JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Influence of Rainfall Distribution on Simulations of Atrazine, Metolachlor, and Isoxaflutole/Metabolite Transport in Subsurface Drained Fields

GAREY A. FOX*

Biosystems and Agricultural Engineering Department, 120 Agricultural Hall, Oklahoma State University, Stillwater, Oklahoma 74078-6016

SRI H. PULIJALA

Dudek Engineering and Environmental, 529 West Blueridge, Orange, California 92865

GEORGE J. SABBAGH

Environmental Research, Bayer CropScience, 17745 South Metcalf, Stilwell, Kansas 66085

This research investigated the impact of modeling atrazine, metolachlor, and isoxaflutole/metabolite transport in artificially subsurface drained sites with temporally discrete rainfall data. Differences in considering rainfall distribution are unknown in regard to estimating agrochemical fluxes in the subsurface. The Root Zone Water Quality Model (RZWQM) simulated pesticide fate and transport at three subsurface drained sites: metolachlor/atrazine field experiment in Baton Rouge, LA (1987), and two isoxaflutole/metabolite field experiments in Allen County and Owen County, Indiana (2000). The modeling assumed linear, equilibrium sorption based on average reported physicochemical and environmental fate properties. Assumed rainfall intensity and duration influenced transport by runoff more than transport by subsurface drainage. As the importance of macropore flow increased, the necessity for using temporally discrete rainfall data became more critical. Long-term simulations indicated no significant difference between average or upper percentile (i.e., <2% difference in percent loss as a function of mass applied) atrazine, metolachlor, or isoxaflutole/metabolite loss through subsurface drainage among the three different rainfall assumptions. It was necessary (i.e., within 7% of predicted loss) to use hourly or average duration storm events as opposed to daily rainfall data for total (i.e., runoff and subsurface drainage) pesticide loss over the long term.

KEYWORDS: Atrazine; environmental exposure; isoxaflutole; metabolite; metolachlor; modeling; rainfall distribution

INTRODUCTION

Subsurface drainage is an important management practice aimed at removing excess water from fields. Subsurface drainage prevents stunted root growth, delayed planting, and possible crop failure. However, concerns exist about the transport of pesticides to subsurface drains and eventually into streams adjacent to drained fields. Therefore, the ability to model pesticide transport in fields with subsurface drains is important to quantify the environmental impact of agrochemicals on adjacent water bodies. The Office of Pesticide Programs (OPP) at the U.S. Environmental Protection Agency (U.S. EPA) utilizes a tiered screening approach for drinking water and aquatic exposure assessments. For tier II surface water screening, the OPP uses the Pesticide Root Zone Model (PRZM), a daily time step, one-dimensional field-scale model that simulates pesticide runoff and leaching. The agency is currently considering the adoption of a tier II screening model for exposure assessments for groundwater sources of drinking water (*1*−*3*).

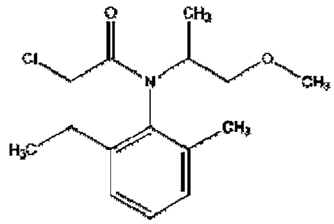
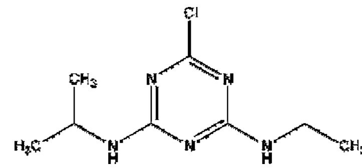
PRZM is one of the models being considered by OPP. PRZM has been evaluated for leaching at numerous field sites with reasonable success (*4*−*7*). However, PRZM does not simulate events on a subdaily time scale, macropore flow, or artificial subsurface drainage, all of which have been shown to influence pesticide transport (*8*). Another model being considered by OPP is Root Zone Water Quality Model (RZWQM), which is a one-dimensional model capable of simulating runoff, leaching, and artificial subsurface drainage on a subdaily time scale (*9*, *10*).

In RZWQM, precipitation that exceeds the infiltration rate is routed into macropores on the basis of a flow capacity limit determined by Poiseuille's law (*11*, *12*). Water entering into

* Corresponding author [e-mail garey.fox@okstate.edu; telephone (405) 744-5431; fax (405) 744-6059].

10.1021/jf063753z CCC: $37.00
Published on Web 06/07/2007

Table 1. Summary of Pesticide Properties Applied on Drained and Nondrained Plots at Ben Hur Research Site (*20*, *21*)

		
chemical name	2-chloro-6′-ethyl-*N*-(2-methoxy-1-methylethyl)-*o*-acetotoluidide	1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine
application amount (kg/ha)	2.16	1.63
molecular weight (g/mol)	283.8	215.7
water solubility (mg/L)	530	33
vapor pressure	1.3×10^{-5} at 25 °C	2.89×10^{-7} at 25 °C
soil K_{oc} (cm^3/g)	190	150
soil surface half-life (days)	20	36

macropores is evenly distributed among the number of effective macropores per unit area. Chemicals are also routed through macropores and allowed to react through chemical partitioning with soil surrounding the macropores. A linear isotherm is assumed for the relationship between chemical absorbed to soil and chemical in solution (*11*). Routines in RZWQM are able to simulate the possible direct connection between macropores and subsurface drains (*8*).

Research has indicated that transport of pesticide in runoff and to the subsurface through macropores is influenced considerably by rainfall intensity and duration (*13*−*17*). However, few, if any, studies attempt to quantify the impact of commonly assumed rainfall distributions in pesticide fate and transport modeling on both annual and long-term simulations over a range of agrochemicals. In fact, a 2005 Federal Insecticide, Fungicide, and Rotencide Act (FIFRA) scientific advisory panel on carbamate cumulative risk assessment explicitly stated that the "...practical differences in considering intensity are unknown with regard to estimating pesticide fluxes in the subsurface over the long-term" (*18*).

MATERIALS AND METHODS

Atrazine, Metolachlor, and Isoxaflutole/Metabolite Field Experiments. This research utilized data collected from three unique subsurface drained field sites in Louisiana and Indiana. The first research site was a field-scale metalochlor and atrazine transport study during the 1987 growing season at the Ben Hur Research Farm located 6 km from Baton Rouge (*19*). Soil was Commerce silt loam (fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) formed in alluvial deposits. Three corrugated polyethylene 102 mm diameter drainage pipes were installed at a depth of 100 cm from the surface. The spacing between the drains was 2000 cm, and the radius of drains was 10 cm. Earth dikes 0.3 m in height were placed so that runoff passed through an H-flume for measurement. For the 1987 growing season, plots were planted with silage corn on April 15−16, and corn was harvested in early August (*20*). Atrazine and metolachlor were applied as a mixture on April 22−24 (**Table 1**) at rates of 1.63 and 2.16 kg/ha, respectively (*20*). Water samples were analyzed for atrazine and metalochlor by extraction with *n*-hexane and analysis by gas chromatography, as discussed in detail by Southwick et al. (*20*, *21*). More details on the sampling are included in numerous literature reports (*20*−*22*).

This research also utilized data from two fate and transport studies with isoxaflutole, (5-cyclopropyl-1,2-oxazol-4-yl)(α,α,α-trifluoro-2-mesyl-*p*-tolyl)methanone, and its daughter product, RPA 202248, α-(cyclopropylcarbonyl)-2-(methylsulfonyl)-*β*-oxo-4-(trifluoromethyl)-benzenepropanenitrile (**Table 2**). Isoxaflutole is registered for use on corn (*23*). Isoxaflutole rapidly degrades (i.e., half-life, $t_{1/2}$, approximately 2 days) into the actual inhibitor of the enzyme *p*-hydroxy phenyl pyruvate dioxygenase (HPPD): RPA 202248. This daughter product is a more persistent compound (**Table 2**).

The first isoxaflutole experimental site was a 30.4 ha isolated field in Allen County, Indiana, with Hoytville silty clay (fine, illitic, mesic Mollic Epiaqualfs) and slopes of <2% (*8*). The second isoxaflutole experimental site was a 10.9 ha field in Owen County, Indiana, with Philo silt loam soil (mixed, active, mesic Fluvaquentic Dystrudepts) and slopes of <1%. Both fields contained subsurface drain lines with an equal spacing of 10 m buried at approximately 1.0 m below ground surface. No-till agricultural management practices were used at both sites in a corn (1998, 2000) and soybean (1999) rotation. Both fields were planted to corn on May 25, 2000. Soil samples collected at both sites were analyzed for particle size distribution, organic matter content, and bulk density (*8*). Soil samples were collected at depth intervals of 15 cm from the surface to approximately 1.5 m below the surface (i.e., 0−15, 15−30, etc.).

A potassium bromide tracer was surface applied at the rate of 39.2 kg/ha on April 29, 2000, for the Allen County site and at the rate of 37.7 kg/ha on May 15, 2000, for the Owen County site. Isoxaflutole was surface applied pre-emergent to bare soil in solid form at the rate of 0.13 kg/ha 5 days after bromide application in the Allen County field and 1 day after bromide application in the Owen County field. Concentrations in soil and subsurface drain flow were monitored for the remainder of the growing season. Water samples were analyzed for isoxaflutole and RPA 202248 using the "Method of Analysis for the Quantification of Isoxaflutole and Its Metabolites in Water Using Isotopically Labeled Internal Standards-Revision 99.3" (April 18, 2000, File No. 46037). The limit of quantification is 0.010 μg L^{-1}, and the limit of detection is 0.003 μg L^{-1}. For the Owen County, Indiana, site, subsurface drain flow was unavailable due to instrument error. Further information on soil and drain flow sampling is outlined by Fox et al. (*8*) for the Allen County site, with the same procedures used at the Owen County site.

Modeling Atrazine, Metolachlor, and Isoxaflutole/Metabolite Transport. Calibration and model evaluation was quantitatively assessed using a normalized objective function (NOF). The NOF is the ratio of the root mean square error (RMSE) to the overall mean of the observed parameter (*1*, *24*, *25*)

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(X_i - Y_i)^2}{n}} \quad (1)$$

$$\mathrm{NOF} = \frac{\mathrm{RMSE}}{X_a} \quad (2)$$

Table 2. Physicochemical and Environmental Fate Properties for Isoxaflutole and Its Metabolite, RPA 202248 (*8*)

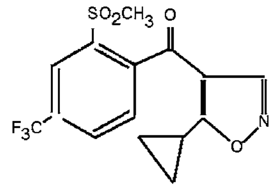
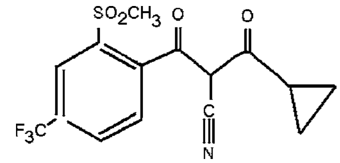
		
CAS Registry No.	141112-29-0	143701-75-1
chemical name	(5-cyclopropyl-4-isoxazolyl) [2-(methylsulfonyl)-4- (trifluoromethyl)phenyl] methanone	α-(cyclopropylcarbonyl)-2-(methylsulfonyl)-β-oxo-4-(trifluoromethyl) benzene-propanenitrile
molecular weight (g/mol)	359	359
water solubility (mg/L)	6.2	326
octanol–water partition coefficient (log *P*)	2.32	–0.37
vapor pressure (mmHg)	1.0×10^{-6} at 25 °C	1.0×10^{-6} at 25 °C
soil K_{oc} (cm^3/g)		
range	102–227	62–204
mean ± 90% confidence interval	155 ± 35	
mean		139 ± 23
laboratory aerobic soil half-life (days)		
range	0.3–4.3	10–39
mean ± 90% confidence interval	1.7 ± 0.9	
mean		27.0 ± 7.0
field dissipation half-life (days)		
range	0.5–3.7	7.0–79.0
mean ± 90% confidence interval	2.0 ± 0.4	
mean	18.0 ± 7.0	
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

Table 3. Soil Characteristics for the Ben Hur Research Site (*19*)[a]

layer	depth (cm)	clay (%)	bulk density (g/cm^3)	K_{sat} (cm/h)
1	30	14–27	1.35–1.65	1.12
2	60	14–39	1.35–1.65	1.12
3	90	14–39	1.35–1.65	3.25
4	100	14–39	1.35–1.65	3.25
5	120	14–39	1.35–1.65	3.9
6	150	14–39	1.35–1.65	4.16

[a] Soil texture data were obtained from the Map Unit Use File (MUUF) Database (*29*).

where X_i and Y_i are the observed and predicted values, respectively; X_a is the mean of observed values; and n is the number of observations. For screening applications, where parameters are not calibrated for the site, model results should be within an order of magnitude of the observed values, which corresponds to an NOF value of <9.0; for site-specific application where data are measured on-site, the model should match observations within a factor of 2, which corresponds to an NOF value of 1.0 (*26*, *27*). Therefore, the criteria used in this evaluation were that the NOF values for hydrology should be equal to or less than unity because the model was calibrated on hydrology. For pesticide transport, the NOF values should be only slightly greater than unity because no calibration was performed on pesticide parameters.

The RZWQM was calibrated on the basis of 1987-measured values of runoff and subsurface drainage at the Baton Rouge site. Model calibration was based on the hourly rainfall data. It is realized that model calibration using distributed rainfall across average storm durations or over a 24 h period could result in a unique set of soil and hydraulic parameters. The soil parameters listed in **Table 3** were used as initial values in the model. The soil was divided into 10 layers with a total profile depth of 300 cm. Initial (i.e., before calibration) values for soil hydraulic properties (i.e., the field capacity and water retention parameters) were derived by the RZWQM. The RZWQM derives estimated hydraulic properties from a soils database based on soil texture class and adjusts these values on the basis of bulk density (*9*). Weather data were available on an hourly time scale as measured by a weather station on site. Soil macroporosity parameters were included to simulate preferential flow. The surface crust conductivity and soil macroporosity parameters including the macropore radius, effective macroporosity, and lateral sorptivity reduction factor were obtained from selected literature (*8*, *10*−*12*). The calibration included adjusting the soil hydraulic parameters (*28*) including the bubbling pressure head, pore six distribution index, residual and saturation water contents, and a macropore−drain express fraction parameter (*8*) until the model-predicted drain flow and runoff met site-specific applicability based on the NOF criterion. No calibration was performed on pesticide fate and transport properties, and the model assumed linear equilibrium sorption. Values of half-life and organic carbon sorption coefficient were taken directly from Southwick et al. (*21*) and Sabbagh et al. (*22*).

Fox et al. (*8*) calibrated a RZWQM model based on observed drain flow for the Allen county site and a 1 year (January 1, 2000−December 31, 2000) simulation period. We followed the same approach in this research (**Table 4**). The same parameters were calibrated as discussed above for Baton Rouge until the model met site-specific applicability (i.e., NOF < 1.0). Values were constrained to be within limits reported by the Map Use Unit File (MUUF) soils database. Hourly weather data were measured by an on-site weather station. After calibration on hydrology, the model was evaluated on the basis of predicted bromide, isoxaflutole, and RPA 202248 transport in subsurface drain flow assuming equilibrium sorption. Transport through the soil matrix and macropores was simulated using the calibrated model and the mean pesticide parameters (**Table 2**). Observed concentrations of bromide, isoxaflutole, and RPA 202248 in edge-of-field subsurface drain flow were compared to predicted concentrations. Further details on the model calibration and evaluation at this site are given in Fox et al. (*8*).

This research also applied RZWQM to the Owen County, Indiana, field site with a 1 year (January 1, 2000−December 31, 2000) simulation period. On the basis of soil samples, the soil profile was divided into six layers: 0−15, 15−30, 30−90, 90−107, 107−152, and 152−256 cm. RZWQM default hydraulic parameters were used initially

Table 4. Default and Calibrated Root Zone Water Quality (RZWQM) Soil Hydraulic Parameters Derived from Input Soil Texture and Bulk Density for the Allen County and Owen County, Indiana, Sites

layer	depth (cm)	moisture contents[a] (cm^3 cm^{-3}) θ_r	θ_s	θ_{33}	θ_{15}	K_{sat}[c] (cm/h)	Brooks–Corey parameters[b] S_2 (cm)	A_2	N_2
				Allen County					
				Default Parameters					
1	15	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
2	30	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
4	107	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
5	152	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
6	296	0.09	0.48	0.38	0.27	0.06	37	0.13	2.15
				Calibrated Parameters					
1	15	0.09	0.48	0.38	0.27	1.0	5	0.05	2.15
2	30	0.09	0.48	0.38	0.27	0.5	5	0.05	2.15
4	107	0.09	0.48	0.38	0.27	0.3	5	0.05	2.15
5	152	0.09	0.48	0.38	0.27	0.1	5	0.05	2.15
6	296	0.09	0.48	0.38	0.27	0.1	5	0.05	2.15
				Owen County					
				Default Parameters					
1	15	0.027	0.574	0.234	0.116	1.32	3.98	0.22	2.66
2	30	0.027	0.574	0.234	0.116	1.32	3.98	0.22	2.66
3	90	0.027	0.558	0.234	0.116	1.32	4.55	0.22	2.66
4	107	0.027	0.543	0.234	0.116	1.32	5.18	0.25	2.66
5	152	0.027	0.570	0.234	0.116	1.32	4.11	0.22	2.66
6	296	0.075	0.464	0.312	0.136	0.23	25.8	0.19	2.58
				Calibrated Parameters					
1	15	0.015	0.574	0.286	0.136	0.68	5.00	0.21	2.63
2	30	0.015	0.574	0.286	0.136	0.68	5.00	0.21	2.63
3	90	0.015	0.558	0.286	0.136	0.68	5.00	0.21	2.63
4	107	0.015	0.543	0.286	0.136	0.68	5.00	0.21	2.63
5	152	0.015	0.570	0.286	0.136	0.68	5.00	0.21	2.63
6	296	0.075	0.464	0.312	0.136	0.23	25.8	0.19	2.58

[a] θ_r and θ_s are the residual and saturated moisture contents, respectively; and θ_{15} and θ_{33} are the moisture contents at 15 and 0.33 bar tensions. [b] S_2 is the bubbling pressure head on the moisture distribution curve, A_2 is the pore size distribution index, and N_2 is the exponent for the unsaturated conductivity curve. [c] K_{sat} is the vertical saturated conductivity; K_{lat}, the lateral saturated hydraulic conductivity, was assumed to be 3 times K_{sat}.

(**Table 4**). Additional soil parameters were available from the MUUF soil database (*29*) for Philo silt loam. Data from the soil database matched laboratory measurements of soil texture, organic matter, and bulk density from the field samples. Soil macroporosity parameters were obtained from selected literature (*10*, *12*). Weather data were input based on measured hourly data from an on-site weather station.

The same parameters were calibrated as discussed above for Baton Rouge and Allen County within limits established by the MUUF soil database and soil samples until model predictions met site-specific applicability (i.e., NOF < 1.0) for bromide (Br) concentrations. As a conservative tracer, bromide should adequately depict hydrologic conditions at the site. Plant uptake of bromide was not considered in the simulations. After calibration on Br, isoxaflutole and RPA 202248 transport through the soil matrix and macropores was simulated using the calibrated model and assuming equilibrium sorption based on the average reported physicochemical and environmental fate properties (**Table 2**). Observed and predicted concentrations of isoxaflutole and RPA 202248 in edge-of-field subsurface drain flow were compared on the basis of the NOF.

Influence of Assumed Rainfall Intensity on Transport. Hourly rainfall data at the three sites were converted into distributed rainfall data across typical rainfall durations and over 24 h. For the Baton Rouge site, the 1987 hourly rainfall data were converted into 24 h rainfall distributions using the Natural Resource Conservation Service (NRCS) 24 h hyetograph approach for a type III geographical area (*30*). On the basis of data in the 1987 hourly rainfall file, average storm duration was calculated. Intensity was assumed to be uniformly distributed across this calculated average rainfall duration. For the Allen County and Owen

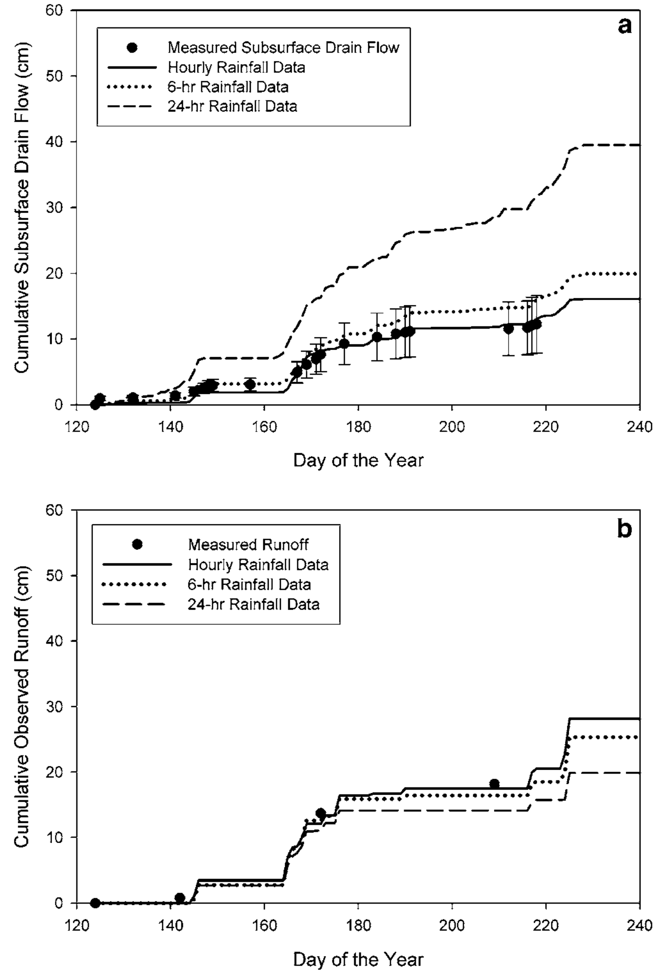


Figure 1. Measured versus predicted Root Zone Water Quality Model (RZWQM) (**a**) subsurface drain flow and (**b**) runoff for the Baton Rouge, LA, field site when using hourly rainfall data, average duration (6 h) uniformly distributed rainfall, and NRCS 24 h distributed rainfall. Error bars on subsurface drain flow represent ± one standard deviation (*20*).

County, Indiana, sites, more detailed time-distribution relationships, which have been suggested to be more appropriate than NRCS methodologies for storm events in the midwestern United States, were used (*31*, *32*). Huff and Angel (*31*) expressed time distributions as cumulative percentages of storm rainfall and storm duration based on a quartile grouping of whether the heaviest rainfall occurred in the first, second, third, or fourth quarter of a storm. Median time distributions of storm rainfall at a point were used to distribute the daily rainfall totals for each day across either the typical rainfall duration or over 24 h. Model-predicted runoff, subsurface drainage, and pesticide concentrations in runoff and subsurface drainage were compared for the 1-year simulations with the assumed rainfall duration based on NOF evaluation criteria.

Long-term (30 year, 1961−1990) simulations were then performed with the calibrated models to quantify differences in pesticide loss as functions of annual rainfall volumes and the assumed rainfall distribution. Hourly rainfall data and average daily weather data were collected from Samson Weather data and state climatologists' offices for locations closest to the field sites: Baton Rouge, LA, Fort Wayne, IN, and Indianapolis, IN. Annual percent losses were calculated at each site for each of the assumed rainfall distributions.

RESULTS AND DISCUSSION

Modeling Atrazine, Metolachlor, and Isoxaflutole/Metabolite Transport. For the Baton Rouge site, minimal calibration of the model resulted in reasonable hydrologic simulation

Table 5. Normalized Objective Function (NOF) Values for Observed versus Model Predicted Flow and Atrazine, Metolachlor, Isoxaflutole, and Metabolite Concentrations at the Three Subsurface Drained Field Sites as a Function of Assumed Rainfall Distribution

	hourly	av duration	24 h
Baton Rouge, LA			
flow			
runoff	0.2	0.2	0.6
subsurface drainage	0.4	0.4	1.9
atrazine			
runoff	0.3	0.3	0.8
subsurface drainage	0.5	1.5	5.8
metolachlor			
runoff	0.3	0.4	0.8
subsurface drainage	0.6	0.5	1.5
Allen County, Indiana			
flow			
subsurface drainage	0.7	0.7	3.3
isoxaflutole			
subsurface drainage	0.9	1.3	1.4
metabolite			
subsurface drainage	1.0	1.7	1.9
Owen County, Indiana			
bromide			
subsurface drainage	0.8	1.0	2.3
isoxaflutole			
subsurface drainage	1.5	1.6	1.6
metabolite			
subsurface drainage	1.7	2.5	2.6

for the subsurface drained site. The saturated conductivity was equivalent to those reported in **Table 3**. Bulk densities were used as reported by Sabbagh et al. (*22*). The bubbling pressure head and pore size distribution index were assumed to be uniform with depth at magnitudes of 60 cm and 0.19, respectively, which falls within ranges for silt loam soil as reported by Rawls et al. (*29*). Lateral saturated hydraulic conductivity was assumed to be equivalent to vertical saturated conductivity. Effective macroporosity (0.00005) matched values used in RZWQM modeling of macropore flow by Malone et al. (*11*). The macropore radius (0.05 cm) fell within the range of reported radii for tilled (0.03 cm) and short-term no-till (0.06 cm) soil (*12*). Surface crust conductivity (0.01 cm h^{-1}) was reasonable for crust conductivities of the top 5 mm of cultivated soils (0.02 cm h^{-1}) and values reported as realistic for RZWQM simulations (*12*). No express fraction was required by the model.

The predicted cumulative drain flow matched measured drain flow and runoff (**Figure 1**) with an NOF of 0.4 for daily measured versus predicted drain flow and 0.2 for runoff (**Table 5**). The model was capable of predicting the timing of peaks in subsurface drainage and runoff shortly after chemical application, which is critical in environmental exposure assessment but, generally, underpredicted the magnitude of these early drainage and runoff events. RZWQM underpredicted metolachlor and atrazine loss in runoff and drain flow shortly after chemical application due to the underprediction of the flow (**Figure 2**). The NOF values were slightly below unity for pesticide losses in subsurface drain flow and runoff, signifying the model satisfied a site-specific application (**Table 5**).

Calibration of the RZWQM for the Allen County, Indiana, site was outlined by Fox et al. (*8*) and is reiterated in **Table 4**. The model was capable of predicting the observed subsurface drain flow on the regression limbs of drain flow hydrographs (**Figure 3**), with an NOF of 0.7 (**Table 5**). Predicted runoff matched observations that runoff at the site was minimal (i.e., <5 cm) during the 2000 growing season. The model captured the dynamics of the leaching when simulating concentrations of isoxaflutole and RPA 202248 (**Figure 4**), but the amplitude

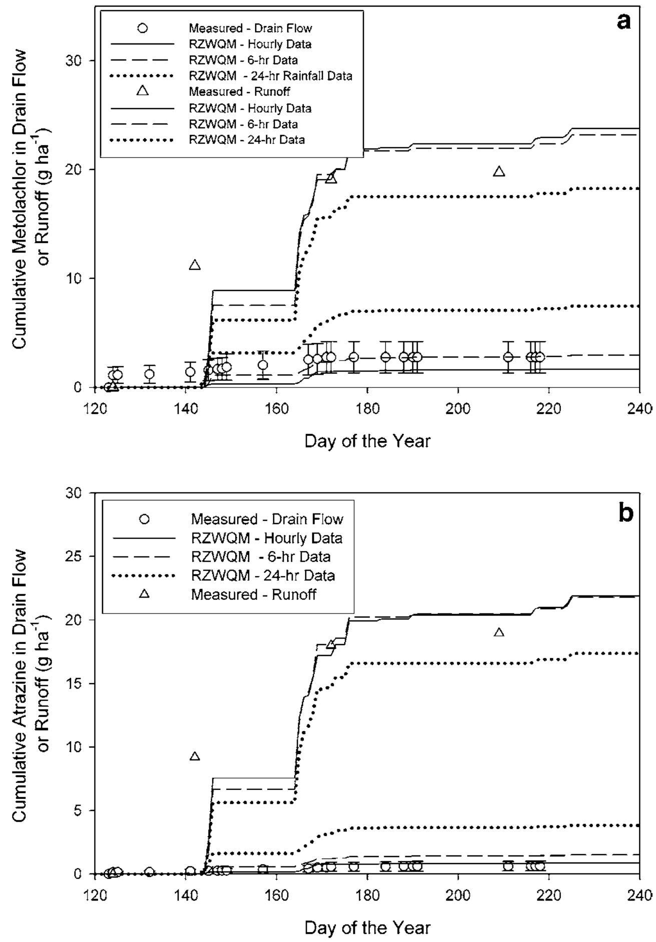


Figure 2. Measured versus predicted Root Zone Water Quality Model (RZWQM) (**a**) metolachlor and (**b**) atrazine for the Baton Rouge, LA, field site when using hourly rainfall data, average duration (6 h) uniformly distributed rainfall, and NRCS 24 h distributed rainfall. Error bars represent ± one standard deviation (*20*).

of the peaks is less evidently reproduced. NOF values for isoxaflutole and RPA 202248 were 0.9 and 1.0, respectively (**Table 5**).

For the Owen County, Indiana, site, minimal calibration of hydraulic parameters predicted the temporal distribution of bromide in edge-of-field subsurface drain flow (**Table 4**; **Figure 5**). Vertical, saturated conductivities were reasonable compared to the MUUF soil database that suggested hydraulic conductivities between 0.5 and 5.0 cm h^{-1}. An EF of 2% was used similar to previous studies (*8*). The NOF suggested site-specific application (**Table 5**). The calibrated model was able to capture the timing of one of the two significant peaks in isoxaflutole, although it should be noted that the peaks had magnitudes of 0.01−0.04 μg L^{-1} and two peaks in RPA 202248 with magnitudes of 5−10 μg L^{-1} (**Figure 6**). The model failed to predict an observed isoxaflutole peak 1 day after application (day 138). This peak occurred during a 0.5 cm rainfall event. Concentrations in edge-of-field subsurface drain flow 1 day after application were most likely due to preferential transport through macropores. However, the model failed to simulate macropore flow for this rainfall event. Simulated isoxaflutole and RPA 202248 concentrations were consistently less than observed concentrations at these peaks (i.e., observed peak of 0.04 μg L^{-1} compared to a simulated peak of 0.02 μg L^{-1} for isoxaflutole; observed peak of 9.0 μg L^{-1} compared to a simulated peak of 6 μg L^{-1} for metabolite). NOF values for isoxaflutole and RPA 202248 were 1.5 and 1.7, respectively

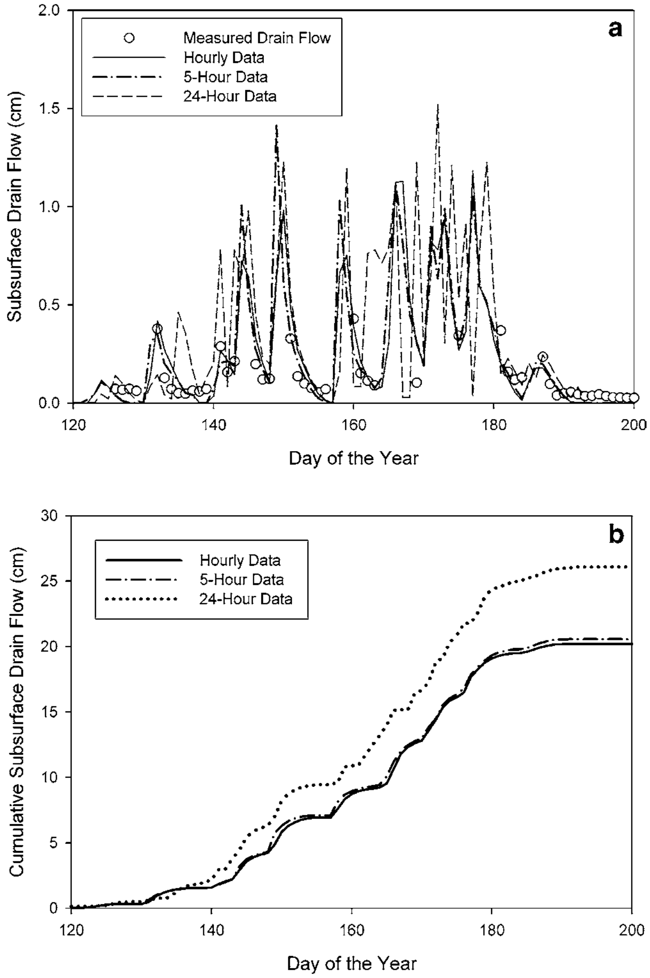


Figure 3. Measured versus predicted Root Zone Water Quality Model (RZWQM) (**a**) daily subsurface drain flow and (**b**) cumulative drain flow for the Allen County, Indiana, field site when using hourly rainfall data, average duration (5 h) distributed rainfall, and 24 h distributed rainfall. The RZWQM was calibrated based on hourly rainfall data.

(**Table 5**). Because the pesticide parameters were not adjusted, these results were acceptable.

Influence of Assumed Rainfall Intensity on Transport. Rainfall duration during the 1987 growing season at Baton Rouge, LA, was log-normally distributed with an average duration of 6.4 h and a standard deviation of 5.9 h. Therefore, average rainfall duration of 6 h with uniform intensity was assumed for the site. Assuming either 24 h rainfall distributions using the NRCS hyetograph approach or uniform 6 h rainfall as opposed to using the hourly rainfall data had a greater influence on predicted flow and pesticide loss through subsurface drainage as compared to runoff (**Figures 1** and **2**; **Table 5**). The 24 h rainfall distribution assumption resulted in greater model-predicted subsurface drainage (approximately 300−400% greater drain flow) and less runoff (approximately 50−80% less runoff) at the end of the simulation period. Greater predicted subsurface drainage resulted in considerably greater metolachlor and atrazine in subsurface drain flow and less in runoff (**Figure 2**; **Table 5**). With rainfall assumed to be distributed across the entire 24 h period, RZWQM failed to simulate transpiration due to the assumption that incoming solar radiation was prohibited by cloud cover, which resulted in greater soil moisture in the profile. Using the uniform-intensity 6 h duration assumption resulted in greater predicted subsurface drain flow as compared to the hourly rainfall data, although flow depths predicted using

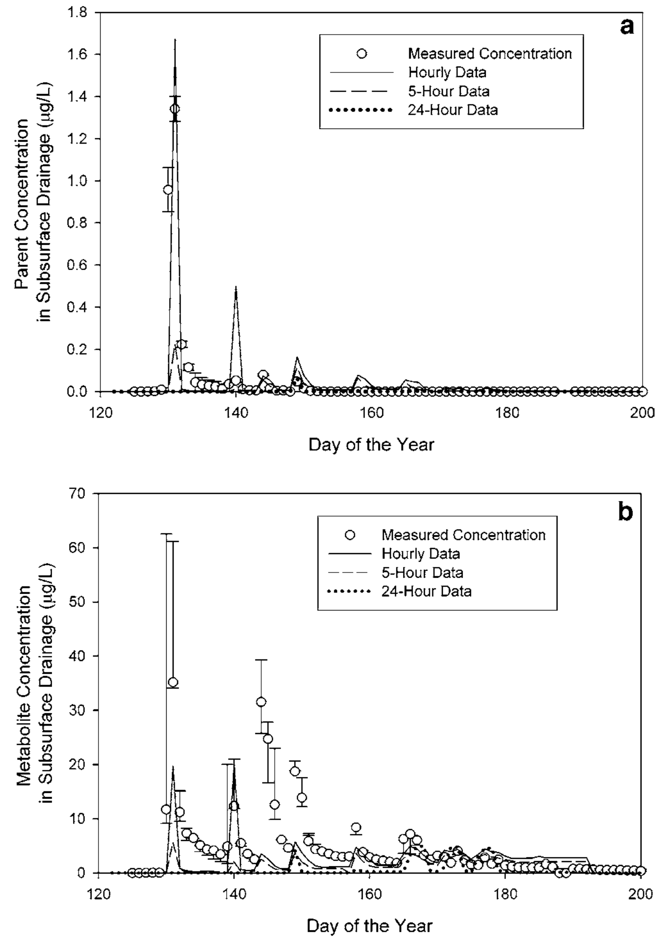


Figure 4. Measured versus predicted Root Zone Water Quality Model (RZWQM) (**a**) isoxaflutole and (**b**) metabolite concentration for the Allen County, Indiana, field site when using hourly rainfall data, average duration (5 h) distributed rainfall, and 24 h distributed rainfall. Error bars represent minimum and maximum concentrations measured by two samplers.

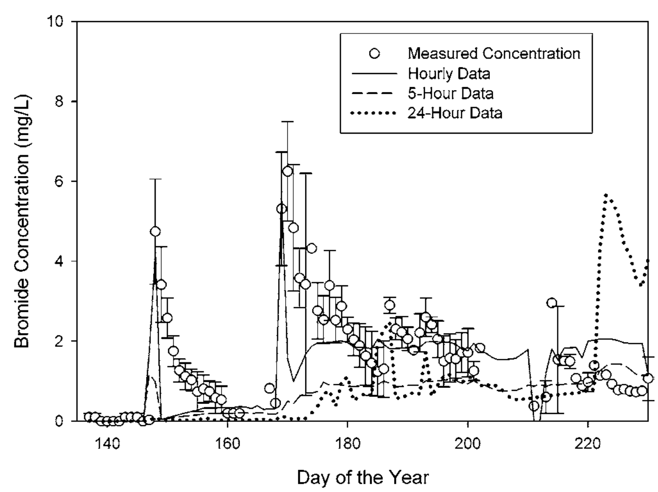


Figure 5. Measured versus predicted Root Zone Water Quality Model (RZWQM) bromide concentration for the Owen County, Indiana, field site when using hourly rainfall data, average duration (5 h) distributed rainfall, and 24 h distributed rainfall. Error bars represent minimum and maximum concentrations measured by two samplers.

this assumption fell within one standard deviation of the average drain flow depth (**Figure 1**; **Table 5**). Differences in runoff between the hourly and 6 h rainfall files were also minimal as documented by the NOF values for each simulation (**Table 5**).

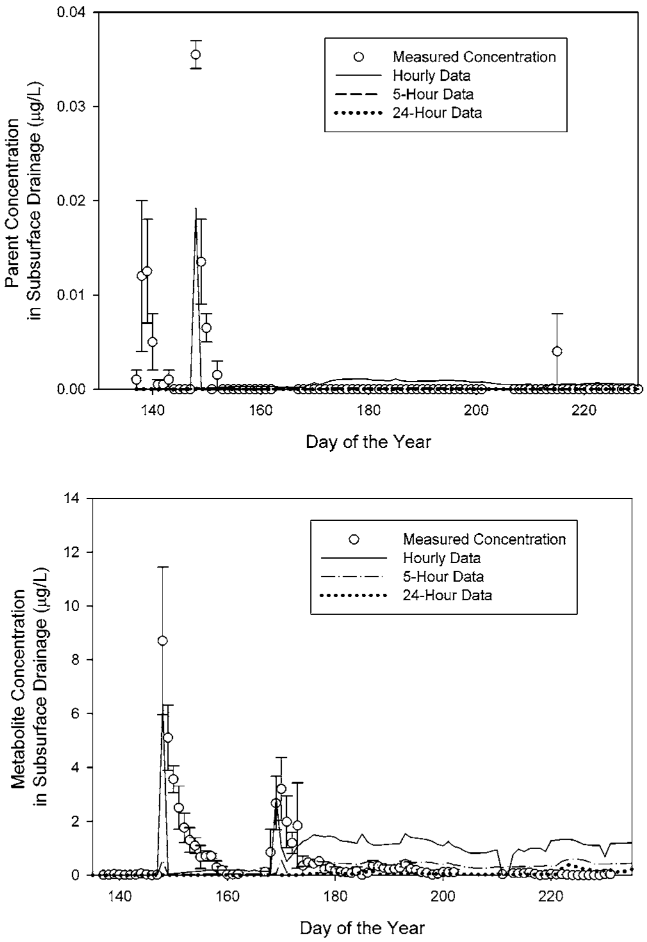


Figure 6. Measured versus predicted Root Zone Water Quality Model (RZWQM) (**a**) isoxaflutole and (**b**) metabolite concentration for the Owen County, Indiana, field site when using hourly rainfall data, average duration (5 h) distributed rainfall, and 24 h distributed rainfall. Error bars represent minimum and maximum concentrations measured by two samplers.

Observed metolachlor concentrations, which were underpredicted using the hourly rainfall data (NOF = 0.6), were more closely predicted when using a uniform 6 h duration (NOF = 0.5) (**Figure 2**). Atrazine concentrations were slightly overpredicted relative to the average and standard deviation with the uniform, 6 h duration rainfall assumption. Runoff losses were statistically equivalent between predictions using the hourly rainfall data and the uniform 6 h duration assumption (**Figure 2**; **Table 5**).

At the Allen County, Indiana, site, the average duration of rain storm events during the 2000 growing season was log-normally distributed with an average duration of 5.1 h and a standard deviation of 5.0 h. Therefore, the typical duration was assumed to be 5 h. Intensity was distributed according to a Huff curve for the 5 and 24 h duration assumptions (*31*). Similar to the Baton Rouge site, minimal differences were predicted in terms of subsurface drain flow and runoff between the hourly and distributed 5 h duration assumption (**Figure 3**; **Table 5**). Also, as expected, subsurface drain flow increased and runoff decreased with the distributed 24 h duration assumption. However, unlike the Baton Rouge site, significant differences were predicted in pesticide transport in subsurface drain flow between the hourly and distributed, 5 h duration assumption due to the prevalence of macropore flow (**Figure 4**; **Table 5**). At this site, macropore flow was critical for predicting the 0.2−1.4 $\mu g\ L^{-1}$ peaks in isoxaflutole and the 20−40 $\mu g\ L^{-1}$ peaks in metabolite shortly after chemical application. The site required a 2% express fraction linking macropores with the subsurface drain lines (*8*). The magnitude of macropore flow with the distributed, 5 h duration was significantly reduced (approximately 10−15%) when compared to the magnitude of macropore flow with the hourly rainfall data, especially on the days with observed peaks in parent and metabolite concentrations (i.e., days 128 and 140). The percent reduction in macropore flow from the hourly data to the distributed 24 h duration assumption was approximately 72%. Macropore flow, in relation to the total magnitude of drain flow, was less prevalent at the Baton Rouge site than at the Allen County site. Differences in predicted runoff and runoff losses were minimal between the model simulations with the three different rainfall data sets.

The Owen County, Indiana, site behaved similarly to the Allen County, Indiana, site in that the transport of pesticides was largely dependent on macropore flow. Average storm duration for the 2000 growing season was 5.1 h with a standard deviation of 5.6 h. Predicted bromide concentrations in subsurface drain flow were fairly equivalent between the hourly, distributed, 5 h assumption and the distributed 24 h assumption except for shortly after chemical application, which were due to differences in predicted macropore flow (**Table 5**). In fact, if the hourly data were not modeled with the proposed express fraction of Fox et al. (*8*), the predicted bromide concentrations were similar for all three rainfall assumptions. The ratio of macropore flow to drain flow at this site was approximately 78%. The distributed 24 h duration assumption predicted minimal (i.e., <1 ppb) metabolite concentrations in drain flow

Table 6. Average and 90th Percentile Percent Pesticide Losses as a Function of the Amount Applied for 30 Year (1961–1990) Simulations at the Baton Rouge, LA, Allen County, Indiana, and Owen County, Indiana, Field Sites

field site	pesticide	rainfall data	av and 90th percentile total loss (%)	av and 90th percentile drain flow loss (%)	av and 90th percentile runoff loss (%)
Baton Rouge	metolachlor	hourly	3.7 (14.0)	0.1 (0.2)	3.6 (14.0)
		6 h	3.0 (13.4)	0.1 (0.3)	2.9 (13.2)
		24 h	2.3 (7.9)	0.3 (0.6)	2.0 (7.3)
	atrazine	hourly	3.5 (11.6)	0.1 (0.2)	3.4 (11.5)
		6 h	3.0 (11.6)	0.1 (0.3)	2.9 (11.4)
		24 h	2.2 (6.8)	0.2 (0.4)	2.0 (6.4)
Allen County	isoxaflutole and metabolite	hourly	5.1 (13.7)	2.4 (4.1)	2.6 (11.7)
		8 h	4.3 (10.4)	2.4 (4.0)	1.8 (7.1)
		24 h	6.4 (15.5)	3.3 (5.6)	3.1 (10.9)
Owen County	isoxaflutole and metabolite	hourly	2.0 (2.7)	0.7 (1.1)	1.3 (2.4)
		8 h	1.8 (3.4)	1.5 (2.4)	0.3 (0.8)
		24 h	2.1 (3.5)	2.0 (3.5)	0.1 (0.1)

until the end of the growing season due to the reduced macropore flow generation (**Table 5**).

Long-Term Simulations. For Baton Rouge rainfall events from 1961 to 1990, the average duration was 6.1 h with a standard deviation of 6.9 h. Therefore, a typical rainfall duration of 6 h with uniform intensity was assumed. Greater predicted loss occurred with the hourly rainfall data as compared to predicted losses with the average duration or 24 h rainfall assumptions (**Table 6**). Such patterns were the result of the site being runoff dominated with percent losses largely dependent on time-discrete rainfall inputs at the soil surface. The years with >10% loss as a function of amount of pesticide applied experienced precipitation events shortly after chemical application. For these long-term (i.e., 30 year) simulations, differences between hourly, average duration, and 24 h rainfall assumptions were less visible based on mean annual percent loss compared to 90th percentile loss. For environmental exposure assessments based on upper percentile percent loss estimates, the use of distributed 24 h rainfall data underpredicted peak losses (**Table 6**). Assuming distributed average storm duration appeared to be appropriate for predicting reasonable upper percentile pesticide losses (**Table 6**).

For the Allen County and Owen County sites, average rainfall durations for the 1961−1990 period were 8.0 h (with a standard deviation of 6.7 h) and 7.4 h (with a standard deviation of 6.9 h), respectively. For these drainage-dominated sites, the 24 h distributed rainfall assumption resulted in the greatest percent loss of pesticide (**Table 6**). Using hourly rainfall data resulted in the greatest percent losses in years when macropore flow occurred shortly after chemical application. Otherwise, 24 h distributed rainfall data allowed the soil profile to more frequently reach saturation by elimination of vegetation transpiration and minimum runoff, which correspondingly increased pesticide transport capacity. The pattern of increased percent loss through runoff with more time discrete rainfall data was not apparent for the Allen County, Indiana, site due to model-predicted saturation excess runoff (i.e., saturation from below). Differences between either the mean or peak pesticide concentrations were <5% at Allen County and <2% at Owen County between the three rainfall assumptions (**Table 6**).

Therefore, long-term simulations suggest that minimal differences would be expected in average or upper percentile pesticide losses when using hourly or average duration rainfall data (i.e., <4% difference) due to the dependence of runoff on time-discrete rainfall. For runoff-dominated sites, long-term simulations required distributed average duration rainfall data to match 90th percentile percent losses as compared to 90th percentile percent losses when using the hourly data. For subsurface drainage dominated sites, the benefit of using temporally discrete rainfall data was less evident. Although macropore flow was important for short-term annual simulations of chemical loss when rainfall occurred shortly after application, these results suggest that modeling macropore flow may not be important for estimating mean or upper percentile total pesticide loss over the long term.

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Received for review December 27, 2006. Revised manuscript received February 19, 2007. Accepted April 25, 2007.

JF063753Z