be useful to supplement existing studies in helping improve confidence in the regulatory use of environmental models for predicting leaching and runoff. Several observations contributed to this decision. None of the published studies used the current version of either model (this is especially relevant to PRZM, where the runoff routines have been changed significantly). Very few of the studies focused on runoff losses (most studies focused on the mobility of crop protection products in the soil profile). The number of studies having quantitative validation results was minimal. Since few of the published studies consider model validation the primary purpose of the field experiments, often data sets were not as extensive as would be desirable for model validation. Modelers were aware of field results in most of the studies (although in some of the studies where the field results were known, modelers claimed to make no adjustments to the input parameters). Therefore, in these studies the comparisons of model predictions and experimental measurements could be considered calibration since in model validation the modeler should have no knowledge of the field results to prevent biasing the selection of input parameters.

Van den Bosch and Boesten [9] independently reviewed validation efforts with PRZM, leaching estimation and chemistry pesticide (LEACHP), GLEAMS, and PELMO. For both PRZM and GLEAMS, they assessed the quality of the validation efforts in six papers (all of which are included in Table 1). They concluded that the validation status of PRZM and GLEAMS was low, especially at concentrations near the European 0.1-μg/L drinking water guideline.

ISSUES IN VALIDATION RESEARCH

The literature review also highlighted some areas requiring careful consideration in a model validation study.

Model validation versus validation of the regulatory modeling process

In regulatory applications, the purpose is usually to predict the amount or concentration of a compound in runoff water or groundwater at a site where extensive research has not been performed. This is in direct contrast to the model developer who usually is trying to fit predictions to existing data obtained from a field experiment. For regulatory applications, the selection of some model parameters (such as soil properties, degradation rates, sorption parameters, or compartment sizes) may not be as straightforward as for the model developer. In regulatory applications, many of the parameters must be ob-

tained from information in databases or estimated from laboratory studies or studies performed at different locations. Since the selection of model input parameters is usually one of the most important factors affecting the accuracy of predicted results, the validation process must be designed so it is not merely an exercise testing the ability of the modeler to select proper input parameters [10]. However, an incorrect assessment in a regulatory application is equally wrong whether resulting from a poor selection of input parameters or from poor model performance. If an incorrect assessment results from the poor choice of input parameters, this is not necessarily an indication of poor model performance. However, if an input parameter to a specific model cannot be selected with sufficient accuracy to ensure satisfactory model predictions, then this model may not be suitable for use in regulatory applications.

Therefore, the validation of a regulatory application of a model must include validation of the procedures for selecting input parameters. This requires that these procedures be exactly described to eliminate (or minimize) the influence of the modeler. As a result, validation of a regulatory application requires an additional step beyond the traditional validation process when the model developer validates (or calibrates) the model by comparing its predictions with available experimental data. In the second step, both the procedure for selecting input parameters and the resulting model predictions are tested. This two-step validation process of testing the model followed by testing of the modeling procedure is necessary to avoid misleading results since the process of selecting the input variables can compensate for faults in a model.

The importance of the modeling process was shown in a ring test of the PRZM, LEACHP, and VARLEACH models [11] that demonstrated that differences in judgment even with experienced modelers can significantly affect model predictions. In this test, five modelers were given the same description of a field experiment and were then asked to model the movement of an experimental pesticide to obtain information on the concentration of the pesticide in the soil profile at 220 d after application and in the soil-water at a depth of 1 m. The authors noted that no two sets of predicted results for a given model were exactly the same. This result is not surprising given the wide variation in the assumed values for many of the input parameters. For example, all five modelers used five different assumptions about the thickness of the various soil segments. The authors pointed out that ''the variation between five simulations was similar to that associated with the measurements of pesticide behavior in the field'' and that this user dependence of modeling should be an important component of evaluating model output. The authors concluded, ''Even where predicted results give an acceptably accurate simulation of field behavior, the findings of this ring test suggest that claims of validity will be misleading unless it can be proved that similarly accurate results would be obtained by a number of independent users'' [11].

Acceptability of model predictions

The acceptability of model predictions compared with field measurements is influenced by use in a regulatory setting. It is critical that regulatory modeling procedures do not significantly underpredict the movement of residues into groundwater or surface water, so that unexpected impacts on the environment do not occur. Model predictions indicating greater movement than what actually occurs are not a problem as long as unnecessary restrictions do not result from the risk assessment. The challenge is to develop a modeling process that produces a conservative set of results while minimizing the difference between model predictions and experimental results.

Quantitative procedures for comparing model predictions with observed values

Most validation/calibration comparisons in the studies in Table 1 are qualitative, using statements such as the data generally agree with the model predictions. Obtaining statistical descriptions of these comparisons is more difficult; however, a number of papers (e.g., Haan et al. [12], Parrish and Smith [13], Walker et al. [7], Boekhold et al. [14], Loague et al. [15]) have been published that examine various procedures for quantifying the ability of model predictions to describe observed values. Boekhold et al. [14] discuss five approaches to assessing model performance: factor *f* approach, comparison of confidence intervals, comparison of mean values, comparison of variances, and graphical methods. For their validation work with pesticide leaching and accumulation (PESTLA), they chose the factor *f* approach, which is based on the capacity index approach described by Parrish and Smith [13]. Walker et al. [7] present several different indices for expressing the overall fit and descriptions of degradation and movement. Loague et al. [15] suggest that summary variables that can be obtained from concentration variables include total mass, center of mass, peak concentration, time for a critical concentration to leach to a depth of interest, and depth of the leaching front and advocate the use of root mean square error as a statistical measure of model performance.

The choice of variables for comparison also must consider the regulatory application. For example, if a model correctly predicts the amount of a chemical moving to the water table but the timing is off a couple of days, the error in timing makes no difference in a risk assessment. Obviously, a model correctly predicting runoff as a function of time within a rainfall event is desirable, but a model that gets only the total loss during an event correct may be adequate in a regulatory application. A model that correctly predicts movement to the water table may be acceptable even if it does not correctly predict soil concentration profiles. However, the fundamental validity of the model processes must be maintained. For example, correctly predicted runoff or leaching losses of crop protection products must be considered irrelevant if water movement is not adequately described. Armstrong et al. [16] describe a multistep validation process that considers water movement, tracer movement, and then movement of the specific chemical.

Separation of modeler from field data

To maximize the credibility of a validation exercise that includes the selection of input parameters, the modeler should have no knowledge of the field results. Otherwise, the validation work will probably be characterized as calibration.

Calibration simulations

If the predictions based on the initial set of input parameters do not provide acceptable agreement (as defined by the objectives of validation exercise), a set of calibration simulations may be performed to help determine whether the source of error is the result of the model or the selection of input parameters. Such calibration should not consist of a simplistic regression of input parameters to minimize difference between

observed and predicted values since most water quality models have enough adjustable parameters to fit a limited set of field observations [12] but rather a systematic variation of input parameters constrained to feasible ranges. Results of sensitivity analyses (such as those described by Fontaine et al. [17] and Walker et al. [7]) can be useful tools in performing such simulations. Calibration simulations should normally be performed as a two-step process: first calibrating parameters affecting movement of water to optimize the hydrology and then changing chemical-specific properties to best describe chemical movement. Haan et al. [12] describe a statistical protocol that transforms parameter uncertainty into prediction uncertainty using probability density functions in order to ''distinguish a good fit that is based on artificial manipulation of an overparameterized model from a good fit that is based on an accurate description of the processes that control contaminant transport.''

Improving the quality of field studies used to validate models

Additional site-specific information (e.g., more detailed soil information, application of a tracer, or soil-specific laboratory sorption and degradation studies) may be useful when a field study is being used to obtain data for model validation. Smith et al. [18] review some of the items that should be considered when conducting field studies for model validation. This subject is important when reviewing existing data sets for inclusion in validation studies as well as in the planning of new studies to be used in model validation.

CONCLUSIONS

Comparisons of PRZM and GLEAMS predictions with field measurements have been made in a number of studies found in the literature. Most of these studies demonstrated that PRZM can be a useful tool in assessing leaching. Although PRZM predictions in surface soil in the early portions of a study are not particularly useful, its overpredicting of residue movement in later stages of an experiment provides conservative assessments suitable for use in estimating potential leaching in regulatory risk assessments. However, because of various limitations of the available literature studies, additional validation research to supplement existing studies would improve the confidence in the runoff and leaching predictions of PRZM and GLEAMS in regulatory applications. This validation research should carefully consider the following: (1) improving and standardizing the process for selection of input parameters (2) developing procedures for performing calibration simulations to determine whether differences between model predictions and field measurements are the result of model inaccuracies or the choice of input parameters (3) devising appropriate procedures for keeping results of field studies from modelers performing simulations to validate model predictions while providing access when calibration simulations are being performed (4) developing quantitative statistical procedures for comparing model predictions with field measurements (5) identifying the combinations of soil properties and weather patterns under which the models provide estimates that are sufficiently accurate for use in regulatory decision making (6) identifying specific areas where each of the models can be improved (7) identifying the type and quantity of measurements that must be made in field studies to ensure suitability for model calibration and/or validation.

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APPENDIX

Summaries of individual papers

The following paragraphs provide a summary of each of the 35 articles listed in Table 1, including relevant conclusions of the papers' authors. See text for explanation of model names.

Barrett [19] examined the leaching of triasulfuron residues in a loamy sand in Kansas, USA, using field results and pesticide root zone modeling (PRZM). The author concluded, ''Modeling of triasulfuron movement with PRZM resulted in a simulation that predicted accurately the time of appearance of triasulfuron residues at lower depths (~60 days) and the mass flux (nearly 10% of applied moving to shallow groundwater within 6 months after application), but underestimated dispersion and therefore overestimated peak concentrations in shallow ground water by a factor of two or three.'' The author noted that PRZM does not simulate preferential flow in structured soils.

Cai et al. [20] examined the leaching of aldicarb residues from a banded application in a cotton field with sandy loam soil in Jiangsu province, China, and compared the results to predictions made by the PRZM model (Ver 1). The model appeared to underpredict the concentration in the soil during the early samplings (a factor of two to three at 30 d); however, the authors noted that ''this may be due to the fact that the field soil sampling core was collected immediately beneath the aldicarb application point, so that the aldicarb residue concentration cannot represent the field-average concentration.'' If converted to ''field-average concentrations, . . . , the predicted results would be close to the measured field concentrations. With increasing sample depth and time, the two results

tend to be more consistent. This is due to aldicarb diffusing and moving downward in the form of a pyramid beneath the application point with lateral dispersion producing a more even aldicarb distribution in the soil profile.''

Carsel et al. [2] examined the use of the PRZM model (Ver 1) to predict the leaching of aldicarb residues in New York, USA. A simulation was first performed that did not use any site-specific data and thus was run as a calibration-free assessment. The model accurately predicted the maximum concentration within less than 10% of the measured value but overestimated the amount of movement through the soil. A series of calibration runs was performed on the individual soil core results and the average of the soil core results. In all three cases, increasing the adsorption coefficient to twice the uncalibrated values and making small adjustments in the degradation rates resulted in predictions of peak concentrations within less than 10% of the measured values and all other values within a factor of two to three.

Carsel et al. [21] compared PRZM (Ver 1) predictions with measured soil concentrations of metalaxyl from sites in Florida and Maryland, USA. The model overpredicted the amount of leaching early in the study at the Florida site (26 d after application) but provided an excellent fit (predicted values were within 30% of measured values) at 55 and 85 d after application. At the Maryland site, both the observed and the predicted values indicated that residues remained in the top 15 cm of the soil. The predicted concentrations were within a factor of two of the observed values, with a general overprediction of the concentrations.

Dibbern and Pestemer [22] examined the ability of the GLEAMS, PRZM, CALF, LEACHM, SESOIL, and EQUI models to describe the leaching of terbuthylazine through a loamy soil in Germany. The GLEAMS model greatly overpredicted the amount of leaching, as indicated by the depth of the peak (predicted peak at 15–20 cm vs observed at 0–3 cm) and greatly underpredicted the concentration of the residues in the upper layers. The PRZM model slightly overpredicted the movement (predicted peak at 3–6 cm vs observed at 0–3) and was able to predict lower concentrations within a factor of two to three, except for a measured value at 24 to 30 cm, which was three times greater than the measured value at 18 to 24 cm.

Dowd et al. [23] compared the dissipation of lindane residues in a forest in Georgia, USA, with predicted values from the PRZM model (Ver 1). The PRZM model was not able to accurately predict the measured concentrations below the top 10 cm. The authors felt that this was probably due to the inability to model preferential flow, which is probably a very important pathway in water movement in the highly structured soils commonly encountered in forests.

Flori et al. [24] examined the leaching of metamitron, chloridazon, ethofumesate, and lenacil residues in a field in the Po Valley of Italy using PRZM (Ver 1). The authors noted that the soil horizon thickness parameter (THKNS) had a major effect on predicting the mobility and persistence of the compounds.

Hegg et al. [25] studied the leaching of aldicarb residues in a Dothan loamy sand in South Carolina, USA. The field data and the predictions of PRZM (Ver 1) were in good agreement since they indicated that detectable residues would be found only in the top 0.6 m of soil.

Jones et al. [28] examined the leaching of aldicarb residues at two sites in Florida using the PRZM model (Ver 1). The PRZM underestimated the depth of the peak at an early time point, two weeks after application (~60 vs 160 cm) but only slightly underestimated the peak locations at six and 11 weeks after application (~210 vs 260 cm and 225 vs 260 cm, respectively). The authors indicated that these slight underpredictions were due to dispersion.

Jones et al. [29] compared the predicted leaching of aldicarb and aldoxycarb residues using the PRZM model (Ver 1) with field data from Arizona, California, Florida, Indiana, Maine, Michigan, Nebraska, New York, North Carolina, South Carolina, Virginia, Washington, and Wisconsin, USA. The maximum leaching depth, defined as the depth below which the average concentration was less than the sensitivity of the analytical method, was compared for 34 field plots. In most cases where the measured leaching depth was greater than 60 cm, the model tended to overpredict the depth of leaching, although the overprediction was generally less than 50%, that is, observed depth of 2 m versus a calculated depth of 3 m. There were two sites, in Arizona and California, where this did not hold; both used flood or furrow irrigation.

Jones et al. [28] investigated the leaching of aldicarb residues through sandy soil in Nebraska and compared the measured values with those predicted by PRZM (Ver 1). The model predictions were conservative in that they tended to slightly overpredict the movement of aldicarb residues, with the predicted values being within a factor of two to three of the measured values.

Khan and Green [29] modeled the leaching of dibromochloropropane (DBCP) in two pineapple fields in Hawaii, USA. The PRZM (Ver 1) correctly predicted the depth of the peak concentration and the general shape of the concentration profile with depth, although it could not predict the magnitude of the concentration. The authors indicated that this was expected because PRZM does not take into account volatilization, which is a major dissipation mechanism for DBCP (later versions of PRZM do include volatilization).

Leonard et al. [30] conducted studies designed to validate the GLEAMS model using field data from Georgia, on fenamiphos and its sulfoxide and sulfone metabolites. Estimated values were used for the hydrology and erosion parameters as well as estimated degradation and adsorption values for the three compounds. The authors concluded that ''GLEAMS-simulated mass of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in the root zone compared favorably with field data within the variability of the data. Simulated and observed concentrations with depth in the soil at selected dates also closely corresponded.'' The predictions of the GLEAMS model slightly overestimated the total amount of fenamiphos and its metabolites in the soil profile but were within the confidence intervals of the measured data.

Loague [31] calibrated the PRZM model (Ver 1) for the leaching of ethylene dibromide (EDB) in a pineapple field on Oahu, Hawaii, using two years of data. The authors examined several methods to compare the results of measured values with modeling results. These include such factors as (1) total mass, (2) center of mass, (3) peak concentration, (4) time for a specific concentration to leach to a certain depth, (5) depth to peak concentration, and (6) depth to the leaching front. They concluded that if they used the data from one year to calibrate the model, the results were poor for the other year. The authors concluded that the poor fit was not surprising because of the deep leaching being simulated and potential problems with the data sets.

Loague et al. [32] used PRZM (Ver 1) to evaluate the leaching of ethylene dibromide (EDB) in two pineapple plantations in Hawaii. This paper is the first of a series of three papers. The results of the comparisons with the data are described in the later two papers in the series, which have also been summarized.

Loague et al. [33] examined the leaching of 1,2-dibromo-3-chloropropane (DBCP), ethylene dibromide (EDB), and 1,2,3-trichloropropane (TCP) in structured soils in Hawaii using the PRZM model (Ver 1). The authors of the paper recognized they were attempting to use the model under conditions (deep soils, volatilization) for which the model was not designed. Despite these severe limitations, when adjustments were made for degradation and/or volatilization, the predicted peak concentrations of EDB in soil were within a factor of two to four of the measured concentrations, with the model overestimating the depth of leaching. Similar results were found for both DBCP and TCP in the top 12 m of the soil, but the model greatly overpredicted the concentrations from 12 to 20 m.

Loague et al. [15] used the PRZM model (Ver 1) to examine the leaching of bromide, chlorpyrifos, and fenamiphos in two sites in Hawaii. The PRZM was generally able to model the movement of bromide and generally gave results that were within a factor of two of the measured results. In one of the test plots, the model was not able to predict the upward movement of bromide by capillary rise.

Lorber and Offutt [34] examined the use of PRZM (Ver 1) in predicting leaching of aldicarb residues in North Carolina and Wisconsin as an assessment tool for predicting the potential for groundwater contamination. A comparison of observed versus predicted values for aldicarb residues at three sites with nine distinct scenarios was excellent, with observed versus predicted values generally within a factor of two and always within a factor of five.

Mueller [35] modeled the leaching of dichlorprop and bentazon through lysimeters in Sweden using PRZM (Ver 1) and compared the results to field data. Bentazon movement was examined in sand and clay, while dichlorprop movement was studied in clay, sand, and loam soils. Two significant modifications were made to two sets of hydrologic parameters. The initial soil-water content was adjusted to match the predicted time of first water discharge to the actual data. Also, the difference between field capacity and wilting point was adjusted in each soil horizon. When these two modifications were made, an excellent agreement was observed between the measured and calculated volume of water leaching from all five soils during one year. The loss of bentazon from the soil columns was accurately predicted over the year of the study, with less than a 10% difference between the observed and predicted values after one year. For dichlorprop, PRZM predicted no dichlorprop in the leachate, while dichlorprop was actually present in the leachate. This difference between predicted and observed was probably the result of significantly slower degradation occurring in the lysimeter than in the laboratory studies.

Mueller et al. [36] examined the ability of the PRZM (Ver 1) and GLEAMS (Ver 1.8.55) models to predict the leaching of alachlor, metribuzin, and norflurazon in a loamy sand soil in Georgia. Both models accurately predicted the observed concentrations of norflurazon in the soil profile with the predicted values equivalent to the observed values at 84 d. For alachlor and metribuzin, both models accurately predicted the observed concentrations in the soil profile within the first 20 d, then overpredicted the movement through the soil profile. For metribuzin, the observed concentrations were within a factor of three for the first 20 d and within a factor of four by day 40, the last day at which measured values were above the limit of detection. For alachlor, the observed concentrations were within a factor of four for the first 20 d and within a factor of seven by day 40, the last day at which measured values were above the limit of detection.

Nicholls [37] studied the movement of bentazon through lysimeters containing a sand using the PRZM and CALF models. The PRZM (Ver 1) was able to accurately predict the total amount of leachate produced over 325 d and the total amount of bentazon leached. Unfortunately, the model overpredicted the amount of leachate produced early in the experiment, but this was due to the modelers not simulating the presence of a crop in the lysimeter, which would have increased the amount of evapotranspiration, and not simulating the two months of freezing conditions, which allowed for the model to predict leaching even though this did not occur under the experimental conditions. Bentazon appeared in the leachate earlier than predicted by the models.

Parrish et al. [38] used the PRZM (Ver 2) and AGGR models to examine the leaching of aldicarb, metolachlor, and bromide in a four-year field study in the Dougherty Plain area of southwestern Georgia. For metolachlor, which was studied for three years, the predicted values using PRZM were within a factor of two of the measured value for over 90% of the measured values and within a factor of five for all of the measured values (up to 10 per year). The few times when the predicted value was greater than twice the measured value occurred when the observed values were very small. For aldicarb, which was studied for four years, more variability was observed in the comparisons. The predicted values using PRZM were within a factor of two of the measured value for 60 to 100% of the measured values and within a factor of five for 82 to 100% of the measured values (up to 15 per year). The model tended to overpredict the movement of aldicarb through the soil profile, which lowered the goodness of fit, especially when very low measured residues were detected. Modeling the movement of bromide was more difficult. The authors concluded, ''The lack of mass balance in bromide suggests that preferential flow is a significant factor that may adversely affect the viability of advection-dispersion models for these soils. Nonetheless, both PRZM and AGGR accurately predicted bromide peak concentrations down to 1 meter, but diverged considerably thereafter by predicting deeper movement than actually occurred.''

Pennell et al. [39] examined the leaching of aldicarb and bromide through a sand in Florida using GLEAMS (Ver 1.8.54) and PRZM (Ver 1). The predicted PRZM values were within approximately 30, 45, and 70% of the measured values for bromide, aldicarb, and total aldicarb related residues, respectively. GLEAMS underestimated the dissipation of bromide and total aldicarb-related residues in the root zone and overpredicted the solute concentrations near the soil surface.

Perry [40] examined the leaching of atrazine, alachlor, metolachlor, trifluralin, and 2,4-D residues in Kansas and compared them to results predicted by the PRZM model (Ver 1). The authors indicated that ''the PRZM was best calibrated to the observed data for the three soil types by treating the sand-and-silt fraction as sand and adjusting the organic-carbon content by a factor of 0.1.''

Sadeghi et al. [41] compared the effects of conventional versus no-till management systems on the leaching of atrazine during three growing seasons in silt loam soils in Maryland using field results and the PRZM model (Ver 1). The modeling results overpredicted, by less than a factor of two, the levels in the top 10 cm of the soil. The modeling was not able to predict the low concentrations, generally less than 25 ppb, detected in 10-cm increments from 20 to 50 cm.

Sauer et al. [42] examined the leaching of atrazine and metolachlor in a field study in Wisconsin and the movement of carbofuran and chlorpyrifos in intact soil columns. The results of the experiments were compared to results from the PRZM model (Ver 1). Starting after the 14-d sampling point, PRZM predicted deeper movement of atrazine residues than were observed. Similar results were found for metolachlor. One of the problems of this study was the lack of mobility of the compounds in the field, which was due to the low rainfall during the study. Shirmohammadi and Knisel [43] examined the leaching of dichloprop and bentazon through lysimeters in Sweden using the GLEAMS model (Ver 2.0). It was necessary to make several major modifications to parameters dealing with hydrology since lysimeters were being modeled rather than a field scale experiment, which is what GLEAMS was designed to simulate. The experimental values showed considerable variability, with three of the four lysimeters not producing any leachate during any given sampling period.

Shirmohammadi et al. [44] used the GLEAMS model to examine the leaching of atrazine, carbofuran, cyanazine, dicamba, metolachlor, and simazine in no-till and conventional tillage systems in Maryland. Predicted leaching of the pesticides was compared to the results of groundwater concentrations of the pesticides. With only one exception, the model predicted higher concentrations than were observed, with the predicted values ranging from two to 10 times the observed values.

Sichani et al. [45] compared the leaching and runoff of alachlor, atrazine, cyanazine, carbofuran, and chlorpyrifos through a tiled drainage field in Indiana with predicted values using the GLEAMS model. The model was able to predict fairly well the total mass of the compounds that moved through the soil profile as well as the overall timing of the movement, except for the first observed values in the drainage after the application. For atrazine, the predicted values were less than the observed values, with the peak differences being within a factor of two to four. For carbofuran, the predicted values were greater than the observed values, with the peak differences being within a factor of two. For cyanazine, the predicted values were within a factor of two to four of the observed values.

Smith et al. [46] compared the leaching of atrazine, alachlor, and bromide on a Lakeland sand in Georgia using GLEAMS (Ver 1.8.55) and PRZM (Ver 2). The authors concluded, ''In all cases, the measured and predicted peak concentrations agreed to within an order of magnitude, and in most cases they agreed to within a factor of 2 or 3.''

Smith et al. [47] compared the leaching of atrazine through intact soil cores in the laboratory with predictions made using the PRZM model (Ver 1). It was necessary to calibrate the model in order to obtain the proper hydrologic balance. The ability of the model to predict the concentration of atrazine in the leachate from four columns varied widely, as did the observed values (measured value of 10.7, 0.1, 0.5, and 1.4 g/L vs predicted values of 0.0, 0.1, 0.3, and 0.1 g/L, respectively). The PRZM underpredicted atrazine concentrations in the upper and lower layers of the soil but overpredicted the concentrations at the middle layers. In three of the four columns studied, the authors noted evidence of preferential flow.

Trevisan et al. [48] used the PRZM model (Ver 1) to examine the leaching of atrazine and metolachlor in a field study in Italy. The model was generally able to predict the experimental data, especially in the top 10 cm. The authors indicated that PRZM underestimated residue levels at 30 cm early in the study, but then agreement was good later in the study. No quantitative indication was seen of the actual values, so that a better comparison could not be made.

Walker et al. [7] examined the ability of several models (GLEAMS, runoff only; PRZM, Ver 2; LEACHP; and VARLEACH, leaching only) to predict the movement of pesticide residues using data from several countries (United Kingdom, six locations; Germany, 10 locations; France, six locations; Italy, four locations). A wide variety of compounds, including alachlor, chloridazon, metribuzin, metsulfuron-methyl, and terbuthylazine, were used. The PRZM2 tended to overpredict, especially at later sampling times, the movement of residues, especially in lysimeter studies. Based on 63 comparisons of the German and French data, PRZM overestimated the mean leaching depth in 25% of the observations, was within 20% of the measured value in 20% of the observations, and underestimated leaching by more than 20% in 55% of the observations. The PRZM overestimated the residual mass in 25% of the observations, was within 20% of the measured value in 55% of the observations, and underestimated leaching by more than 20% in 25% of the observations. A wide difference was observed in the ability to predict the values from the French versus the German data sets as measured by model efficiency, with the French data giving 49% acceptable values, while the German data only gave 28% acceptable values. GLEAMS validation efforts were limited to runoff data from one site for three seasons.

Walker et al. [49] compared the results of lysimeter studies with alachlor, atrazine, and metribuzin to predicted values from PRZM (Ver 2), VARLEACH, and LEACHP. For all three compounds, PRZM2 overpredicted the movement at later points (112 and 156 d) in the study. Although PRZM underpredicted the concentrations of the compounds in the leachate at early sampling events, because of its inability to predict preferential flow, the cumulative losses predicted were within 20% of the measured losses over the length of the study for metribuzin, with no data given for the other compounds.

Zacharias and Heatwole [53] examined the leaching of bromide, atrazine, and metolachlor over a five-month period in a field plot that had been planted to no-till corn in the coastal plain of Virginia using GLEAMS (Ver 1.8.55) and PRZM (Ver 2). The modeling used uncalibrated and calibrated simulations. Both the GLEAMS and PRZM models were unable to accurately predict the initial movements of the bromide tracer. The authors felt that this was due to both models' inability to model preferential flow.