# Prediction of Pesticide Losses in Surface Runoff from Agricultural Fields Using GLEAMS and RZWQM

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**Abstract.** *Seepage zones have been shown to be of critical importance in controlling contaminant export from agricultural watersheds. To date, no multipurpose agricultural water quality model has seepage zones incorporated into its process-level representations. We chose to test two widely used models of agricultural water quality, the Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) and the Root Zone Water Quality Model (RZWQM), by seeing how well each predicted solution pesticide concentration and loss in surface runoff from two agricultural fields: one with and one without seepage zones. Daily simulated atrazine and metolachlor concentration and loss in surface runoff from both calibrated and default (or non-calibrated) GLEAMS and RZWQM were compared with three years of measured data from the two fields. The results of the study show that GLEAMS and RZWQM using default input parameters were not capable of predicting atrazine and metolachlor concentration and loss in surface runoff from the fields with and without seepage zones (modeling efficiency <0.16). Site-calibrated GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from both fields (coefficient of determination >0.52, index of agreement >0.83, and modeling efficiency >0.53) and can be used for assessing the effects of seepage zones on pesticide loss in surface runoff from agricultural fields.*

***Keywords.*** *Atrazine, Metolachlor, Model, Pesticides, Predicted, Surface runoff.*

Although variable source area processes (seepage zones) have been well studied in forested and range land systems (Grayson and Blöschl, 2001; Walter et al., 2000), the impacts of these processes on agricultural processes have only recently been closely investigated and only in a limited number of settings (Gburek and Sharpley, 1998; Daughtry et al., 2001). Seepage zones occur when subsurface flow pathways emerge on the surface and are common to agricultural lands bordering streams; however, their impacts on agricultural water quality have not been effectively modeled because of lack of data (Gburek et al., 2002; Gish et al., 2001). Seepage zones can strongly influence surface runoff and chemical fluxes from agricultural fields. Studies have shown that watersheds with seepage zones generated more surface runoff and lost more nitrate-nitrogen and pesticides than watersheds without seepage zones (Gburek and Sharpley, 1998; Walthall et al., 2000). Some subsurface flow pathways come close to the soil surface (but do not emerge on the surface) and increase soil moisture content in the topsoil layers. The increased soil moisture contents in the top layers have been found to impact chemical loss and crop yield (Gish et al., 2005). These seepage zone studies demonstrate the dramatic impact that subsurface stratigraphy can have on surface runoff-chemical fluxes, even when soil properties, yield distributions, and climate are similar.

Computational agricultural water quality models provide an opportunity to evaluate the response of soil and water resources to different farming practices, climatic conditions, soil, and topographic properties in an efficient and cost-effective way. However, the reliability of these models depends on how well each process is represented and on the accuracy of the model parameters used. To determine if the model adequately simulates the real conditions and to gauge model usefulness, an assessment of its performance for a variety of soil, crop, management practices, hydrologic, and climatic conditions is needed.

Correlation and correlation-based measures (e.g., $r^2$) have been widely used to evaluate model performance by measuring the "goodness-of-fit" of hydrologic and water quality models. However, correlation-based measures are oversensitive to extreme values (outliers) (Legates and McCabe, 1999; Ott, 1993). In general, a single evaluation measure can indicate that a model is a good predictor, when in reality it is not. Because of these limitations, additional evaluation criteria, e.g., relative percent error ($E_r$), coefficient of efficiency (E), index of agreement (*d*), root mean square error (RMSE), and absolute maximum error ($|E_{max}|$), have been proposed by different researchers to assess model performance (Buchleiter et al., 1995; Haan et al., 1993; Legates and McCabe, 1999; Chinkuyu et al., 2004).

In this study, two well-known and comprehensive models, the Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) v. 3.0.1, and the Root Zone Water Quality Model (RZWQM) 98 v.1.0.2000.830, were calibrated and evaluated using data from two agricultural fields

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(field C with seepage zones, and field A without seepage zones) at the USDA Beltsville Agricultural Research Center in Beltsville, Maryland. Although GLEAMS and RZWQM do not explicitly have seepage zone processes incorporated into them, these models were chosen for this study because: (1) they have not been evaluated on agricultural fields with seepage zones due to lack of data, (2) no agricultural water quality models have saturated and seepage zone processes incorporated into them, (3) these models are widely used to evaluate agricultural management practices under different soil, climatic, and hydrologic conditions, and (4) the hydrologic and chemical concepts of these models are passed on to other larger-scale models such as the Soil and Water Assessment Tool (SWAT) model (Arnold et al., 1998). Few scientists have the equipment to identify, define, and study subsurface flow pathways and seepage zones in agricultural lands, and thus there is little data to develop or test models for seepage zones. To our knowledge, no agricultural nonpoint-source pollution model represents saturation and seepage zone processes in addition to the important biological and chemical controls on agricultural water quality (e.g., nutrient dynamics and pesticide processes).

The main objective of this study was to use different evaluation techniques to determine whether GLEAMS and RZWQM can adequately model atrazine and metolachlor concentration and loss in surface runoff from agricultural fields with and without seepage zones.

## Background on the GLEAMS Model

The GLEAMS model was developed to simulate edge-of-field and bottom-of-root-zone loadings of water, sediment, pesticides, and plant nutrients from complex climate-soil-management interactions (Knisel, 1993). As a field-scale water quality model, GLEAMS has been evaluated for nutrient and pesticide losses under different conditions and management practices with varied successful and unsuccessful results (Chinkuyu and Kanwar, 2001; Bakhsh et al., 2000). The ability of GLEAMS to represent variable source area processes (seepage zones) is limited to generating compensating hydrologic parameter values to represent these processes in a limited manner. Thus, there is no direct representation of chemical loss through seepage zones in GLEAMS.

Although GLEAMS has different components, only the pesticide component is of interest to this study. For detailed description of the other components, such as hydrology, nutrients, sediments, and erosion, refer to Knisel (1993). The pesticide component of GLEAMS simulates pesticide losses in surface runoff, sediments, and percolation below the root zone. Pesticide application methods include: surface application, soil incorporation, injection, irrigation water (chemigation), and application to foliage or crop canopy. Pesticides washed off from plants result in changed concentrations in the surface soil. The pesticide concentration in the surface soil determines the amount that is available for extraction into surface runoff and/or movement into the soil profile. Pesticide adsorption characteristics are coupled with the water storage routing technique of the hydrology component to route pesticides within and through the root zone. Upward movement of pesticides and plant uptake are simulated with soil evaporation and plant transpiration, respectively. Pesticide distribution between the solution phase and the soil phase is a simple linear adsorption isotherm. The partitioning coefficient is based on percent soil organic matter and is assumed to be linear with concentration. Pesticide dissipation or degradation rate in the soil is assumed to obey first-order kinetics. The degradation rate used in GLEAMS is a "lumped" parameter that describes the net effect of many individual processes. Degradation processes include volatilization, photolysis, hydrolysis, biological degradation, and chemical reactions.

## Background on the RZWQM Model

The USDA-ARS Root Zone Water Quality Model (RZWQM) is a physically based simulation model designed to predict hydrologic and chemical responses, including potential groundwater contamination of agricultural management systems (Ahuja et al., 2000; RZWQM Team, 1995). RZWQM is sufficiently comprehensive to predict the relative response of plants and interactions among system processes to changes in water balance, temperature, nutrient cycling, plant growth, soil chemistry, and management practices. Management practices include tillage and application of manure, pesticides, and crop residues. Specific details of RZWQM components are given in the model documentation (Ahuja et al., 2000).

Similar to GLEAMS, seepage zone processes are not explicitly represented in RZWQM98 v. 1.0.2000.830 model and must be represented by adjusting the effective hydrologic and chemical parameters of the model (within the parameter range). Chemical transport within the soil matrix is calculated using a sequential partial displacement and mixing approach in 1 cm increments during water infiltration. During the successive infiltration steps, the displacement of solution in the saturated soil layers occurs only in mesopore regions in the manner of piston displacement, and diffusion between mesopore and micropore regions is allowed to occur. Mixing is also allowed to occur within all mesopores after each displacement step. Pesticides in the top two 1 cm soil layers are subject to non-uniform mixing by raindrops during precipitation and transfer to surface runoff. The degree of mixing between rainwater and soil solution is assumed to be complete at the soil surface (equal to unity) and to decrease exponentially with depth (as deep as 2 cm). For a soil-adsorbed pesticide, either a linear isotherm and an instantaneous equilibrium adsorption or a first-order reversible kinetic adsorption-desorption is assumed to occur between the solution and adsorbed phases in both mesopore and micropore regions (Ahuja et al., 1996). At the end of an infiltration event, the mesopore and micropore regions are allowed to equilibrate. Pesticides applied on plant and plant residues are subject to wash-off and degradation. Pesticide degradation on these surfaces and in/on soil is generally assumed to follow a lumped first-order degradation process.

RZWQM has been evaluated for pesticide losses under different conditions with different results. Ahuja et al. (1996) and Azevedo et al. (1997) found that individual soil concentration predictions (depth and time) were generally within an order of magnitude of those observed. Jaynes and Miller (1999) observed that RZWQM did not adequately predict soil pesticide distribution because observed peak concentrations were at the soil surface (0 to 7.5 cm), but the predicted peak concentrations were at 15 cm (using the equilibrium-only model). Azevedo et al. (1997) also observed that the simulated pesticide concentrations in deeper soil (below 20 cm) were generally higher than the observed (using the equilibrium-only pesticide model within RZWQM). Most assessments found RZWQM to simulate soil-water content adequately, but restricting layers in the soil profile were sometimes blamed for less accurate simulations because they are not adequately parameterized and represented in the model (Cameira et al., 1998; Wu et al., 1999). Cracks specified in RZWQM cannot be changed (as a function of soil moisture) during the simulation period. This limitation produces poor surface runoff and chemical concentrations in runoff from clay soils where there is cracking (during dry periods) and no cracking (during wet periods) (Ghidey et al., 1999). Malone et al. (2004) reviewed RZWQM validation studies and found that: (1) accurate parameterization of restricting soil layers (low permeability horizons) improved simulated soil-water content, (2) calibrating pesticide sorption kinetics improved simulated soil pesticide concentration with time (persistence) and depth, and (3) calibrating the pesticide half-life was generally necessary for accurate pesticide persistence simulations.

## Materials and Methods

### Description of the Experimental Site

Five years of data (1999 to 2003) for calibration and evaluation of GLEAMS and RZWQM were obtained from two fields (A and C), which are part of a 21 ha agricultural research site located at the USDA Beltsville Agricultural Research Center in Beltsville, Maryland. The site is part of the Optimizing Production inputs for Economic and Environmental Enhancement ($OPE^3$) study. $OPE^3$ seeks to compare agricultural production systems at a scale large enough to capture the spatial variability of crop and soil parameters, yet small enough for fields to be in similar climatic and geologic settings. The site has a weather station that measures several weather parameters at different time intervals, such as soil and air temperature, relative humidity, wind speed, rainfall, solar radiation, and evapotranspiration. The five-year average annual precipitation measured at the research site is about 99 cm. Annual total precipitation values in 1999, 2000, 2001, 2002, and 2003 were approximately 95, 91, 87, 89, and 135 cm, respectively. In 1999, no significant amount of rainfall fell until September, when major storms, including Hurricane Floyd, generated significant surface runoff. During the other years, precipitation was uniformly distributed during the growing season (between April to mid-November), which resulted in some surface runoff throughout the season.

The fields at the $OPE^3$ site drain into a riparian wetland forest, which contains a first-order stream. About 74% of the site has <2% slope, and only 2% of the site has >3% slope. The soils are sandy textured with buried clay lens (coarse-loamy, siliceous, semiactive, mesic, Typic Hapludult). Soil cores (12.6 $cm^2$ by 1 m long) and auger samples as deep as 2.5 m were collected at the site to provide soil property data (Gish et al., 2002). The samples were analyzed for pH, texture, organic matter content, and major ions (K, Ca, and Mg). The soil profile predominantly consists of sandy loam Ap horizon for the top 0.30 m, followed by a loam Bt horizon that continues down to 0.80 m, a loamy sand C horizon from 0.80 to 1.20 m, and fine textured clay loam lens from about 1.20 to 2.50 m (Gish et al., 2002). Selected physical soil properties measured at the research site are presented in table 1 (Daughtry et al., 2001). The two fields (A and C) used in this study have similar soils, climate, and agricultural management practices. Field C (4.0 ha) has large natural seepage zones, and field A (3.6 ha) has no seepage zones. Seepage zones are common to agricultural lands bordering streams and occur when subsurface flow emerges on the surface. Subsurface flow pathways were identified and delineated using ground-penetrating radar (GPR) data and digital elevation maps (DEM). For a detailed description of delineation of subsurface flow pathways, refer to Gish et al. (2002). Water from seepage zones mixes with surface runoff before leaving the field. These seepage zones result in higher surface runoff, nutrient, and pesticide losses from the field (Daughtry et al., 2001).

Both fields were tilled in early spring using chisel plow. Digested dairy cow liquid manure was applied to the fields from 1999 and 2003. Immediately after application of manure, the soil was disked to incorporate the manure and minimize N loss through volatilization. After disking, corn (*Zea mays* L.) was planted each year in both fields. Atrazine and metolachlor were applied to both fields to control weeds on 1 June 1999, 13 June 2000, 20 June 2001, 24 April 2002, and 14 June 2003. The application rates of atrazine and metolachlor were 1.31 and 1.51 kg $ha^{-1}$, respectively. Surface runoff water (including runoff from seepage zones) from each field was measured at the outlet with a 45.7 cm H-flume equipped with a flowmeter and a water sampler (ISCO, Lincoln, Neb.). The amount of surface runoff was measured automatically and continuously recorded whenever there was a runoff event. Surface runoff water samples were collected after every 5000 L passed through the flume. Surface runoff water samples were collected and analyzed for solution atrazine and metolachlor concentrations. Sediments in surface runoff water were rare because the surface soil at the study site is mostly coarse sandy loam. Therefore, sediments in surface runoff water were not analyzed for atrazine and metolachlor.

### GLEAMS and RZWQM Data Input

Climatic data measured at the $OPE^3$ experimental site and used as input to both GLEAMS and RZWQM models include daily minimum, maximum, and mean air temperatures; daily and break point precipitation; mean monthly maximum and minimum temperatures; solar radiation; wind speed; and relative humidity. Data on clay, silt, sand, and organic matter contents were measured at the site and used as inputs to the models (table 1). Porosity, field capacity, wilting point, and hydraulic conductivity were obtained from the GLEAMS and RZWQM databases (default values) and used as inputs to the respective models. In both GLEAMS and RZWQM, an effective rooting depth of 120 cm was used and divided into five horizons based on soil texture of the site. All management (tillage, planting, harvesting) information was col−

**Table 1. Selected physical soil properties measured at the study site and used as inputs in the models (Daughtry et al., 2001).**

| Soil Depth (cm) | Clay (%) | Silt (%) | Sand (%) | Organic Matter (%) |
|---|---|---|---|---|
| 0 - 15 | 5 | 15 | 80 | 3.5 |
| 15 - 30 | 11 | 18 | 71 | 3.2 |
| 30 - 75 | 7 | 10 | 83 | 3.0 |
| 75 - 90 | 6 | 16 | 78 | 2.0 |
| 90 - 120 | 10 | 25 | 65 | 2.0 |

lected each year at the site and used as input to both models. Other crop characteristics data, such as leaf area index, crop height, dry matter ratio, and C:N ratio, were taken from the model's respective databases.

### Sensitivity Analysis

GLEAMS and RZWQM simulations were first performed using default input parameters, as is done when no data is available for calibration. These default parameters were obtained from the GLEAMS databases (Knisel, 1993) and RZWQM databases (Ahuja et al., 2000) based on local site information from the Prince George's County, Maryland, soil survey and from laboratory and field measurements made at this research site. Simulations were first conducted from 1 January 1999 to 31 December 2003 using default model input parameters. Data collected in 2001, 2002, and 2003 were used to compare model simulations based on the default parameters.

Model parameters were then tested for sensitivity based on the model users' manuals (Knisel, 1993; Ahuja et al., 2000). Sensitive input parameters for GLEAMS and RZWQM were identified using on-site field surface runoff, soil moisture, and atrazine and metolachlor concentration and loss in surface runoff data for 1999 and 2000. The test ranges for each parameter are given in table 2. These test ranges were based on data from the literature and the models' respective databases. Sensitive model parameters were identified by observing the change in model output as a result of a change in a parameter value. A normalized sensitivity coefficient between standard deviations of the parameter and model output was computed (Ma et al., 2000). The normalized sensitivity coefficient can be defined as:

$$\beta_i = \frac{b_i S_{Xi}}{S_{Yi}} \qquad (1)$$

where $S_{Xi}$ and $S_{Yi}$ are the standard deviations of the *i*th model parameter ($X_i$) and the *i*th model output ($Y_i$), respectively, and $b_i$ is the corresponding coefficient. A sensitivity coefficient of 1.0 means that one standard deviation change in the model parameter will lead to a standard deviation change in the model output. Only parameters that resulted in a sensitivity coefficient greater than $\pm 0.5$ were considered sensitive.

### GLEAMS and RZWQM Model Calibration

In water quality modeling, the hydrology component (e.g., surface runoff and percolation) is calibrated first before the chemical components because hydrology determines water quality. Surface runoff and percolation water moves chemicals on the soil surface as well as through the soil profile. In this study, brief discussions of the calibration and results of the hydrology component (surface runoff) are given to explain the relevance of the pesticide results. For detailed presentation of sensitive parameters, calibration, and results of the hydrology component (surface runoff and soil moisture content), refer to Chinkuyu et al. (2004).

**Table 2. Sensitive parameters used in calibrating pesticide components of GLEAMS and RZWQM models.**

| | GLEAMS | | | | RZWQM | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Calibrated[d] | | | | Calibrated | |
| Pesticide and Parameter[a] | Parameter Range[b] | Def.[c] | Field A | Field C | Parameter Range | Def. | Field A | Field C |
| Atrazine | | | | | | | | |
| Initial concentration on crop residues (μg $g^{-1}$) | 0 - 50 | 0.45 | 0.80 | 0.02 | | | | |
| Wash-off fraction (fraction) | 0 - 1 | 0.10 | 0.20 | 0.15 | | | | |
| Fraction applied to foliage (fraction) | 0 - 1 | 0.10 | 0.30 | 0.56 | | | | |
| Fraction applied to soil (fraction) | 0 - 1 | 0.90 | 0.70 | 0.44 | | | | |
| Partitioning coefficient (mL $g^{-1}$) | 0 - 1000 | 100 | 110 | 105 | 0 - 1000 | 100 | 110 | 200 |
| Water solubility (mg $L^{-1}$) | 0 - 1000 | 33 | 40 | 34 | 0 - 1000 | 33 | 30 | 28 |
| Soil half-life (days) | 0 - 300 | 60 | 68 | 53 | 0 - 200 | 60 | 62 | 75 |
| Foliar lumped half-life (days) | 0 - 100 | 5 | 10 | 4 | 0 - 100 | 3 | 12 | 15 |
| Wash-off foliage power (1 $mm^{-1}$) | | | | | 0 - 1 | 0.005 | 0.003 | 0.003 |
| Wash-off residue power (1 $mm^{-1}$) | | | | | 0 - 1 | 0.005 | 0.003 | 0.003 |
| Soil surface aerobic half-life (days) | | | | | 0 - 100 | 0 | 12 | 15 |
| Crop residue lumped half-life (days) | | | | | 0 - 100 | 3 | 12 | 15 |
| Metolachlor | | | | | | | | |
| Initial concentration on crop residues (μg $g^{-1}$) | 0 - 50 | 0.60 | 0.75 | 0.80 | | | | |
| Wash-off fraction (fraction) | 0 - 1 | 0.10 | 0.15 | 0.12 | | | | |
| Fraction applied to foliage (fraction) | 0 - 1 | 0.10 | 0.30 | 0.18 | | | | |
| Fraction applied to soil (fraction) | 0 - 1 | 0.90 | 0.70 | 0.82 | | | | |
| Partitioning coefficient (mL $g^{-1}$) | 0 - 1000 | 200 | 220 | 210 | 0 - 1000 | 200 | 230 | 210 |
| Water solubility (mg $L^{-1}$) | 0 - 1000 | 530 | 550 | 540 | 0 - 1000 | 530 | 450 | 550 |
| Soil half-life (days) | 0 - 300 | 90 | 110 | 120 | 0 - 200 | 90 | 95 | 95 |
| Foliar lumped half-life (days) | 0 - 100 | 5 | 20 | 20 | 0 - 100 | 0 | 5 | 20 |
| Wash-off foliage power (1 $mm^{-1}$) | | | | | 0 - 1 | 0.013 | 0.005 | 0.050 |
| Wash-off residue power (1 $mm^{-1}$) | | | | | 0 - 1 | 0.013 | 0.005 | 0.050 |
| Soil surface aerobic half-life (days) | | | | | 0 - 100 | 0 | 5 | 20 |
| Crop residue lumped half-life (days) | | | | | 0 - 100 | 0 | 5 | 20 |

[a] No other parameters were calibrated in the model.
[b] Values from models databases and literature.
[c] Def. = default, i.e., initial parameter values obtained from models' databases before calibration.
[d] Calibrated = final parameter values after calibration for years 1999 and 2000. Calibrated values were used to simulate 2001, 2002, and 2003.

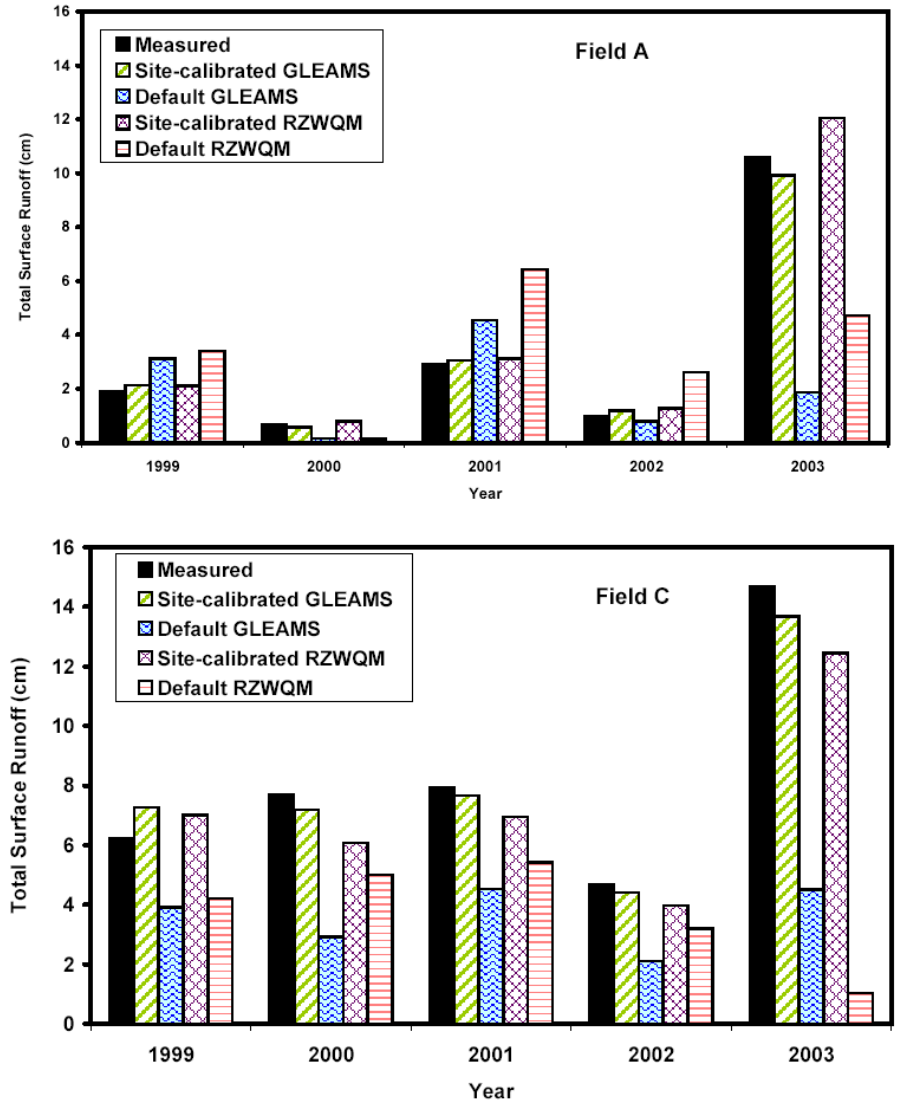


**Figure 1. Total growing-season measured and simulated surface runoff from fields A (top) and C (bottom) from 1999 to 2003. Note that 1999 and 2000 data were used for model calibration, and 2001, 2002, and 2003 data were used for model evaluation.**

Sensitive parameters were calibrated for each model and field. Calibration of GLEAMS hydrologic parameters included the Natural Resources Conservation Service (NRCS) curve number for soil moisture condition II (CN2), field capacity, permanent wilting point, and effective rooting depth (RD). Saturated hydraulic conductivity, field capacity, and rooting depth were calibrated for surface runoff, evapotranspiration, and soil moisture content in RZWQM. After calibration of the hydrology components of both GLEAMS and RZWQM, parameters affecting atrazine and metolachlor concentration and loss in surface runoff were calibrated next. Atrazine and metolachlor initial concentration on crop residues, water solubility, wash-off fraction, wash-off foliage power, wash-off residue power, partitioning coefficient, fraction applied onto foliage or soil, soil half-life, soil surface aerobic half-life, foliar lumped half-life, and crop residue lumped half-life were identified as sensitive parameters and calibrated for atrazine and metolachlor concentration and losses in surface runoff from GLEAMS and RZWQM.

Data measured and predicted in 1999 and 2000 were used for calibrating the models. If daily predicted surface runoff, and atrazine and metolachlor concentration and loss in surface runoff, did not match the daily observed values (within a relative percent error range of ±25%), then the sensitive parameters were adjusted repeatedly until suitable responses were obtained. Thus, the models were considered calibrated when the overall relative percent errors between daily predicted and measured values were between −25% and 25% for both 1999 and 2000 data (Hanson et al., 1999; Bakhsh et al., 2000; Chinkuyu et al., 2004). Note that only data collected in 1999 and 2000 were used for model calibration, and data collected in 2001, 2002, and 2003 were used for model validation.

After calibration, fields A and C had different parameter values for hydrology and pesticide components because of the presence and absence of seepage zones. Field studies at the research site and other seepage zone study sites have shown high surface runoff and pesticides losses in surface runoff from fields with seepage zones (Daughtry et al., 2001; Gish et al., 2001; Gburek et al., 2002). Higher pesticide

**Table 3. Measured and simulated surface runoff and atrazine and metolachlor concentration and loss in surface runoff from field A from 1999 to 2003.**

| | | GLEAMS | | | | RZWQM | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Default | | Calibrated | | Default | | Calibrated | |
| Year[a] | Measured | Pred.[b] | $E_r$[c] | Pred. | $E_r$ | Pred. | $E_r$ | Pred. | $E_r$ |
| Total surface runoff (cm) | | | | | | | | | |
| 1999 | 1.91 | 3.11 | 63 | 2.14 | 12 | 3.40 | 78 | 2.10 | 10 |
| 2000 | 0.66 | 0.05 | −92 | 0.57 | −14 | 0.04 | −94 | 0.79 | 20 |
| 2001 | 2.91 | 4.54 | 56 | 3.04 | 5 | 6.44 | 121 | 3.11 | 7 |
| 2002 | 0.98 | 0.79 | −19 | 1.11 | 13 | 2.62 | 167 | 1.26 | 28 |
| 2003 | 10.59 | 1.88 | −82 | 9.91 | −6 | 4.72 | −55 | 12.05 | 14 |
| 2001-2003 | 14.48 | 2.20 | −85 | 14.07 | −3 | 5.32 | −63 | 16.42 | 17 |
| Average daily atrazine concentration (μg $L^{-1}$) | | | | | | | | | |
| 1999 | 8.4 | 0.3 | −96 | 6.8 | −19 | 0.1 | −99 | 7.6 | −10 |
| 2000 | 112.5 | 0.1 | −100 | 102.5 | −9 | 0.2 | −100 | 86.4 | −23 |
| 2001 | 90.7 | 0.4 | −99 | 75.9 | −16 | 7.6 | −92 | 70.1 | −22 |
| 2002 | 42.8 | 4.5 | −89 | 33.5 | −22 | 0.4 | −99 | 36.2 | −15 |
| 2003 | 10.5 | 5.0 | −52 | 12.3 | 17 | 18.7 | 78 | 9.2 | −12 |
| Average daily atrazine loss (g $ha^{-1}$) | | | | | | | | | |
| 1999 | 0.038 | 0.001 | −97 | 0.036 | −5 | 0.003 | −92 | 0.034 | −11 |
| 2000 | 0.111 | 0.001 | −99 | 0.099 | −11 | 0.001 | −99 | 0.085 | −23 |
| 2001 | 0.773 | 0.002 | −100 | 0.547 | −29 | 0.022 | −97 | 0.497 | −36 |
| 2002 | 0.132 | 0.018 | −86 | 0.108 | −18 | 0.001 | −99 | 0.091 | −31 |
| 2003 | 0.372 | 0.032 | −91 | 0.275 | −26 | 0.292 | −21 | 0.414 | 11 |
| Average daily metolachlor concentration (μg $L^{-1}$) | | | | | | | | | |
| 1999 | 23.3 | 2.0 | −91 | 18.2 | −22 | 10.3 | −56 | 27.2 | 17 |
| 2000 | 60.3 | 4.4 | −93 | 51.7 | −14 | 0.6 | −99 | 55.9 | −7 |
| 2001 | 164.2 | 3.5 | −98 | 121.4 | −26 | 377.7 | 130 | 130.4 | −21 |
| 2002 | 25.7 | 11.4 | −57 | 19.8 | −23 | 6.9 | −73 | 19.7 | −23 |
| 2003 | 27.2 | 8.1 | −70 | 16.1 | −40 | 244.8 | 800 | 15.9 | −42 |
| Average daily metolachlor loss (g $ha^{-1}$) | | | | | | | | | |
| 1999 | 0.104 | 0.010 | −90 | 0.129 | 24 | 0.240 | 130 | 0.082 | −21 |
| 2000 | 0.100 | 0.002 | −98 | 0.084 | −16 | 0.002 | −98 | 0.091 | −9 |
| 2001 | 0.688 | 0.025 | −96 | 0.501 | −27 | 1.242 | 81 | 0.453 | −34 |
| 2002 | 0.226 | 0.045 | −80 | 0.228 | 1 | 0.001 | −99 | 0.181 | −20 |
| 2003 | 0.297 | 0.060 | −80 | 0.309 | 4 | 0.973 | 228 | 0.271 | −9 |

[a] Note that 1999 and 2000 measured and predicted data were used for model calibration.
[b] Pred. = predicted values.
[c] $E_r$ = relative percent error (%).

volatilization losses were also observed in wet than in dry areas (J. Prueger, 2005, personal communication). Therefore, in field C, sensitive parameters were adjusted extensively (within the parameter test ranges) to try to represent the higher pesticide losses due to seepage zone processes. Although field C had large natural seepage zones in the middle and close to the field outlet (over 70% of the field), the whole field was assumed to be homogeneous (just like A), thus using one parameter value, e.g., one curve number. This decision was made since subdividing the field into wet and dry areas would increase model complexity (by having many parameters) and limit a fair comparison between fields A and field C. Initial and final calibrated pesticide parameter values are given in table 2.

### Model Evaluation and Data Analysis

Default and site-calibrated GLEAMS and RZWQM models were evaluated using daily measured data from field A (without seepage zones) and field C (with seepage zones) over a three-year evaluation period (2001 to 2003). Several techniques, based on objective and subjective approaches, were used to test the performance of the models (Bakhsh et al., 2000; Chinkuyu et al., 2001). Subjective criteria included graphical display of simulated and measured solution atrazine and metolachlor concentration and loss in surface runoff. The subjective criteria were used to locate anomalies in model predictions and to provide an insight into temporal response of the models for the entire simulation period. Several statistical criteria were used that account for differences over the whole simulation, ignoring differences between simulations and observations over time.

Objective criteria included: coefficient of determination ($r^2$), relative percent error ($E_r$), coefficient of efficiency or modeling efficiency (E), and index of agreement (*d*). For each evaluation technique, a benchmark that the model should outperform for each of these statistics was established based on other studies. A model was considered to have performed well when: (1) relative percent error was between −25% and +25%, (2) modeling efficiency was greater than 0.50, (3) coefficient of determination was greater than 0.50, and (4) index of agreement was greater than 0.50. These benchmark values were chosen based on other studies that gave similar "acceptable" values showing good model performance (Bakhsh et al., 2000; Hanson et al., 1999; Ma et al., 2000; Leavesley et al., 1983; Ott, 1993; Wilcox et al., 1990).

For each model output (atrazine and metolachlor concentration and loss), the model received a score of 1 for each of the evaluation techniques that met the conditions specified above. The scores were then added for each model and model output to get the total score. There was a possible maximum total score of 4 (four evaluation methods) and a possible minimum score of zero for each combination of model, field, and model output of interest (e.g., metolachlor loss in surface runoff from field A). The model with the highest total scores for a given output and field of interest was considered to be superior to the other. By using graphical comparison, several statistical tests, and the combined scoring from the statistical tests, we hoped to get a more robust picture of model performance than if we had just used graphical comparison and a single statistical test, as is done for most water quality modeling studies.

## Results and Discussion

### Simulation with Default Model Parameters

#### *Field without Seepage Zones*

Note that only the 2001, 2002, and 2003 evaluation period data were used in the statistical evaluation of the performance of GLEAMS and RZWQM. Both GLEAMS and RZWQM using default input parameters were not capable of predicting surface runoff from field A (fig. 1). GLEAMS using default input parameters underpredicted surface runoff in 2002 and 2003 with absolute errors greater than 19% (table 3). Default RZWQM overpredicted surface runoff in 2001 and 2002 with errors greater than 121%. Overall results from 2001 to 2003 show that both GLEAMS and RZWQM underpredicted surface runoff from field A ($E_r > -63\%$).

The poor performance of the default models in predicting surface runoff contributed to poor predictions of atrazine and metolachlor concentration and loss in surface runoff from field A (tables 3 and 4). The results in figure 2 show that GLEAMS and RZWQM with default input parameters consistently underpredicted daily atrazine loss in surface runoff from field A. GLEAMS using default input parameters underpredicted daily atrazine concentration in surface runoff from field A with errors of −87%, coefficient of determination of 0.01, modeling efficiency of −0.04, and index of agreement of 0.17 (table 4). Similarly, RZWQM with default input parameters also underpredicted atrazine concentration in surface runoff from field A with relative percent errors of −81%, modeling efficiency of −0.02, coefficient of determination of 0.02, and index of agreement of 0.04 (table 4). These results clearly show that GLEAMS and RZWQM with default input parameters failed to predict daily atrazine concentration and loss in surface runoff from field A.

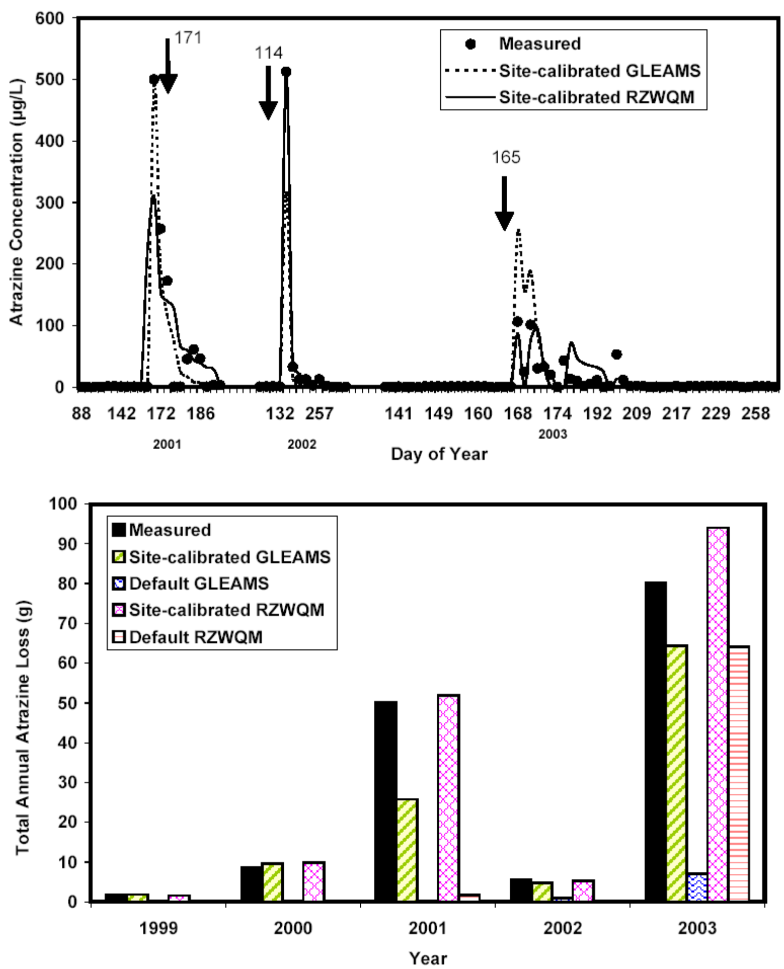


**Figure 2. Measured and simulated atrazine concentration and loss in surface runoff from field A. Only 2001, 2002, and 2003 data were plotted in the atrazine concentration comparison graph. The arrows indicate dates when atrazine was applied. Note that 1999 and 2000 data were used for model calibration, and 2001, 2002, and 2003 data were used for model evaluation.**

Table 4. Statistical comparison of daily measured and simulated atrazine and metolachlor concentration and loss in surface runoff from field A during the evaluation period (from 2001 to 2003).

| | Atrazine | | | | Metolachlor | | | |
|---|---|---|---|---|---|---|---|---|
| | GLEAMS | | RZWQM | | GLEAMS | | RZWQM | |
| Parameters | Def.[a] | Cal.[b] | Def. | Cal. | Def. | Cal. | Def. | Cal. |
| Average daily concentration (μg $L^{-1}$) | | | | | | | | |
| Field-observed data[c] | 31.72 | 31.72 | 31.72 | 31.72 | 30.51 | 30.51 | 30.51 | 30.51 |
| Simulated value | 3.89 | 23.86 | 5.55 | 24.22 | 7.73 | 27.47 | 121.50 | 18.93 |
| Number of observations | 93 | 93 | 93 | 93 | 83 | 83 | 83 | 83 |
| Coefficient of determination ($r^2$) | 0.01 | 0.74 | 0.02 | 0.72 | 0.001 | 0.81 | 0.27 | 0.88 |
| Index of agreement (*d*) | 0.17 | 0.93 | 0.17 | 0.88 | 0.15 | 0.94 | 0.50 | 0.92 |
| Modeling efficiency (E) | −0.04 | 0.74 | −0.02 | 0.69 | −0.10 | 0.80 | −4.98 | 0.79 |
| Relative percent error ($E_r$) | −87 | −6 | −81 | −5 | −73 | 20 | 341 | −20 |
| Total score[d] | 0 | 4 | 0 | 4 | 0 | 4 | 1 | 4 |
| Average daily loss (g $ha^{-1}$) | | | | | | | | |
| Field-observed data | 0.420 | 0.420 | 0.420 | 0.420 | 0.344 | 0.344 | 0.344 | 0.344 |
| Simulated value | 0.024 | 0.376 | 0.191 | 0.438 | 0.052 | 0.234 | 0.898 | 0.254 |
| Number of observations | 90 | 90 | 90 | 90 | 83 | 83 | 83 | 83 |
| Coefficient of determination ($r^2$) | 0.001 | 0.68 | 0.001 | 0.89 | 0.01 | 0.56 | 0.01 | 0.52 |
| Index of agreement (*d*) | 0.11 | 0.89 | 0.09 | 0.97 | 0.24 | 0.83 | 0.16 | 0.83 |
| Modeling efficiency (E) | −0.03 | 0.68 | −0.23 | 0.89 | −0.07 | 0.56 | −8.74 | 0.53 |
| Relative percent error ($E_r$) | −94 | 9 | −52 | 24 | −84 | −10 | 186 | −2 |
| Total score | 0 | 4 | 0 | 4 | 0 | 4 | 0 | 4 |

[a] Def. = default model with input parameters based on databases, soil surveys, and site-specific information.
[b] Cal. = calibrated model.
[c] Data observed or measured in the field.
[d] Total number of evaluation techniques that meet the scoring criteria described in the Model Evaluation and Data Analysis section above.

GLEAMS and RZWQM using default input parameters were also not capable of predicting metolachlor concentration and loss in surface runoff from field A (tables 3 and 4 and fig. 3). Default GLEAMS underpredicted daily metolachlor concentration and loss in surface runoff from field A with relative percent error of <−73%, coefficient of determination of <0.01, and modeling efficiency of <−0.07 (table 4). The coefficient of determination (0.27), modeling efficiency (−4.98), and relative percent error (341%) indicate that default RZWQM overpredicted metolachlor concentration in surface runoff from field A. RZWQM also overpredicted metolachlor loss in surface runoff from field A with a relative percent error of 186% because of the high predicted metolachlor concentration (table 4). The total scores (<1) indicate that both GLEAMS and RZWQM using default input parameters failed to predict atrazine and metolachlor concentration and loss in surface runoff from field A. Although GLEAMS and RZWQM were developed to evaluate management practices in homogenous fields (such as field A), the results of this study show that the models using default input parameters failed to predict atrazine and metolachlor concentration and loss in surface runoff.

### *Field with Seepage Zones*

GLEAMS and RZWQM using default input parameters underpredicted surface runoff from the field with seepage zones (field C) with errors <−32% (table 5 and fig. 1). The low predictions of surface runoff resulted in high predicted atrazine concentration in runoff water from field C (table 5). Thus, there was no dilution of atrazine in runoff water. The relative percent error (29%), coefficient of determination (0.02), and modeling efficiency (−3.52) show that GLEAMS with default input parameters was not capable of predicting daily atrazine concentration in surface runoff from field C (table 6). Default GLEAMS underpredicted atrazine loss in surface runoff from field C showing coefficient of determination of 0.04, modeling efficiency of −0.01, and relative percent error of −77% (table 6). RZWQM using default input parameters overpredicted atrazine concentration in surface runoff from field C with relative percent error of 99% and modeling of efficiency of −3.20 (table 6). Although RZWQM overpredicted atrazine concentration, the model underpredicted atrazine loss in surface runoff from field C with modeling efficiency of −0.17 and relative percent error of −32%. GLEAMS and RZWQM using default input parameters underpredicted metolachlor concentration in surface runoff from field C with relative percent error of <−48% (table 6). GLEAMS and RZWQM using default input parameters underpredicted metolachlor loss in surface runoff from field C with relative percent error of <−86% and modeling efficiency of <0.06 (table 6).

GLEAMS and RZWQM with default input parameters were not capable of predicting daily atrazine and metolachlor concentration and loss in surface runoff from the fields with and without seepage zones (tables 3 through 6). Because of the poor performances of the default GLEAMS and RZWQM, these models were calibrated by adjusting several sensitive hydrologic and pesticide parameters (table 2) and best fitting the daily model outputs to the 1999 and 2000 data sets (tables 3 and 5). The atrazine and metolachlor results of site-calibrated GLEAMS and RZWQM are presented in the following sections. Note that three years of pesticide data (2001 to 2003) were used for model evaluation. Brief discussions of surface runoff results are also presented in this article. The amount of surface runoff produced determines atrazine and metolachlor concentration and loss in the runoff water. For detailed and complete discussion of surface runoff results, refer to Chinkuyu et al. (2004).

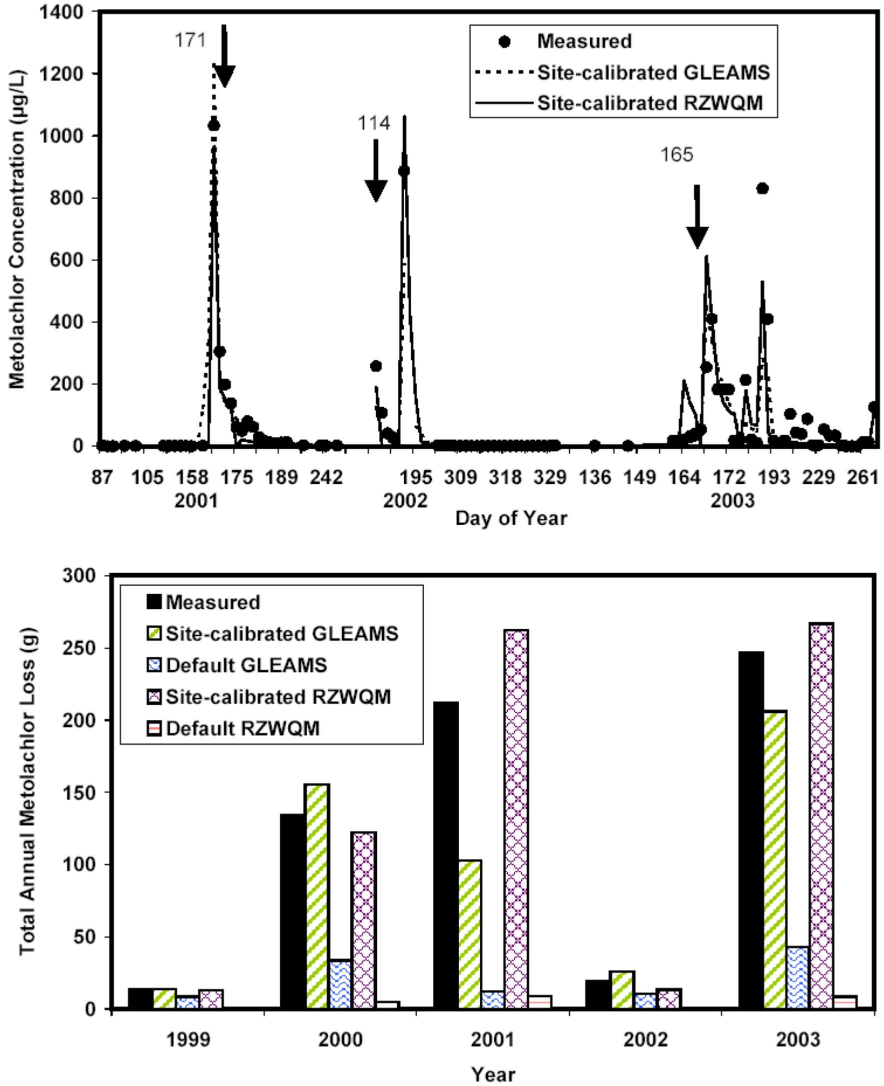


**Figure 3. Measured and simulated metolachlor concentration and loss in surface runoff from field A. Only 2001, 2002, and 2003 data were used in the metolachlor concentration comparison graph. The arrows indicate dates when metolachlor was applied. Note that 1999 and 2000 data were used for model calibration, and 2001, 2002, and 2003 data were used for model evaluation.**

## Simulation with Calibrated Model Parameters

### *Field without Seepage Zones*

Note that data and predictions for 1999 and 2000 were used to adjust model parameters (calibration) so that model outputs would match the observations. Data for 2001, 2002, and 2003 were used for model validation. Calibrated GLEAMS and RZWQM predicted daily and annual surface runoff from field A with relative percent errors of <28% (table 3). During the evaluation period (2001 to 2003), calibrated GLEAMS and RZWQM adequately predicted overall annual surface runoff from the field without seepage zones (field A) with relative percent errors of −3% and 17%, respectively.

The good performance of site-calibrated GLEAMS and RZWQM in predicting surface runoff contributed to better performance of the models in predicting daily atrazine and metolachlor concentration and loss in surface runoff from field A (tables 3 and 4 and figs. 1 through 3). Site-calibrated GLEAMS and RZWQM predicted daily atrazine concentration in surface runoff from field A (fig. 2). In 2001 and 2002, RZWQM underpredicted atrazine loss in surface runoff with errors <−31% (table 3). However, the index of agreement (>0.88), modeling of efficiency (>0.68), coefficient of determination (>0.68), and relative percent error (<24%) show that GLEAMS and RZWQM were capable of adequately predicting daily atrazine concentration and loss in surface runoff from field A (table 4). Calibrated GLEAMS and RZWQM (total score of 4) performed much better than the models using default input parameters (total score of zero) in predicting atrazine concentration and loss in surface runoff.

Both GLEAMS and RZWQM predicted metolachlor concentration and loss in surface runoff from field A (fig. 3 and tables 3 and 4). Although in 2003, both calibrated GLEAMS and RZWQM underpredicted daily metolachlor concentration in surface runoff from field A (error of <−40%) (table 3), the coefficient of determination (>0.56), index of agreement (>0.83), modeling efficiency (>0.56), and relative percent error (<20%) indicate that calibrated GLEAMS adequately predicted daily metolachlor concentration and loss in surface runoff from field A (table 4). Calibrated RZWQM predicted metolachlor concentration in surface runoff from field A with relative percent error of −20%,

**Table 5. Measured and simulated surface runoff and atrazine and metolachlor concentration and loss in surface runoff from field C from 1999 to 2003.**

| | | GLEAMS | | | | RZWQM | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Default | | Calibrated | | Default | | Calibrated | |
| Year[a] | Measured | Pred.[b] | $E_r$[c] | Pred. | $E_r$ | Pred. | $E_r$ | Pred. | $E_r$ |
| Total surface runoff (cm) | | | | | | | | | |
| 1999 | 6.23 | 3.92 | −37 | 7.26 | 16 | 4.21 | −32 | 7.01 | 12 |
| 2000 | 7.71 | 2.93 | −62 | 7.19 | −7 | 5.01 | −35 | 6.08 | −21 |
| 2001 | 7.94 | 4.53 | −43 | 7.67 | −3 | 5.42 | −32 | 6.95 | −12 |
| 2002 | 4.69 | 2.10 | −55 | 4.40 | −6 | 3.20 | −32 | 3.98 | −15 |
| 2003 | 14.67 | 4.50 | −69 | 13.67 | −7 | 1.04 | −93 | 12.45 | −15 |
| 2001-2003 | 27.30 | 7.72 | −72 | 25.75 | −6 | 2.14 | −92 | 22.38 | −18 |
| Average daily atrazine concentration (μg $L^{-1}$) | | | | | | | | | |
| 1999 | 1.0 | 5.1 | 410 | 1.1 | 10 | 165.5 | 16450 | 0.8 | −20 |
| 2000 | 13.6 | 19.5 | 43 | 11.7 | −14 | 277.9 | 1943 | 11.0 | −19 |
| 2001 | 24.3 | 39.1 | 61 | 19.6 | −19 | 274.5 | 1029 | 18.2 | −25 |
| 2002 | 16.7 | 7.3 | −56 | 13.7 | −18 | 149.5 | 795 | 24.9 | 49 |
| 2003 | 32.2 | 29.8 | −7 | 24.7 | −23 | 137.0 | 325 | 20.7 | −36 |
| Average daily atrazine loss (g $ha^{-1}$) | | | | | | | | | |
| 1999 | 0.035 | 0.021 | −40 | 0.027 | −23 | 2.599 | 7326 | 0.029 | −17 |
| 2000 | 0.173 | 0.090 | −48 | 0.170 | 2 | 0.139 | −20 | 0.197 | 14 |
| 2001 | 0.632 | 0.038 | −94 | 0.388 | −39 | 0.813 | 29 | 0.431 | −32 |
| 2002 | 0.070 | 0.029 | −59 | 0.061 | −13 | 0.053 | −24 | 0.074 | 6 |
| 2003 | 0.653 | 0.189 | −71 | 0.494 | −24 | 0.386 | −41 | 0.514 | −21 |
| Average daily metolachlor concentration (μg $L^{-1}$) | | | | | | | | | |
| 1999 | 8.5 | 14.1 | 66 | 7.2 | −15 | 0.1 | −99 | 6.7 | −21 |
| 2000 | 50.2 | 20.3 | −60 | 39.4 | −21 | 73.0 | 45 | 44.8 | −11 |
| 2001 | 70.1 | 44.5 | −36 | 55.9 | −20 | 17.7 | −75 | 47.5 | −32 |
| 2002 | 49.6 | 15.5 | −69 | 36.3 | −27 | 0.1 | −100 | 62.6 | 26 |
| 2003 | 90.8 | 28.9 | −68 | 58.5 | −35 | 46.9 | −48 | 92.1 | 1 |
| Average daily metolachlor loss (g $ha^{-1}$) | | | | | | | | | |
| 1999 | 0.189 | 0.117 | −38 | 0.164 | −13 | 0.005 | −97 | 0.179 | −5 |
| 2000 | 0.551 | 0.138 | −75 | 0.637 | 16 | 0.019 | −96 | 0.502 | −9 |
| 2001 | 1.824 | 0.087 | −95 | 1.585 | −13 | 0.074 | −96 | 1.338 | −26 |
| 2002 | 0.169 | 0.071 | −58 | 0.159 | −6 | 0.001 | −99 | 0.093 | −45 |
| 2003 | 1.669 | 0.214 | −87 | 1.237 | −26 | 0.054 | −97 | 1.334 | 20 |

[a] Note that 1999 and 2000 measured and predicted data were used for model calibration.
[b] Pred. = predicted values.
[c] $E_r$ = relative percent error (%).

coefficient of determination of 0.88, index of agreement of 0.92, and modeling efficiency of 0.79 (table 4). RZWQM predicted metolachlor loss in surface runoff from field A with an error of −2% and index of agreement of 0.83. Calibrated GLEAMS and RZWQM (total scores of 4) predicted metolachlor concentration and loss in surface runoff from field A and performed much better than the models using default input parameters (total scores <1).

Although predicted daily atrazine and metolachlor concentrations did not perfectly match daily atrazine and metolachlor concentrations (figs. 2 and 3), the statistical results in tables 3 and 4 show that GLEAMS and RZWQM were capable of predicting atrazine and metolachlor concentration and loss in surface runoff from the field without seepage zones ($E_r$ < 24%). The good performance of the models is not surprising because these models were developed to simulate homogenous fields such as field A (Knisel, 1993; Ahuja et al., 2000). Although GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from field A, the various evaluation methods used in this study show that calibrated GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from field A with various capabilities. For example, GLEAMS performed better than RZWQM in predicting atrazine concentration in surface runoff from field A with a modeling efficiency of 0.74 and index of agreement of 0.93 (table 4). However, RZWQM performed better than GLEAMS in predicting atrazine loss in surface runoff from field A with a modeling efficiency of 0.89 and index of agreement of 0.97. Both GLEAMS and RZWQM predicted metolachlor concentration ($d$ > 0.92) and loss ($d$ = 0.83) in surface runoff from field A (table 4). The differences in level of model performance can be attributed to the fact that: (1) the two models did not have the same relative percent error values during the calibration years of 1999 and 2000 (it was just relative percent errors between −25% and +25%), and (2) the models predicted different amounts of surface runoff during the evaluation period (2001 to 2003).

### *Field with Seepage Zones*

Good surface runoff predictions are required for better predictions of atrazine and metolachlor concentration and loss in surface runoff water. Detailed discussion of surface runoff results are presented in Chinkuyu et al. (2004) and are not repeated in this article. However, site-calibrated

Table 6. Statistical comparison of daily measured and simulated atrazine and metolachlor concentration and loss in runoff from field C during the evaluation period (from 2001 to 2003).

| | Atrazine | | | | Metolachlor | | | |
|---|---|---|---|---|---|---|---|---|
| | GLEAMS | | RZWQM | | GLEAMS | | RZWQM | |
| Parameters | Def.[a] | Cal.[b] | Def. | Cal. | Def. | Cal. | Def. | Cal. |
| Average daily concentration (μg $L^{-1}$) | | | | | | | | |
| Field-observed data[c] | 24.33 | 24.33 | 24.33 | 24.33 | 72.76 | 72.76 | 72.76 | 72.76 |
| Simulated value | 34.93 | 16.34 | 46.51 | 15.96 | 29.43 | 44.81 | 9.09 | 48.59 |
| Number of observations | 114 | 114 | 114 | 114 | 95 | 95 | 95 | 95 |
| Coefficient of determination ($r^2$) | 0.02 | 0.67 | 0.15 | 0.64 | 0.23 | 0.78 | 0.01 | 0.83 |
| Index of agreement (*d*) | 0.31 | 0.88 | 0.50 | 0.90 | 0.59 | 0.92 | 0.33 | 0.94 |
| Modeling efficiency (E) | −3.52 | 0.54 | −3.20 | 0.65 | 0.16 | 0.71 | −0.15 | 0.77 |
| Relative percent error ($E_r$) | 29 | −19 | 99 | −15 | −48 | −7 | −87 | −4 |
| Total score[d] | 0 | 4 | 1 | 4 | 1 | 4 | 0 | 4 |
| Average daily loss (g $ha^{-1}$) | | | | | | | | |
| Field-observed data | 0.445 | 0.445 | 0.445 | 0.445 | 1.259 | 1.259 | 1.259 | 1.259 |
| Simulated value | 0.087 | 0.309 | 0.289 | 0.296 | 0.134 | 0.670 | 0.044 | 0.931 |
| Number of observations | 110 | 110 | 110 | 110 | 95 | 95 | 95 | 95 |
| Coefficient of determination ($r^2$) | 0.04 | 0.57 | 0.11 | 0.55 | 0.28 | 0.69 | 0.12 | 0.80 |
| Index of agreement (*d*) | 0.40 | 0.87 | 0.54 | 0.83 | 0.42 | 0.88 | 0.30 | 0.93 |
| Modeling efficiency (E) | −0.01 | 0.53 | −0.17 | 0.56 | 0.06 | 0.66 | −0.08 | 0.74 |
| Relative percent error ($E_r$) | −77 | −13 | −32 | −15 | −86 | −22 | −96 | 5 |
| Total score | 0 | 4 | 1 | 4 | 0 | 4 | 0 | 4 |

[a] Def. = default model with input parameters based on databases, soil surveys, and site-specific information.
[b] Cal. = calibrated model.
[c] Data observed or measured in the field.
[d] Total number of evaluation techniques that meet the scoring criteria described in the Model Evaluation and Data Analysis section above.

GLEAMS and RZWQM performed better than the models with default input parameters in simulating surface runoff from the field with seepage zones (field C) with absolute relative percent errors <18% (table 5). The good performance of the models in predicting surface runoff is also observed in the predicted daily atrazine concentration and atrazine loss in surface runoff (figs. 4 and 5). The index of agreement (>0.87), modeling efficiency (>0.53), coefficient of determination (>0.57), and relative percent error (>−19%) indicate that GLEAMS predicted atrazine concentration and loss in surface runoff from field C (table 6). Calibrated RZWQM overpredicted daily atrazine concentration in 2002 with an error of 49% and underpredicted daily atrazine concentration in 2003 with an error of −36% (table 5). However, overall results from 2001 to 2003 indicate that RZWQM predicted atrazine concentration in surface runoff from field C with relative percent errors of −15%, index of agreement of 0.90, coefficient of determination of 0.64, and modeling efficiency of 0.65 (table 6). The coefficient of determination (0.55), index of agreement (0.83), modeling efficiency (0.56), and relative percent error (−15%) show that RZWQM predicted atrazine loss in surface runoff from field C.

The results presented in figure 5 show that calibrated GLEAMS and RZWQM predicted metolachlor concentration and loss in surface runoff from field C. However, RZWQM underpredicted metolachlor loss in 2002 with relative percent error of −45%. The coefficient of determination (>0.69), index of agreement (>0.88), modeling efficiency (>0.66), and relative percent error (<−22%) show that GLEAMS predicted metolachlor concentration and loss in surface runoff from field C (table 6). RZWQM also predicted metolachlor concentration and loss in surface runoff from field C with index of agreement of >0.93, coefficient of determination of >0.80, modeling efficiency of >0.74, and relative percent error of <5% (table 6). Calibrated GLEAMS and RZWQM (with totals scores of 4) performed better than the default models (with totals scores of <1) in predicting metolachlor concentration and loss in surface runoff from field C. However, these results show that the models are not perfect because they barely passed some of the evaluations tests used in this study. For example, both GLEAMS and RZWQM had coefficients of determination and modeling efficiencies of <0.56 for metolachlor loss in field A (table 4) and coefficients of determination and modeling efficiencies of <0.57 for atrazine loss in field C (table 6). Although calibrated GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from field C, their performances were different. In field C, RZWQM predicted metolachlor concentration and loss better than GLEAMS, showing coefficient of determination >0.80, index of agreement >0.93, and modeling efficiency >0.74 (table 6). RZWQM also performed better than GLEAMS in predicting atrazine concentration. However, GLEAMS performed better than RZWQM in predicting atrazine loss in surface runoff from field C with relative percent error of −13 (table 6). The differences in level of model performance can be attributed to the fact that: (1) the two models did not have the same relative percent error values during the calibration years of 1999 and 2000 (it was just relative percent errors between −25% and +25%), and (2) the models predicted different amounts of surface runoff during the evaluation period (2001 to 2003).

## Implications of Modeling Results

The main objective of this study was to use different evaluation techniques to determine whether GLEAMS and RZWQM can adequately model daily atrazine and metolachlor concentration and loss in surface runoff from agricultural fields with and without seepage zones. The various evaluation methods used in this study show that calibrated

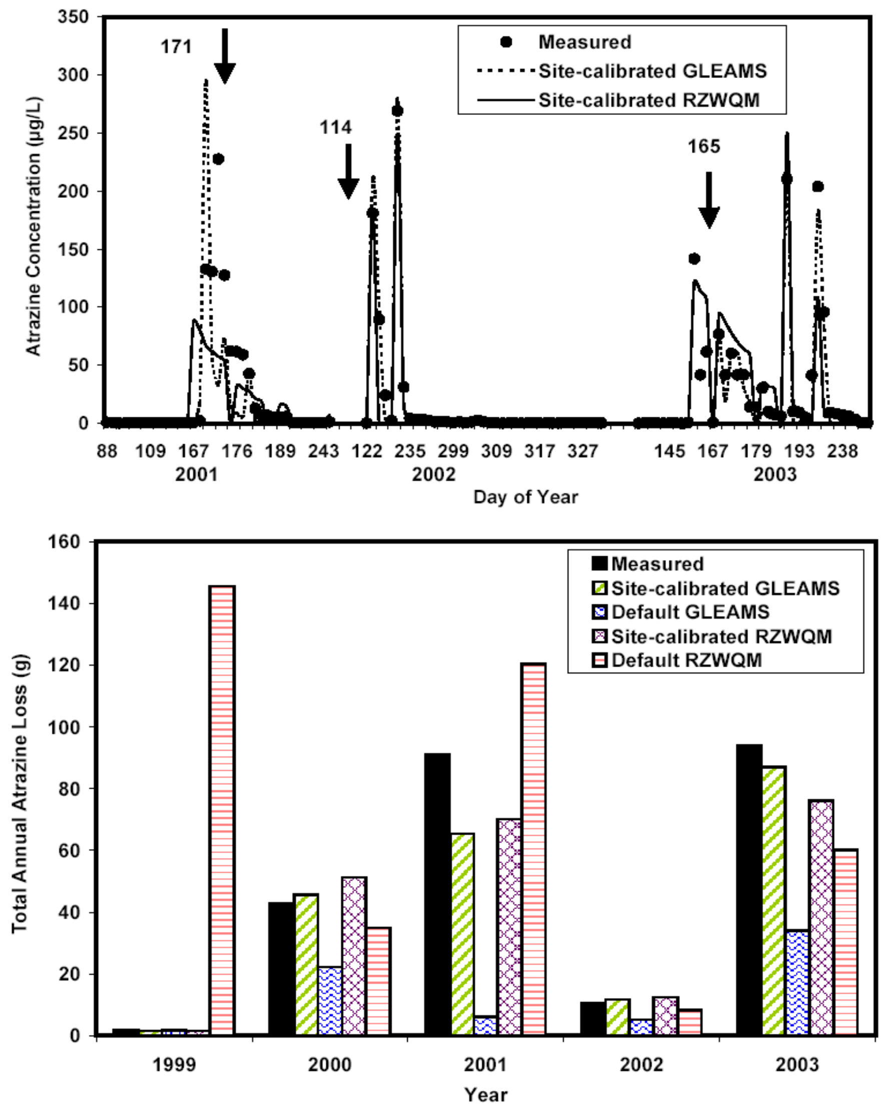


**Figure 4. Measured and predicted atrazine concentration and loss in surface runoff from field C. Only 2001, 2002, and 2003 data were plotted in the atrazine concentration comparison graph. The arrows indicate dates when atrazine was applied. Note that 1999 and 2000 data were used for model calibration, and 2001, 2002, and 2003 data were used for model evaluation.**

GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from the fields with and without seepage zones with various capabilities. For example, GLEAMS performed better than RZWQM in predicting atrazine concentration in surface runoff from field A with a modeling efficiency of 0.74 and index of agreement of 0.93 (table 4). However, RZWQM performed better than GLEAMS in predicting atrazine loss in surface runoff from field A with a modeling efficiency of 0.89 and index of agreement of 0.97. In field C, RZWQM performed better than GLEAMS in predicting metolachlor concentration in surface runoff with coefficient of determination >0.80. However, GLEAMS performed better than RZWQM in predicting atrazine loss in surface runoff from field C. Although there were differences in the level of performance of GLEAMS and RZWQM, overall results show that based on the various evaluation methods used in this study, calibrated GLEAMS and RZWQM predicted atrazine and metolachlor concentration and loss in surface runoff from fields with and without seepage zones with $E > 0.53$, $E_r < 20\%$, $r^2 > 0.52$, and $d > 0.83$ (tables 4 and 6). Both GLEAMS and RZWQM predicted daily atrazine and metolachlor concentrations in surface runoff from the fields with and without seepage zones (figs. 2 through 5). These results are important because they show that although GLEAMS and RZWQM displayed different abilities, the models can be used to predict atrazine and metolachlor loss in surface runoff from fields with seepage zones.

Although both calibrated GLEAMS and RZWQM predicted pesticide concentration and loss in surface runoff from the fields with and without seepage zones, the results show that the models are not perfect because some of the evaluation standards were barely met. Both models had equal or slightly better performance in field A than in field C. For example, GLEAMS predicted atrazine concentration in field A with a modeling efficiency of 0.74, while in field C the modeling efficiency was reduced to 0.54 (tables 4 and 6). The better performance of these models in field A is not surprising because GLEAMS and RZWQM are lumped models that were developed to handle homogeneous fields such as field

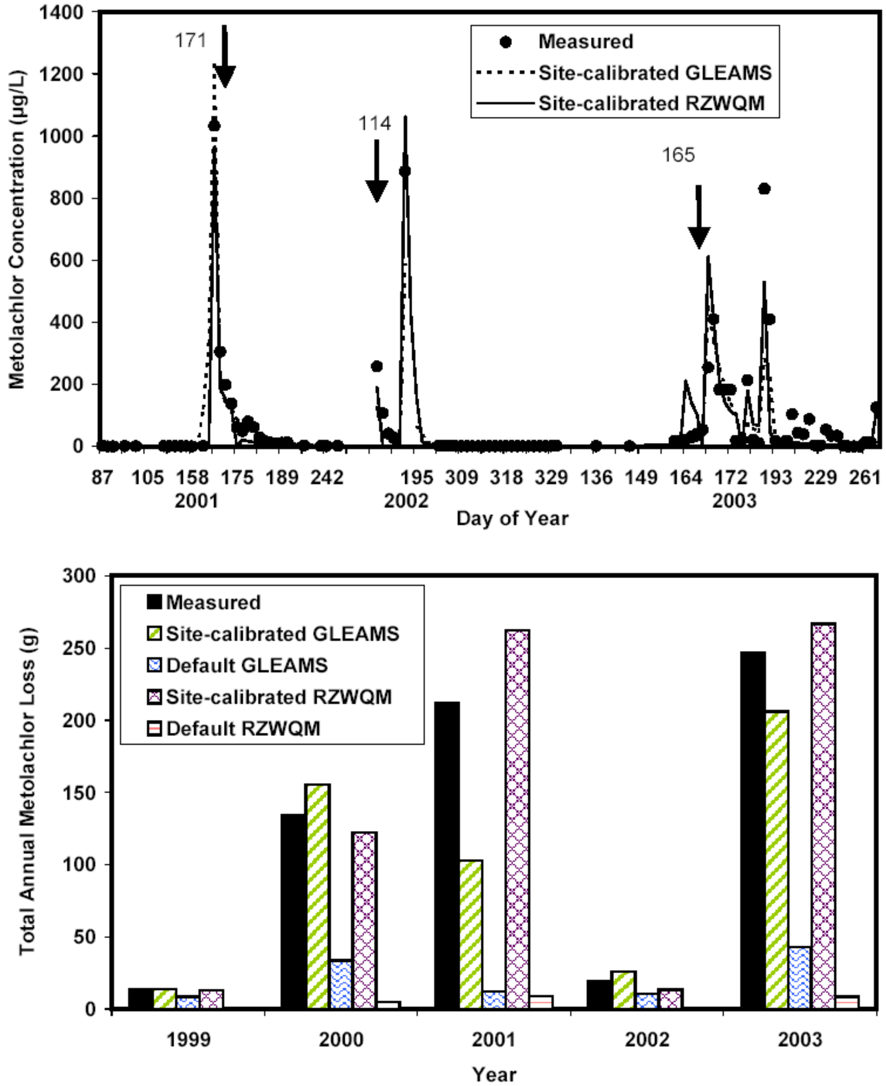


**Figure 5. Measured and predicted metolachlor concentration and loss in surface runoff from field C. Only 2001, 2002, and 2003 data were plotted in the metolachlor concentration comparison graph. The arrows indicate dates when metolachlor was applied. Note that 1999 and 2000 data were used for model calibration, and 2001, 2002, and 2003 data were used for model evaluation.**

A. On the other hand, the models did not perform as well in field C because they do not have seepage zone processes incorporated into them. These models do not integrate all aspects of hydrologic controls from the runoff flow perspective (variable sources), much less from interactions between surface runoff and water quality from different sources (Grayson and Blöschl, 2001). Because seepage zone processes are not represented in GLEAMS and RZWQM, sensitive hydrologic and pesticide parameters for field C were adjusted extensively (within the test ranges) to match pesticide losses from the field with seepage zones compared to the same parameters in field A (without seepage zones) (table 2). The extensive adjustment of the parameters enabled the models to better predict pesticide concentration and loss in surface runoff from field C than the models using default input parameters. Thus, based on the results of this and previous (Chinkuyu et al., 2004) studies, sensitive hydrologic parameters (e.g., curve number, field capacity, effective rooting depth) and pesticide parameters (e.g., partitioning coefficient, water solubility, soil half-life) must be adjusted extensively for GLEAMS and RZWQM to be able to predict high surface runoff and pesticide losses from fields with seepage zones.

Based on the fact that GLEAMS and RZWQM were not perfect in this study, more data from different sites are needed to evaluate these models and assess whether there is a need for model developers to consider incorporating upward movement of water and chemicals in the soil profile and redistribution of the chemicals among surface runoff, percolation, and seepage zones. The data being collected at OPE[3] is a good starting point for long-term data that can be used to evaluate and possibly incorporate seepage zone processes in the GLEAMS and RZWQM models. Data from other research sites are also needed to evaluate GLEAMS and RZWQM before incorporation of seepage zone processes into these models.

## Summary and Conclusions

The GLEAMS and RZWQM models were used to predict daily atrazine and metolachlor concentration and loss in surface runoff from two agricultural fields: one with and one without seepage zones. The results of this study have particular importance in using the two models to assess the impacts of various management practices on agricultural fields that have seepage zones.

First, daily simulated pesticide concentration and loss in surface runoff from both default and site-calibrated GLEAMS and RZWQM were compared with measured pesticide concentration and loss in surface runoff from the two fields from 2001 to 2003. The results show that GLEAMS and RZWQM using default input parameters were not capable of predicting pesticide concentration and loss in surface runoff in fields with and without seepage zones. The poor performance of both models was probably due to poor representation of measured soil and pesticide properties, or the structure of the two models may not properly represent hydrological and pesticide processes occurring in the fields. Additional field data on the spatial distribution of physical soil, hydrologic, and pesticide properties might improve the models using default input parameters, but there is little question that field-based parameterization or calibration would need to be incorporated into the application of these water quality models to ensure optimal model performance.

Second, the results show that site-calibration of GLEAMS and RZWQM improved the performance of both models. Based on the various evaluation techniques used in this study, calibrated GLEAMS and RZWQM predicted daily atrazine and metolachlor concentration and loss in surface runoff from both fields ($r^2 > 0.52$, $d > 0.83$, and $E > 0.53$) and can be used to assess the effects of seepage zones on atrazine and metolachlor losses in surface runoff from agricultural fields.

Third, based on the fact that GLEAMS and RZWQM were not perfect in this study, there is a need for the models to be tested with long-term data from several sites before incorporating upward movement of water and chemicals in the soil profile and redistribution of chemicals among surface runoff, percolation, and seepage zones. Therefore, the data being collected at $OPE^3$ sites are a good starting point for modeling studies to investigate the problem of seepage zones in agricultural systems.


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