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Characterization of Fate and Transport of Isoxaflutole, a Soil-Applied Corn Herbicide, in Surface Water Using a Watershed Model

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The objective of this study is to conduct a comprehensive assessment of the transport of isoxaflutole and RPA 202248 and their accumulation potential in semistatic water bodies, using a distributed watershed scale model and observed water quality data. A conceptual model was developed to characterize the fate and transport of isoxaflutole residues to and in surface water. The soil and water assessment tool (SWAT), a continuous daily time-step watershed model, was used to simulate the processes identified in the conceptual model. Monitoring data were available for a number of surface water bodies within the major product use area as a result of extensive and intensive residue monitoring. Detailed product use information at the zip-code level was obtained through dealer sales and a grower survey. The hydrologic and chemical transport results from the SWAT model were validated by comparison to available monitoring data from selected water bodies. Upon validation, the model was used to simulate the fate of isoxaflutole-derived residues in the water bodies using long-term historical weather data. The results from this investigation indicate no evidence of long-term accumulation of isoxaflutole and its metabolite RPA 202248 in semistatic water bodies.

KEYWORDS: Isoxaflutole; watershed assessment; water quality modeling; SWAT; flushing index

INTRODUCTION

Herbicides are an important component of economic agricultural production in the United States. Isoxaflutole is a low use rate, pre-emergence corn herbicide registered for use in 18 states in the United States to control grass and broad-leaf weeds since 1999. The typical application rate of isoxaflutole is in the range of 0.05−0.11 kg/ha, which is much lower than that of the conventional corn herbicides such as atrazine (0.9−1.8 kg/ha) and metolachlor (0.7−1.4 kg/ha) (*1*). Isoxaflutole degrades rapidly (half-life < 4 days) in the field and aquatic environments to its biologically active metabolite, RPA 202248 (*2*). RPA 202248 has a relatively longer half-life in an aquatic environment than in the terrestrial environment (**Table 1**). Therefore, the fate of biologically active residues of isoxaflutole in the environment, particularly in semistatic water bodies, is of interest. Hence, the objective of this study is to conduct a comprehensive assessment of the transport of isoxaflutole and RPA 202248 and their accumulation potential in semistatic water bodies, using a distributed watershed scale model and observed water quality data.

Distributed watershed scale models such as the soil and water assessment tool (SWAT) have been widely used for assessing nonpoint source nutrient loadings across the watershed (*3*−*9*). However, herbicide/pesticide transport has rarely been modeled at this large scale. As indicated by Muller et al. (*10*), most of the watershed scale studies on pesticide pollution focused on estimating the pesticide loads on rivers, streams, and lakes and documented the level of surface water pollution with various pesticides (*11*, *12*), and pesticide transport processes were not modeled or analyzed at this scale. Most of the modeling studies on pesticide transport were conducted at an individual field scale or landscape scale.

Models such as the pesticide root zone model (PRZM) (*13*), groundwater loading effects of agricultural management systems (GLEAMS) (*14*), and chemicals, runoff, and erosion from agricultural management systems (CREAMS) (*15*) have been extensively used to simulate pesticide transport at field scale. Within a regulatory framework, these field scale models are typically used to estimate edge-of-field pesticide loadings, and the loads are directly fed into another surface water body simulation model for ecological and drinking water exposure assessments. However, to understand the impact of distributed usage of pesticide across a large watershed, the field scale models have to be integrated with a watershed scale model such as SWAT for a comprehensive assessment.

PRZM was integrated with a geographical information system (GIS) for statewide assessment of groundwater vulnerability from atrazine use on agricultural lands (*16*). The main emphasis of this study was assessing the groundwater vulnerability, and

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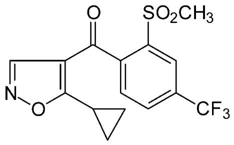
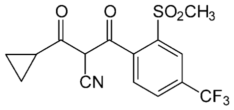
Table 1. Summary of Environmental Fate Information for Isoxaflutole and Diketonitrile (*2*)

property	isoxaflutole	RPA 202248
mol structure		
mol wt (g/mol)	359	359
water solubility (mg./L)	6.2	325
octanol/water partition coeff (log *P*)	2.32	–0.40
vapor pressure (Pa)	1.0×10^{-6} (at 25 °C)	not available
soil K_{OC} at initial soil concn (∼0.29 ppm)	102–227	62–204
lab aerobic soil half-life (days)	0.3–4.3	10–39
field dissipation half-life (days)	0.4–4.5	6.5–21
hydrolysis half-life at pH 7 (days)	0.84	stable
dissipation half-life from water phase in sediment/water system (days)	0.5–0.6	66–89
aquatic photolysis half-life (natural sunlight at pH 7) (days)	6.7	stable

hence the modeling component did not include pesticide transport and routing through surface water in streams and the associated losses. Gustafson et al. (*17*) used a fractal-based scaling approach to model pesticide transport in rivers. In this study the PRZM model's edge-of-field prediction was transformed to a watershed scale using a convection−dispersion equation. However, the major assumption in this study is that the pesticide was applied at a uniform rate on a single date on all agricultural fields, which is often not the case. Neitsch et al. (*18*) integrated the GLEAMS approach for pesticide transport with watershed scale model SWAT and used it for assessing three pesticides, atrazine, metolachlor, and trifluralin. This study showed that such an integrated approach of a field scale model with a watershed scale model could realistically predict the movement and transport of pesticide in a watershed along with the impact of land management practices such as tillage and timing of pesticide application.

MATERIALS AND METHODS

Conceptual Model. Transportation of an agricultural chemical and its distribution through each environmental compartment are governed by several drivers. A conceptual model that describes the distribution processes within a compartment, the distribution of a chemical between compartments, and the drivers that control these processes is illustrated in **Figure 1**. The behavior within each compartment is driven by four major factors: anthropogenic, environmental fate, morphological, and meteorological. Although anthropogenic factors would typically cover all human activities that could affect the distribution of a product within a watershed, only direct influences such as product use, management practices, and reservoir pumping were considered in this study. As isoxaflutole degrades rapidly to RPA 202248, both of these compounds were combined and treated as one combined compound and designated as total relevant residues (TRR) for the modeling analysis in this study.

Watershed Modeling. Once developed by identifying the environmental pathways, distribution processes, and drivers, the conceptual model can then be represented within the framework of a mathematical environmental-fate model. The mathematical model selected for this study is SWAT, developed by the U.S. Department of Agriculture (USDA) for assessment of nonpoint source pollution from agriculture (*19*). SWAT was chosen for this study because (1) it is capable of simulating most of the processes identified in the conceptual model, (2) it is a physically based distributed parameter watershed-scale model, (3) it has been integrated with a GIS and can use readily available GIS data on soils, land use, and elevation, and (4) it has been integrated with the "better assessment science integrating point and nonpoint sources" (BASINS) watershed assessment tool, which is being successfully used by the U.S. Environmental Protection Agency (EPA) and state agencies in water resources and water quality assessments.

SWAT is a physically based, continuous daily time-step, basin-scale hydrologic and water quality model that uses spatially distributed data on soil, land use, terrain (digital elevation model, DEM), and meteorology. Major components of the model include weather, hydrology, soil temperature, plant growth, nutrients, pesticides, and land management. A complete description of the SWAT model components (version 2000) is found in Arnold et al. (*19*) and Neitsch et al. (*20*). The relationships used to simulate the movement of pesticide in the terrestrial phase of the hydrologic cycle were adopted from the GLEAMS model (*14*). Pesticide transport by water and sediment is calculated for each runoff event, and pesticide leaching is estimated for each soil layer when percolation occurs.

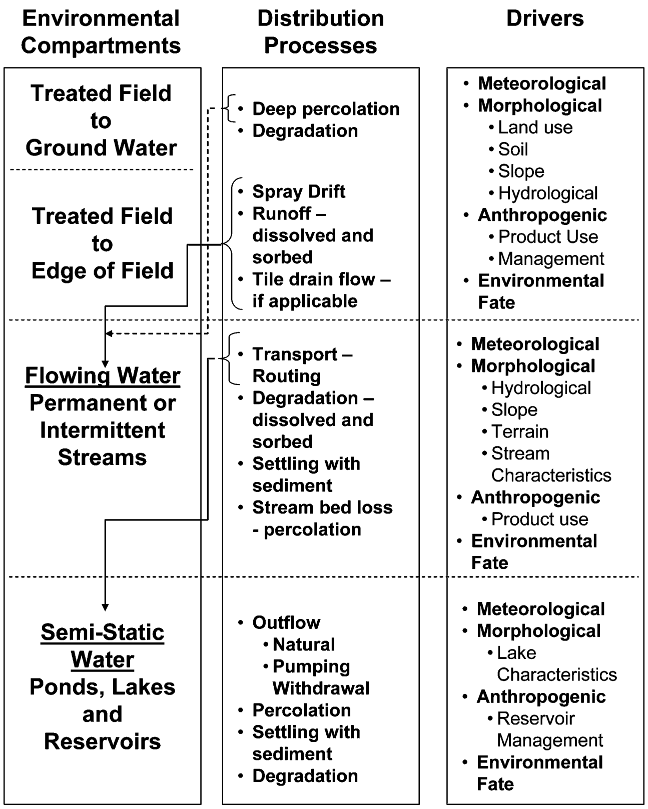


Figure 1. Conceptual model for fate and transport of an agricultural chemical.

The methodology for simulating in-stream pesticide processes in SWAT was adopted from Chapra (*21*). The total pesticide load in the channel is partitioned into dissolved and sorbed components. Whereas the dissolved pesticide is transported with water, the sorbed phase undergoes sediment transport and deposition processes. Pesticide transformations in the dissolved and sorbed phases are simulated by first-order degradation relationships. The fate of isoxaflutole residues in ponds, lakes, and reservoirs was simulated using the reservoir

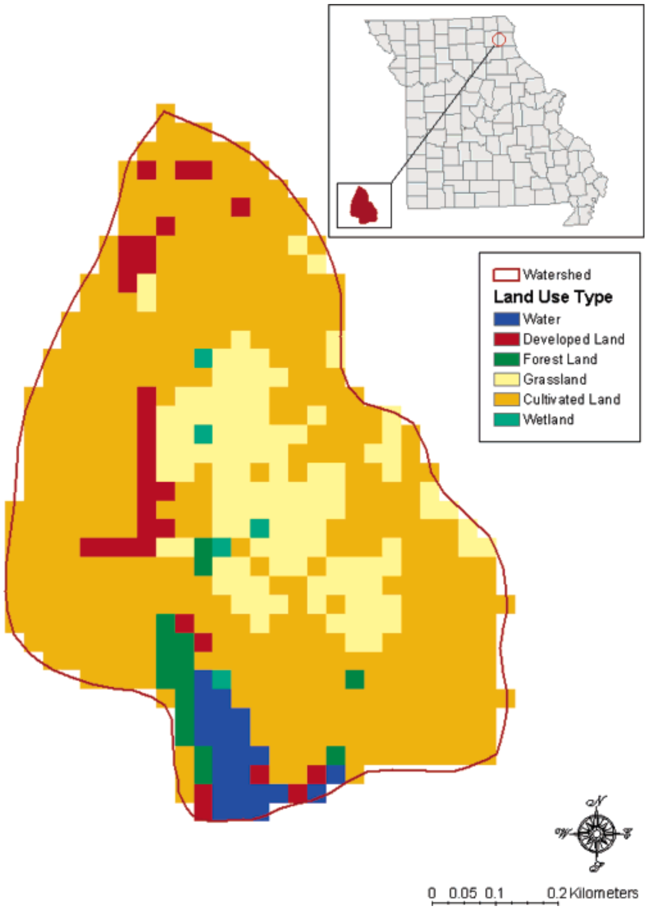


Figure 2. Location and general land use within La Belle Lake watershed, Missouri.

component of SWAT, which was adopted from Chapra (*21*), assuming well-mixed conditions in the surface water layer and sediment layer. The pesticide is partitioned into dissolved and sorbed phases in both the water and sediment layers. Similar to the in-stream processes, major processes simulated by the reservoir model are inflow, outflow, transformation, volatilization, settling, diffusion, resuspension, and burial. The outflow from the reservoir may be caused by natural overflow or by water withdrawal due to pumping.

Isoxaflutole Monitoring Program and Study Area. An extensive water monitoring program that collected >3500 samples from 315 semistatic water bodies during the period 2000–2004 was conducted in the states of Missouri, Iowa, Nebraska, Illinois, Kansas, and Kentucky. The Missouri program began with the assistance of the Missouri Department of Natural Resources in 2000 and continued at a more intensive level through a collaborative program with the Missouri Corn Growers Association and the Environmental Resources Coalition (ERC) that started in 2002. The Nebraska Department of Environmental Quality (NE DEQ) conducted an intense sampling program in 2003, resulting in 423 samples from 50 different sampling points. The Iowa Department of Natural Resources sampled 139 semistatic water bodies across the state during 2002 and 2003, and the Illinois Environmental Protection Agency conducted a monitoring program that included sampling of 24 lakes and reservoirs in 2003. All of the samples were analyzed by Bayer CropScience for TRR (isoxaflutole and RPA 202248) and RPA 203328, which is not biologically active.

Among the 315 water bodies monitored, the original watershed assessment included 19 water bodies and their watersheds (Missiouri, 5; Iowa, 10; Nebraska, 1; and Illinois, 3). For the sake of brevity, this paper highlights the modeling assessment conducted for four watersheds (**Figures 2**–**5**) that represent diverse watershed morphologic conditions. The general watershed characteristics of the four watersheds are given in **Table 2**. According to the National Agricultural Statistical Service (NASS), corn is the major crop grown in most of the cropland located within the study area, followed by soybeans (*23*).

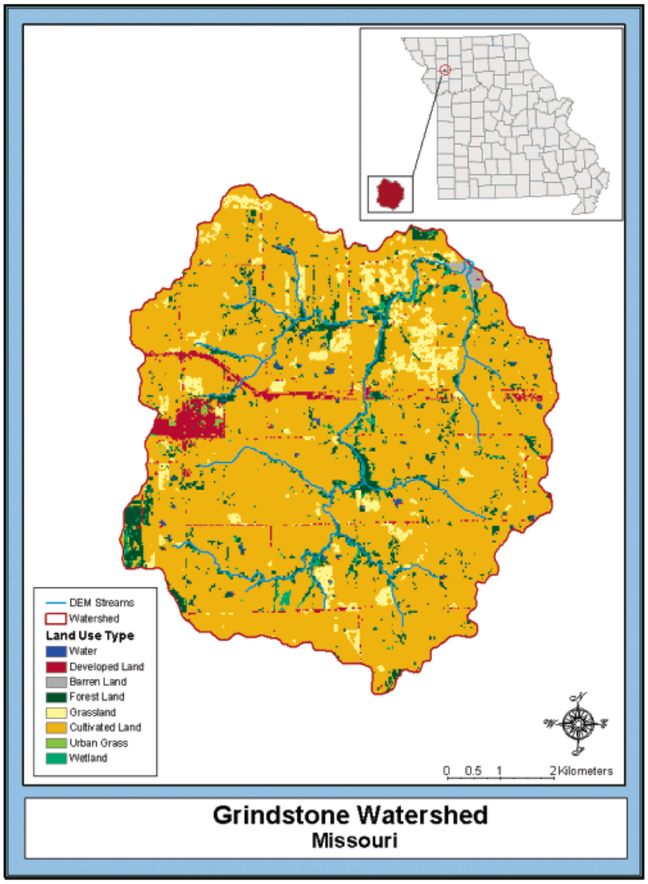


Figure 3. Location and general land use within Grindstone Reservoir watershed, Missouri.

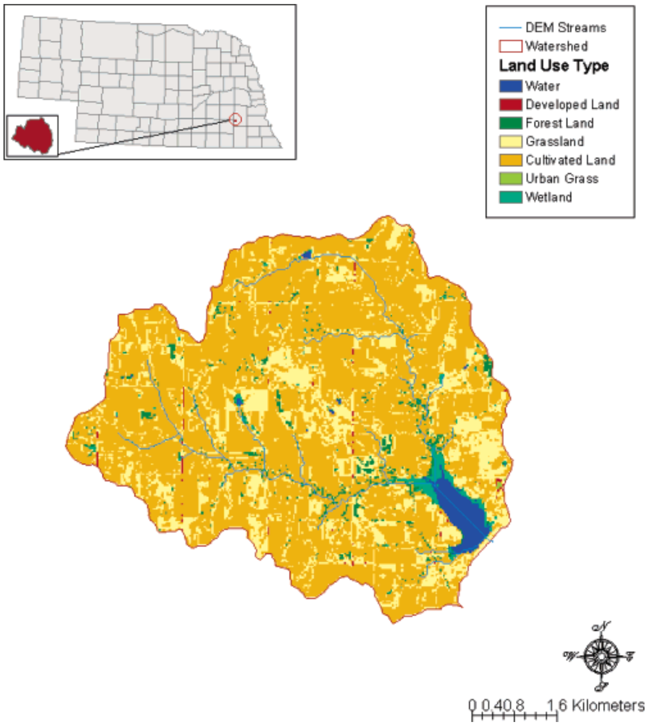


Figure 4. Location and general land use within Bluestem Reservoir watershed, Nebraska.

Product Use Estimation. Isoxaflutole is used as a pre-emergence herbicide only in corn and not in soybeans. The product use information within the Missouri watersheds was collected at a higher level of detail through a grower and dealer survey (**Table 3**). The La Belle watershed did not have any product use. For the Rathbun (Iowa) and Bluestem

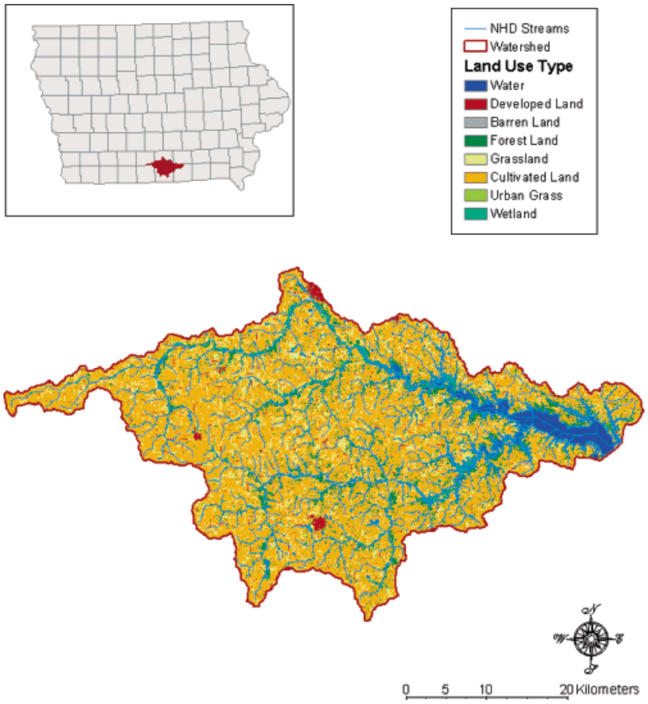


Figure 5. Location and general land use within Rathbun Reservoir watershed, Iowa.

(Nebraska) watersheds, such detailed product use information was not available. Therefore, the product use within those watersheds was estimated on the basis of zip-code level product sales data. From the zip-code level, the product use at the watershed level was derived by calculating the cropland acreage within the watershed using the National Land Cover Data (NLCD; *22*) and the proportion of corn acreage from NASS, by adopting GIS overlay techniques. It should be noted that the underlying assumption in this procedure is that there is uniform product usage on all of the corn acres estimated within a zip-code area. However, in reality, only part of the fields within the watershed might have received product applications. Hence, it was necessary to adjust (calibrate) the use rate within the Bluestem and Rathbun watersheds to achieve reasonable comparison of monitored and simulated residue concentrations in the water body. The product use estimated by GIS overlaying techniques explained above was either reduced or increased until there was satisfactory agreement between the observed and simulated results. Considering the uncertainties with estimating the product use from the product sales information, this adjustment is reasonable. It should be noted that in the case of Grindstone Reservoir, where product use information was available at the field level, it was not necessary to adjust the product use to achieve acceptable comparison of simulated and monitored residues. The product use rate estimated from the zip-code-based sales data and calibrated use rates are given in **Table 3**.

Input Data Used in Watershed Modeling. *Hydrologic Information.* Historical daily weather data such as precipitation and air temperature (daily maximum and minimum) were obtained from the National Weather Service (NWS) cooperative weather stations from 1951 until the end of August 2003. The weather data were then screened for missing values and filled from the nearest weather station from which the data were available. The USDA−NRCS detailed soil dataset, Soil Survey Geographic (SSURGO), and datasets based on 7.5′ quadrangle maps (1:24000 scale) were used for obtaining soil attributes for most of the watersheds (*24*). However, in cases when detailed soil information was not available, a regional scale soil dataset, State Soil Geographic (STATSGO), based on 1° × 2° quadrangle maps (1:250000 scale), was used for obtaining soil attributes (*25*). The physical soil properties needed by SWAT are texture, bulk density, available water capacity, saturated hydraulic conductivity, and soil albedo for up to 10 soil layers. The soil parameters required by SWAT were estimated from STATSGO and SSURGO databases using the Map Unit Use File (MUUF) software. MUUF (*26*) provides a series of tools for generating soil properties in the absence of measured data from generally available soils data and may be used with several hydrologic models.

The land use/land cover information was derived from the 1992 National Land Cover Data (NLCD) at a 30 m resolution (*22*). The NLCD provided a consistent classification of 21 land cover types across the United States, derived from satellite data collected from the early to mid 1990s and other auxiliary data. The spatial resolution of the data is 30 m. The classification of interest in this study is row crops (class 82 in NLCD), which includes corn. Assuming that the row crop land cover has not changed significantly from the time when the land cover data were collected, the proportion of corn within the row crop was estimated using the agricultural statistics data from NASS.

The elevation data used was the 7.5′ digital elevation model (DEM), obtained at 30 m resolution from USGS (*27*). The SWAT GIS interface, AVSWAT, was used to extract model parameters from the GIS layers and weather data. The watershed area contributing to each lake was delineated from the DEM. Each watershed was then divided into subbasins, and the topographic parameters and stream channel parameters for each subbasin were estimated from the DEM by AVSWAT. Each subbasin was further subdivided into hydrologic response units (HRUs) having unique land use and soil combinations. Once the subbasins were delineated, the nearest weather station to the centroid of each subbasin was used to model the hydrology. Watershed management operations such as tillage, pesticide application, planting and harvesting, and lake characteristics were input into the model.

Table 2. Watershed Characteristics

			land cover (%)				soil hydrologic group (%)		
state	watershed name	area (acre)	crop land	forest land	water + wetland	other	B	C	D
Missouri	La Belle Lake 1	122	23	4	13	60		25	75
	Grindstone Reservoir	13235	41	7	2	50	7	93	
Nebraska	Bluestem Reservoir	10150	52	3	3	43	10		87
Iowa	Rathbun Reservoir	354345	31	9	9	51	11	68	19

Table 3. Estimated Product Use in the Study Watersheds

	estimated use (kg of ai[a])				estimated application area (ha)			
watershed name	2000	2001	2002	2003	2000	2001	2002	2003
La Belle Lake 1	0.0	0.0	0.0	0.0	0	0	0	0
Grindstone Reservoir	0.0	0.0	8.8	0.0	0	0	176	0
Bluestem Reservoir[b]	NA[c]	7.2	23.5 (7.2)	38.3 (14.3)	NA	1398	1398	1096
Rathbun Reservoir	NA	37.7	19.4	42.0	NA	10108	9750	8156

[a] Active ingredient. [b] Numbers in parentheses indicate calibrated product use. [c] Not available.

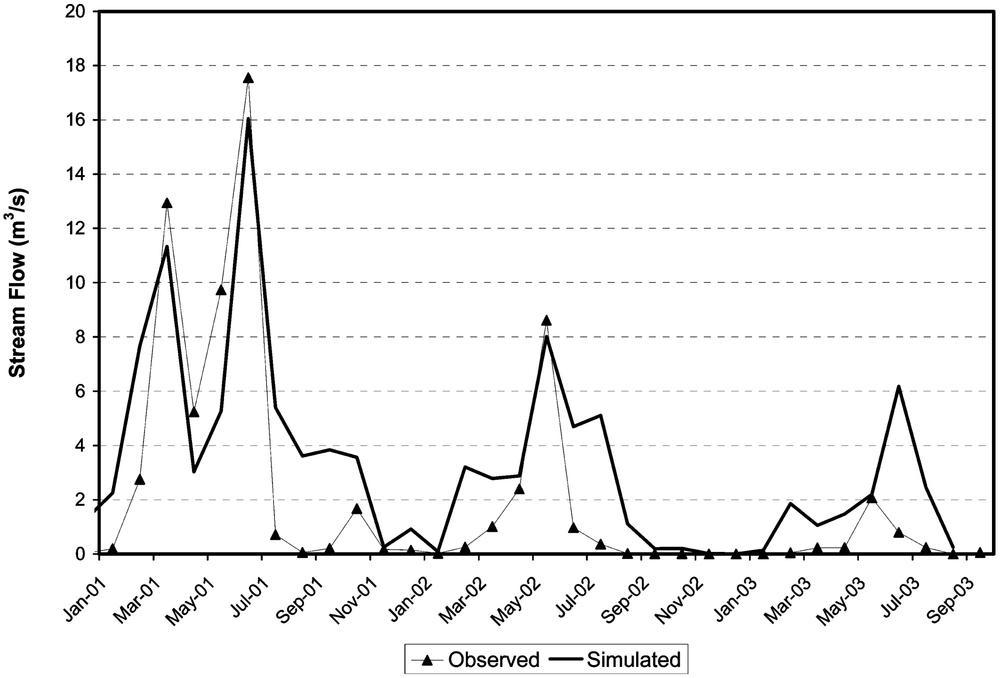


Figure 6. Comparison of observed and simulated average monthly streamflow in Rathbun watershed at USGS gauge 06903400.

Lake and Reservoir Characteristics. Water body characteristics such as lake storage volume at principal and emergency spillways, lake surface area, and maximum flow rate of the principal spillway and drainage area were obtained from state agencies, ERC, and National Inventory of Dams (NID) from the U.S. Army Corps of Engineers (*28*). The SWAT model simulates the lake volume as mass balance between the runoff inflow, overflow through principal and emergency spillways, evaporation, percolation, and lake withdrawal. Withdrawal for drinking water from Grindstone Reservoir was an important component of the water balance within the lake and influenced the concentration of agricultural chemicals in the water body. Average monthly withdrawal rates from Grindstone Reservoir were obtained from the city of Cameron through ERC.

Management Practices. The product use survey conducted on Missouri watersheds provided the product application date within the fields that received isoxaflutole applications. In these fields, simulated corn planting was scheduled 10 days after the application. In fields that did not receive isoxaflutole applications within these watersheds, and in other watersheds where the exact date of product application was not available, corn planting and isoxaflutole application simulations were based on heat unit scheduling available in the SWAT model. On the basis of the fraction of potential heat units (PHU) specified, the heat unit scheduling allowed the model to schedule the operations as a function of temperature. The fraction of PHU for scheduling isoxaflutole application and corn planting was set to 0.12 and 0.15, respectively. It should be noted that corn in these watersheds is cultivated under zero tillage or conservation tillage conditions, which was incorporated in the management practice inputs of the model.

Model Calibration. Acceptable simulation of hydrology is important for any water quality model, which needs to be validated and sometimes, when necessary, calibrated. Calibration and validation of hydrology require measured hydrological information such as runoff volume or streamflow measurements. Except for the Rathbun watershed, streamflow information was not available for model calibration at other watersheds. The streamflow outputs from SWAT were compared with the observed measurement at two stream gauges located within the Rathbun Reservoir watershed to verify SWAT predictions. It should be noted that extensive calibration and validation of the SWAT model have previously been conducted by Srinivasan and Arnold (*29*) as a part of the Hydrologic Unit Model for the United States (HUMUS) project, by comparing the simulated streamflow to measurements from over 5900 stream gauging stations across the United States.

Isoxaflutole residues were first detected in the La Belle Lake in 2001. However, the detailed grower survey showed that there was no product use at this watershed since the time of product registration in 1999. The lake monitoring record since 2001 showed the presence of isoxaflutole residues from an unknown source, which dissipated continuously during the course of the monitoring with no additional input of isoxaflutole-derived residues. The TRR data (isoxaflutole plus RPA 202248) from La Belle Lake provided an ideal source of information for calibrating the degradation rate of TRR in a natural water body. The calibrated degradation rate was used in the simulation for other watersheds.

Long-Term Simulation. One of the objectives of this study was to determine the long-term fate of TRR—isoxaflutole and its metabolite, RPA 202248—in lakes and reservoirs due to its use in the corn acres within the watershed. For this study, a period of 20 years from 1983 to 2002 was chosen for model simulations. The following conditions were employed for the long-term simulations in order to consider realistic worst-case situations:

- The product was applied in the watershed each year of the simulation.
- The highest calibrated use rate during 2001−2003 was used for each of the years of the simulation.
- The spatial pattern for product application within the watershed established during the highest year of use was used for each of the years during the long-term simulation.

As La Belle was a small watershed and did not have any product use, long-term simulations were, therefore, conducted on only the other three watersheds, Grindstone, Bluestem, and Rathbun.

The long-term model simulations were evaluated in terms of flushing index for each watershed. Jones et al. (*30*) defined the flushing index as a ratio of average annual runoff volume to the lake volume. In other words, it indicates the number of times on average per year that the lake volume is replenished by the runoff from the watershed. This depends directly on the lake capacity, watershed area, precipitation in the watershed, and runoff potential of the watershed and indirectly depends on the land use, land cover, and soil characteristics of the watershed. The flushing index will significantly influence the magnitude and duration of the compounds' concentration in the water body.

Time-series analysis was also conducted on the model simulations to determine any long-term trend in the data. Time series of predicted concentration at the water body was decomposed into a *trend* series, a *seasonal* variation series, and a *random* component. An accumulation of residues with time in a water body would be demonstrated by a continual increase in the trend component.

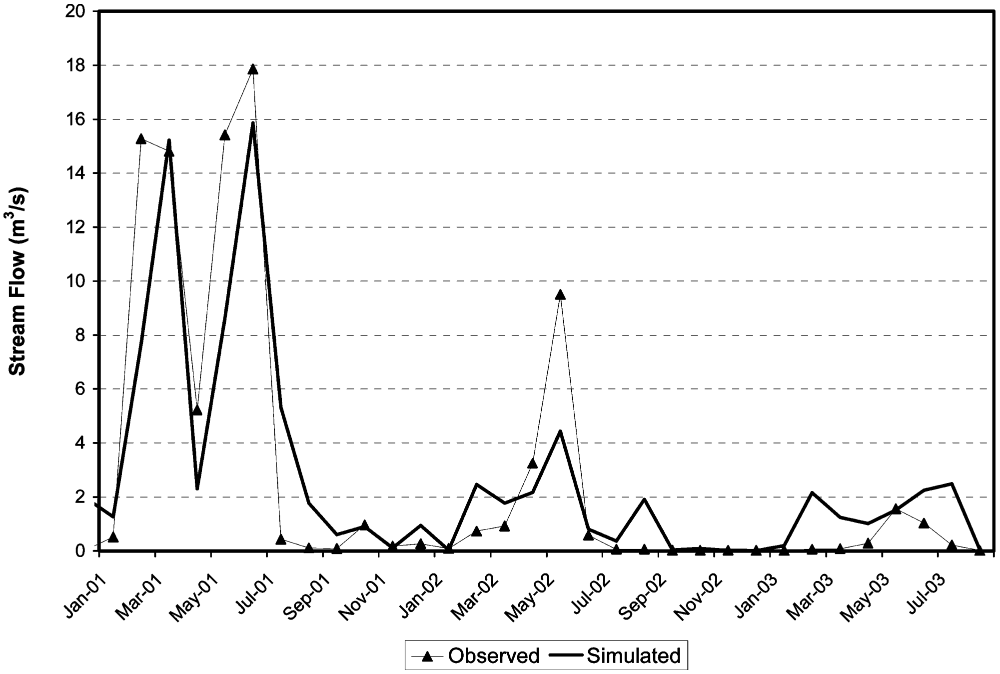


Figure 7. Comparison of observed and simulated average monthly streamflow in Rathbun watershed at USGS gauge 06903700.

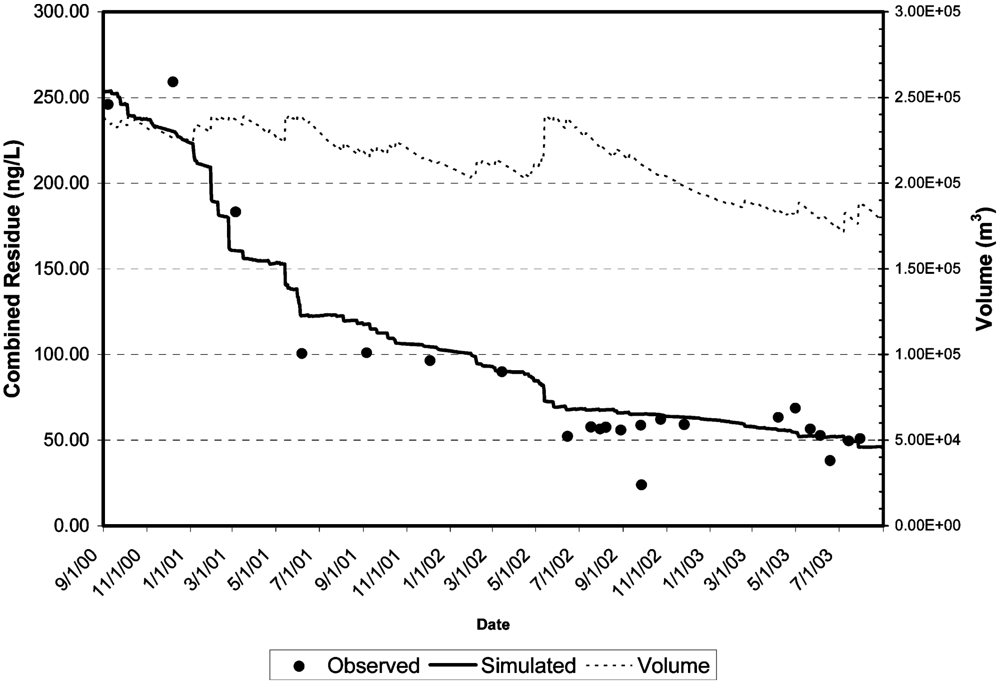


Figure 8. Comparison of monitored and simulated TRR concentration in La Belle Lake.

RESULTS AND DISCUSSION

Hydrologic Verification. The streamflow predictions made by SWAT were compared with observed streamflow data at two USGS stream gauges (06903400 and 06903700) in the Rathbun watershed to verify the model's hydrologic predictions. **Figures 6** and **7** show the comparison of average monthly streamflow simulated by SWAT and that observed at gauges 06903400 and 06903700, respectively. The figures show that the flows simulated by SWAT compare well with the observed flows, indicating satisfactory simulation of hydrology within the watershed. It should be noted that these simulations were obtained by using default hydrologic parameters obtained using the DEM, soil, and land use data from readily available data sources, without any calibration. Furthermore, the use of default model inputs from spatially distributed data sources will help to adopt a consistent approach for all of the watersheds to evaluate the risk of pesticide accumulation potential under diverse morphologic and management conditions. As Rathbun was the biggest watershed simulated in this study and due to

Table 4. Mass Balance of TRR in Water Bodies Derived from Watershed Modeling

watershed name	% dissipated through outflow and pumping	% degraded	% remaining dissovled	% remaining sorbed
La Belle Lake	20	66	14	<1
Grindstone Reservoir	77	18	5	<1
Bluestem Reservoir	81	9	10	<1
Rathbun Reservoir	44	23	32	<1

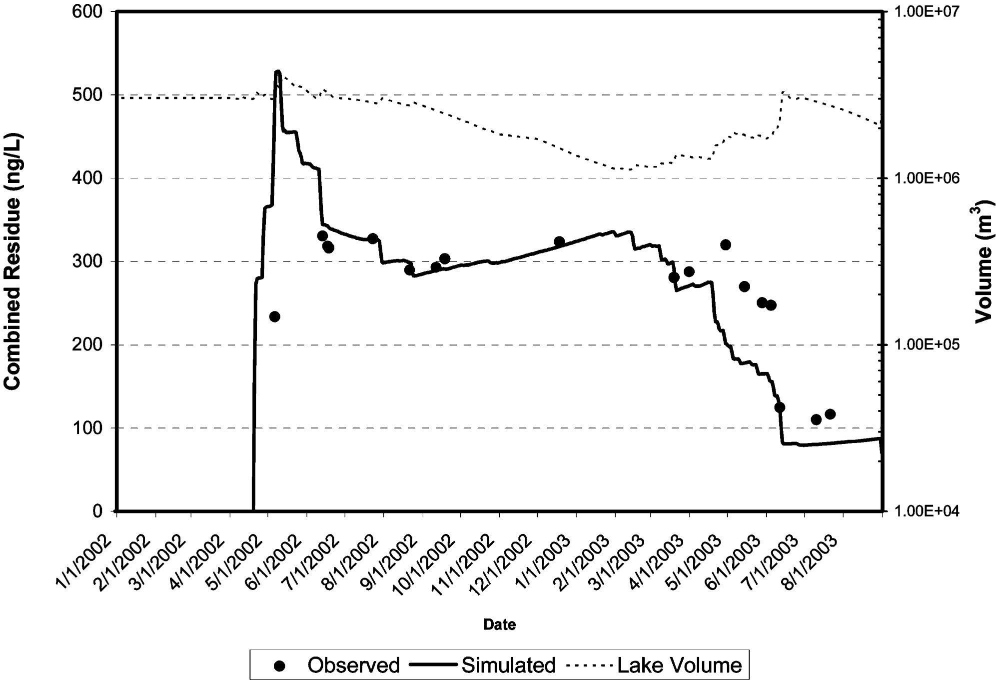


Figure 9. Comparison of monitored and simulated TRR concentration in Grindstone Reservoir.

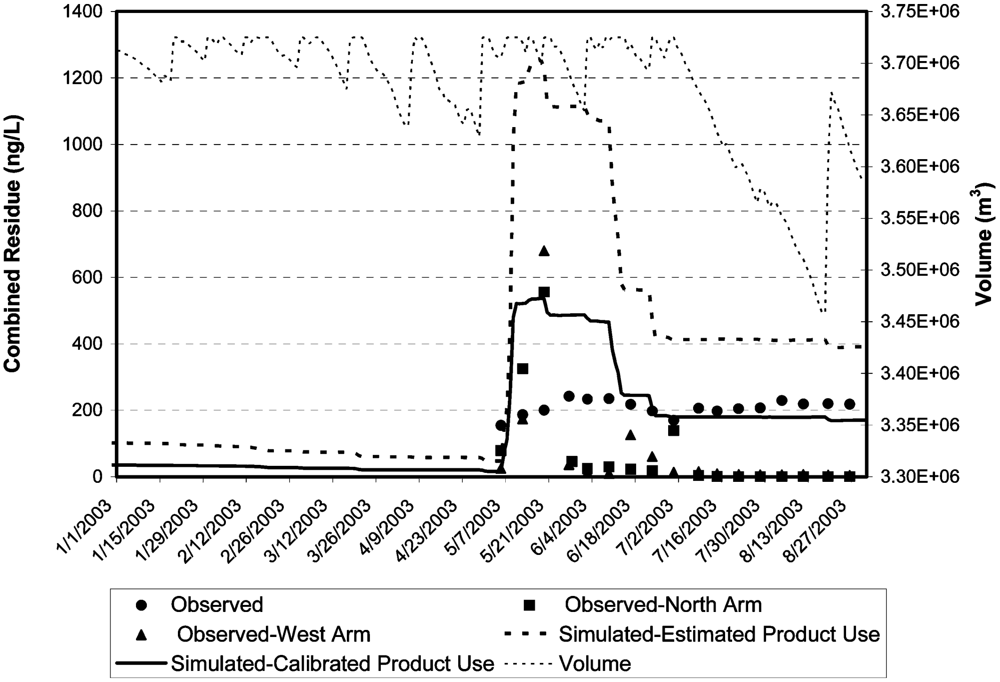


Figure 10. Comparison of monitored and simulated TRR concentration in Bluestem Reservoir.

Table 5. Flushing Index of Water Bodies Based on Long-Term Simulation

watershed name	lake area (ha)	lake vol (10^4 m^3)	av annu rainfall (mm)	av annu runoff (mm)	runoff (% of rainfall)	av lake flushing index (year^{-1})
Grindstone Reservoir	71.6	303.8	943.4	278.2	29.5	4.9
Bluestem Reservoir	131.5	372.5	818.7	225.5	27.5	2.5
Rathbun Reservoir	4456.9	25330.6	941.6	266.8	28.3	1.5

the fact that model streamflow simulations compared well with the observed data, physically based models such as SWAT will be able to simulate the hydrology without much calibration in contrast to empirically derived models.

Calibration of Pesticide Degradation Rate. Using the default hydrologic parameters, the fate and transport of isoxaflutole TRR in the La Belle Lake watershed and lake were simulated using the SWAT model. As input, the simulation assumed no product use within the watershed (**Table 3**). However, the initial TRR concentration in the lake was set to a value of 250 ng/L, which was equal to the monitored value. The model simulated the runoff volume loaded to the lake along with the chemical and water mass balance within the lake. The aquatic degradation rate parameter in the reservoir water quality component of SWAT was calibrated until an acceptable comparison of model estimated and monitored concentration of TRR was achieved (**Figure 8**). The calibrated degradation rate of TRR was equivalent to a first-order half-life of 460 days.

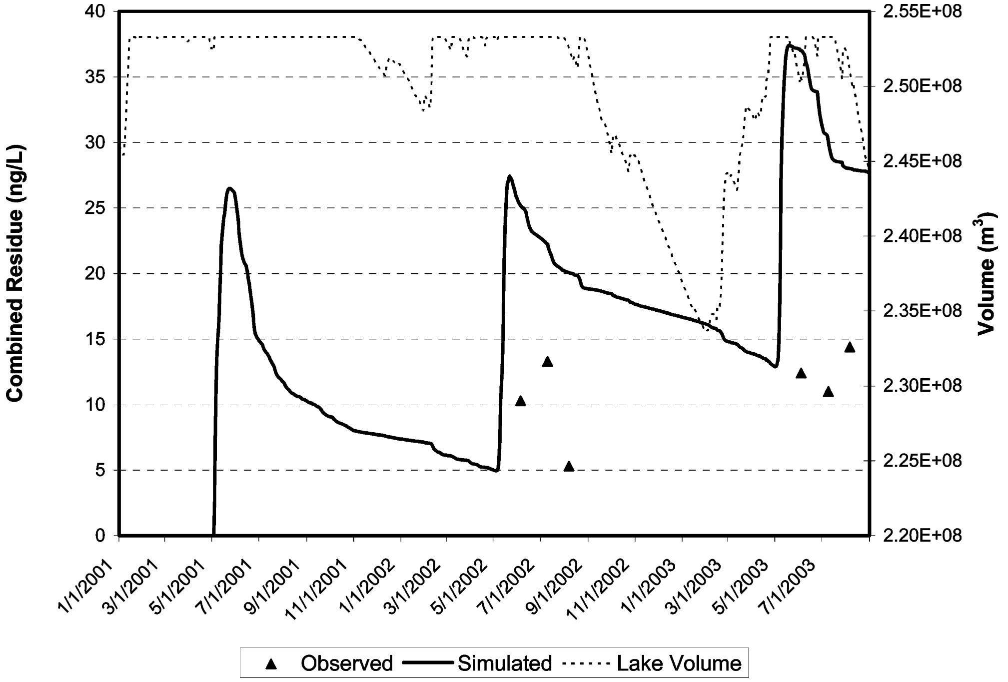


Figure 11. Comparison of monitored and simulated TRR concentration in Rathbun Reservoir.

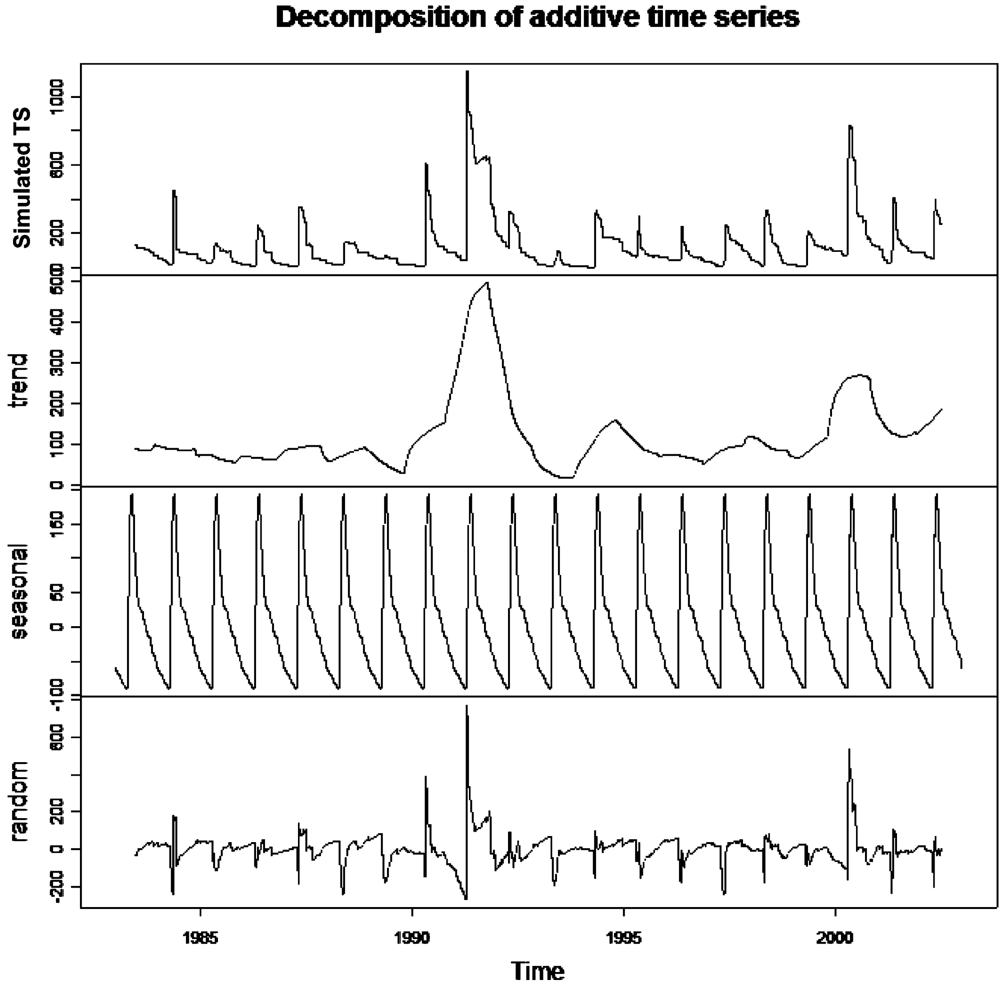


Figure 12. Results from the decomposition of a daily concentration (ng/L) of TRR during 20 years in Grindstone Reservoir.

The resultant degradation rate complements the results from an outdoor aquatic degradation study (*31*). It should be noted that the calibrated degradation rate does not reflect the dissipation of TRR through outflow from the lake, but reflects only a simple first-order degradation of the residues within the lake. The calibrated degradation rate is deemed conservative because SWAT does not account for the effects of temperature on degradation. The first-order half-life of 460 days was used in

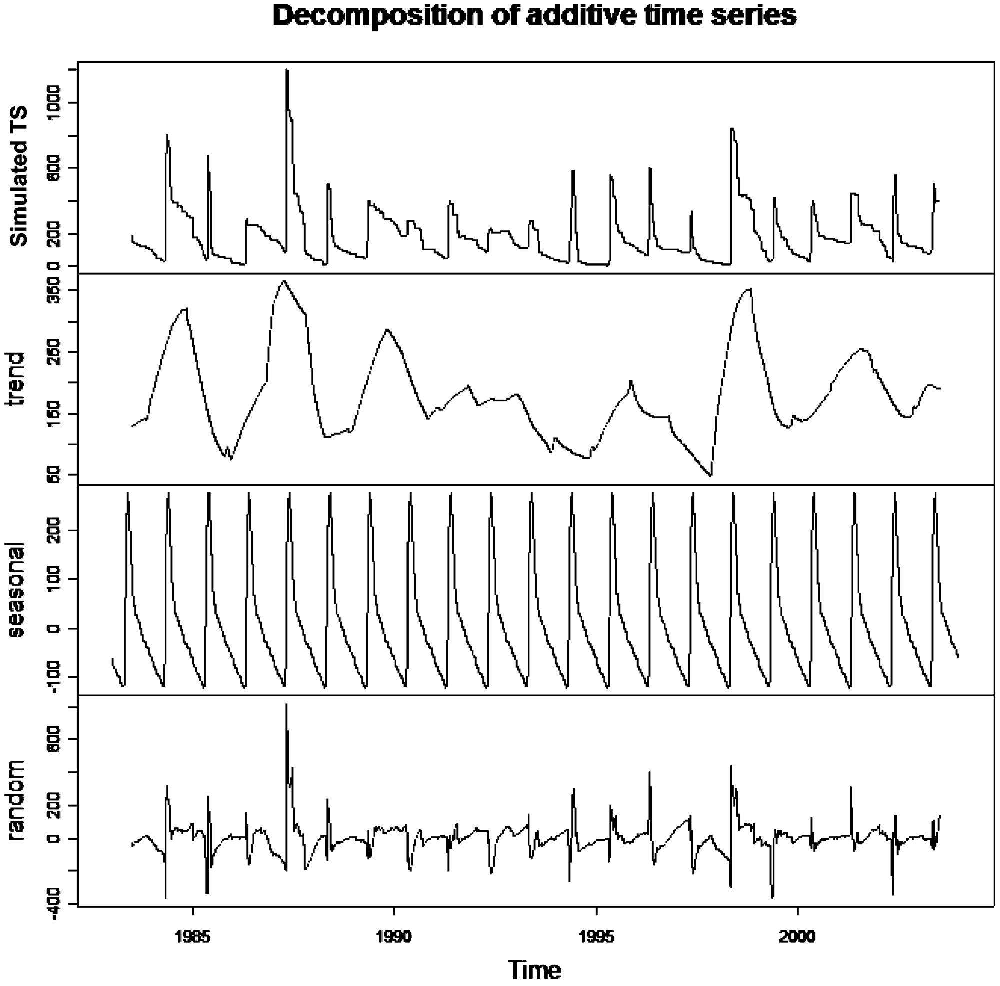


Figure 13. Results from the decomposition of a daily concentration (ng/L) of TRR during 20 years in Bluestem Reservoir.

all other simulations in this study. As noted in **Table 4**, in the case of La Belle Lake, dissipation through outflow was a minor route with degradation in water accounting for the major loss (66%). Discounting the chemical dissipation through outflow and degradation, the amount remaining in the reservoir at any time point would be a combination of the chemical in dissolved and sorbed phases.

Simulation of TRR at Other Watersheds. *Grindstone Reservoir.* The Grindstone Reservoir exhibited a marked response to precipitation events and runoff from the watershed due to the high flushing index (**Table 5**) of the reservoir. **Figure 9** shows a good correspondence between the monitored TRR and simulated concentrations and also shows that the model simulated the lake flushing characteristics very well, particularly after the spring rains during 2002 and 2003. Residue levels increased rapidly in response to fresh inputs of isoxaflutole-derived residues soon after application in early spring 2002. The concentration levels, after sustaining through the summer of 2002, declined in response to fresh inputs of water containing no residues from fall 2002 through spring 2003. It should be noted that there was product use only in 2002 in the watershed (**Table 3**). Dissipation through outflow is clearly the predominant contributor to mass loss (**Table 4**).

Bluestem Reservoir. In general, without any calibration of input parameters to the model, the temporal pattern of the simulated results matched with the observed results, but the magnitude did not (**Figure 10**). The estimated product use for the Bluestem watershed had to be reduced by 60−70% of the estimated value to achieve a satisfactory comparison of monitored and simulated concentrations in the lake (**Table 3**). The resultant simulated concentration in the lake compares favorably with the observed concentrations (**Figure 10**). The simulated residue concentrations in the north arm, west arm, and main reservoir peaked early in the season and, thereafter, fluctuated slightly, reflecting the fluctuations in the lake volume but demonstrating an overall decrease in concentration with time. The watershed simulation suggested that dissipation through outflow was the major route of mass loss (81%), with no evidence of accumulation (**Table 4**).

Rathbun Reservoir. The streamflow verification at two USGS stream gauges at Rathbun Reservoir was presented earlier (**Figures 6** and **7**). **Figure 11** shows the comparison of observed and simulated concentrations of the TRR in the reservoir. It is evident that the model overestimated the concentration in the reservoir, which may be due to higher estimated product use in the watershed. Because the variations between observed and simulated TRR concentrations are within reasonable ranges, no attempts were made to calibrate the product use. By considering the simulation, it is evident that residues in the reservoir occur according to the same pattern observed in most of the other reservoirs analyzed. Residues flow to the reservoir primarily as a result of the first major rainfall event. Thereafter, residues dissipated through a combination of outflow (44%) and degradation (23%).

Long-Term Simulation. *Flushing Index.* The long-term simulation was conducted using SWAT for the Grindstone, Bluestem, and Rathbun watersheds. Twenty years of weather data (1983−2002) were used for this purpose, and simulation

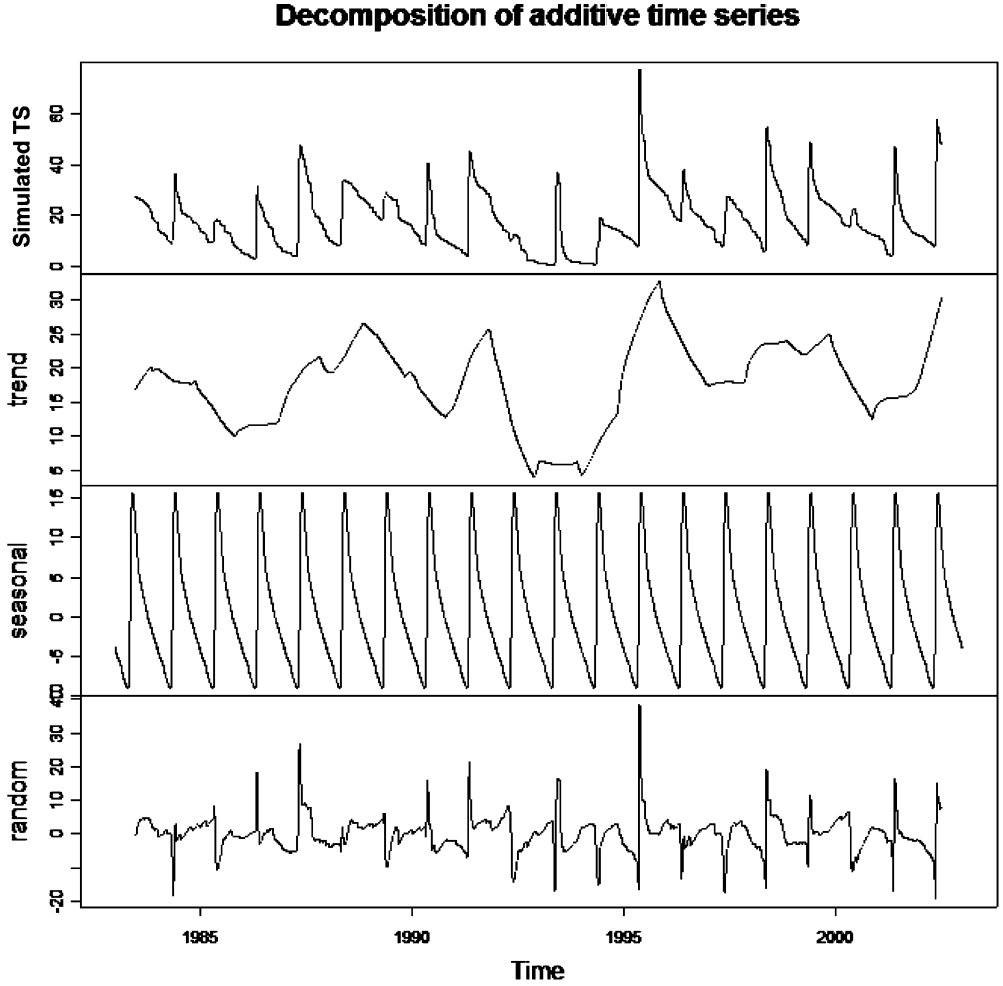


Figure 14. Results from the decomposition of a daily concentration (ng/L) of TRR during 20 years in Rathbun Reservoir.

resulted in daily TRR concentrations in the three reservoirs. From the long-term simulations, an important characteristic that was derived for these watersheds was the flushing index (**Table 5**). Depending on the degradation properties of a compound in aquatic systems, the flushing index will significantly influence the magnitude and duration of the compound's concentration in the water body soon after a loading event. Clearly, for a lake with a high flushing index, the duration of the high concentration in the lake after a loading event will be shorter than that for a lake with a lower flushing index. Accordingly, for Grindstone Lake (flushing index = 4.9), the mean and median of the ratio of annual maximum to minimum concentration, during the simulation period (20 years), are 28.6 and 21.4, respectively, whereas for Rathbun Reservoir (flushing index = 1.5), the mean and median of the ratio of annual maximum and minimum TRR concentrations for the same period are 10.9 and 7.9, respectively. This is because the residues dissipate more quickly through the outflow in lakes with a high flushing index than in lakes with a low flushing index.

Time-Series Analysis. The daily concentration time series obtained from the long-term simulations were decomposed into *trend*, *seasonal*, and *random* series using the *decompose* module of a statistical tool, *R*, version 1.9.1 (*32*). **Figures 12−14** show the results from the decomposition of the daily TRR concentration time series from the three water bodies considered for long-term simulation analyses. In these figures, the *simulated TS* series are the simulated daily residue concentration time series in nanograms per liter (ppt) in the respective water bodies obtained from the long-term simulations.

It can be seen in these figures that the highest concentrations in the time series correspond to the rainfall events (*random* component). The high concentration dissipates quickly in Grindstone Reservoir and Bluestem Reservoir, which have relatively high flushing indices (**Table 5**). In the case of Rathbun Reservoir with a low flushing index, the duration of the combined residue concentration is relatively more prolonged than that of the lakes with a high flushing index. The *trend* components of the time series do not show any significant long-term upward trend for any of the water bodies irrespective of the magnitude and duration of the residue concentration during individual years. This shows that the potential for long-term accumulation of TRR (isoxaflutole plus RPA 202248) in semistatic water bodies is very low.

Conclusions. On the basis of the comprehensive analyses of the fate and transport of isoxaflutole-derived residues in semistatic water bodies, we conclude the following:

- The watershed modeling using SWAT adequately characterized the fate and transport of isoxaflutole-derived residues in the watershed and the water body. A carefully parametrized model such as SWAT can adequately explain the fate and transport of pesticides, thus eliminating or minimizing the need for extensive water quality monitoring.
- Four factors primarily influence the magnitude and trend of isoxaflutole-derived residues in semistatic water bodies: (a) management practices, (b) watershed morphology, (c) magnitude and timing of runoff or drainage events, and (d) rate of degradation in the water body. The use of a surface water hydrological model that takes into account the pesticide transport

and dissipation processes facilitates a holistic analysis of the influence of these factors on the residue patterns in water bodies.

- Lake monitoring data and SWAT simulations both support the hypothesis of degradation of RPA 202248 in the natural water bodies.
- The degradation rate of 460 days for TRR (isoxaflutole plus RPA 202248) estimated in this study may indicate persistence in water bodies. However, a comprehensive evaluation that accounted for all of the dissipation pathways in reality indicates no evidence for long-term accumulation of isoxaflutole-derived residues in semistatic water bodies.

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