USING RZWQM TO PREDICT HERBICIDE LEACHING LOSSES IN SUBSURFACE DRAINAGE WATER

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ABSTRACT. *Improvements have been made in the pesticide component of the Root Zone Water Quality Model (RZWQM) since its release in 1999 for the Management System Evaluation Areas (MSEA) project. This study was designed to evaluate the herbicide leaching component of the model using data on subsurface drainage flow and herbicide leaching losses for a 6−year (1992 to 1997) period. A sensitivity analysis was conducted for the key parameters important in the pesticide calibration process. The model was calibrated using 1992 data and validated using 1993 to 1997 data collected from a tile−drained field within the Walnut Creek watershed in central Iowa. The model evaluation criterion was based on percent difference between the predicted and measured data (%D), root mean square error (RMSE), and model efficiency (EF). Atrazine and metolachlor were applied to corn in 1993, 1995, and 1997, and metribuzin was used during the soybean growing seasons in 1992, 1994, and 1996 at the standard application rates used in Iowa. The predicted subsurface drainage volumes were in close agreement with the measured data showing %D = 1, RMSE = 8, and EF = 0.99, when averaged over the validation years. Herbicide half−life* ($t_{1/2}$) *and soil organic based partitioning coefficient* (K_{oc}) *were found to be the most sensitive parameters for simulating herbicide leaching losses in subsurface drainage water. Both* $t_{1/2}$ *and* K_{oc} *affected the mass and temporal distribution of the herbicide leaching losses in subsurface drainage flows. The predicted herbicide leaching losses in subsurface drainage water were the same order of magnitude as the measured data, when averaged across the validation years. The study also revealed that herbicide leaching losses were significantly* ($P < 0.05$) *controlled by the drainage volume* ($R^2 = 0.97$)*. The model, however, underpredicted herbicide leaching losses after crop harvest and during early spring, possibly because of preferential flow paths developed during these periods. More improvements may be needed in the RZWQM to consider the dynamics of the preferential flow paths development in cultivated soils similar to that of the study area.*

Keywords. *Herbicides, RZWQM, Subsurface drainage, Water quality.*

Nonpoint−source contamination of surface and ground water resources with herbicide losses from agricultural fields has become a serious environmental concern (Kanwar et al., 1997; Hatfield et al., 1999). Atrazine [6−chloro−N−ethyl−N'−(1−methylethyl−1,3,5−triazine−2,4−diamine], metolachlor [2−cholor−N−(2−ethyl−6−methylphenyl)−N−(2−methoxy− 1− methylethyl)acetamide], and metribuzin [4−amino−6−(1,1−dimethylethyl)−3−(methylthio)−1,2,4−triazine−5(4H)−one] are the most commonly used herbicides in corn−soybean growing regions of the U.S. (Larson et al., 1999). Atrazine is also one of the commonly detected compounds in groundwater in Iowa, where nearly 3.2×10^6 kg (a.i.) is applied annually (Jayachandran et al., 1994), although its use is decreasing. Exposure to atrazine may cause irritation in the eyes, nose, and throat, and the compound has been reported to be a possible human carcinogen (Yuan et al., 2000). These herbicides are mobile in the soil, and their contamination potential through surface and subsurface water flow paths has been well documented (Hallberg, 1989; Topp et al., 1994). Several studies have reported the leaching of herbicides via subsurface drainage water, and they therefore pose a direct threat to surface water contamination (Kanwar et al., 1999; Jayachandran et al., 1994; Jaynes et al., 1999).

Subsurface drainage systems have provided a shortcut to the transport of agricultural chemicals from the bottom of the root zone to the edge of the field (Bakhsh et al., 2001a; Hatfield et al., 1998). Therefore, monitoring and evaluation of subsurface drainage water quality and quantity is useful in developing best agricultural management practices that can minimize the contamination potential of water resources from the use of herbicides. Understanding the fate and transport of herbicides within the soil profile and leaching from the bottom of the root zone to the streams through tile lines can help in developing better management options to reduce the contamination potential.

In addition to laboratory and field experiments, computer simulation models offer an alternative approach to study the impact of various farming practices on the fate and transport mechanism of herbicides losses from agricultural areas (Ma et al., 2001; Azevedo et al., 1997). In characterizing the contamination potential from pesticide use, computer models can be more economical, faster, and environmentally safe

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screening tools in comparison with large field−scale experiments (Jaynes and Miller, 1999). These models, however, need to represent the effects of complex interactions among climate, soil, and management factors on the degradation, transport, and fate of the herbicides applied to the fields (Ahuja et al., 1999). Herbicide persistence has been modeled as directly correlated to soil water content and soil temperature (Walker, 1991). Moreover, models can be useful only when their predictions have been verified against field−measured data.

Various models such as GLEAMS (Leonard et al., 1987), PRZM (Carsel et al., 1984), OPUS (Smith and Ferreira, 1986), and LEACHM (Hutson and Wagnet, 1992) have been developed to assess the effects of agricultural chemicals on water quality. Another such soil−plant−atmosphere system model, the Root Zone Water Quality Model (RZWQM), has been developed to assess agricultural management effects on both water quality and crop production (Ma et al., 2000). The model integrates physical, chemical, and biological processes to simulate the effects of various agricultural management practices on plant growth, water movement, and chemical movement within and through the soil profile (Ahuja et al., 1999).

A team of USDA−ARS scientists is working to refine various algorithms of the RZWQM to better represent the complex interaction of soil, climate, and management factors on soil and water quality. The evaluation of various modules of the upgraded version of the RZWQM is an on−going process to improve its performance using field−measured data. In addition, many refinements have been made in the pesticide component of the model since its release for MSEA project studies (Ma et al., 2000). This study was designed to evaluate the pesticide component of the latest version of the RZWQM model with the following specific objectives:

- Calibrate and validate the subsurface drainage flow component of the RZWQM using data from 1992 through 1997 for a field within the Walnut Creek watershed in central Iowa.
- Calibrate and validate the pesticide component of the model by simulating atrazine, metolachlor, and metribuzin leaching losses with subsurface drainage water from 1992 through 1997.
- Conduct sensitivity analysis of the RZWQM using key parameters important in herbicide transport and leaching losses with subsurface drainage water.

WATER AND CHEMICAL TRANSPORT PROCESSES IN THE RZWQM

The RZWQM is a process−based agricultural system model that can be used to assess the effects of different management options on the soil and water quality. It is a one−dimensional field−scale model (vertical in the soil profile) and assumes a layered soil profile that is uniform in the simulated field. The model uses the Green−Ampt equation to simulate infiltration and the one−dimensional Richard’s equation to redistribute water within the soil profile. The model uses the modified Brooks−Corey equations to numerically represent the soil water retention and hydraulic conductivity relationships (Ahuja et al., 1999). The model divides the soil profile horizons into 10 mm depth increments down to the bottom of the profile to simulate water and chemical movements during infiltration. Surface runoff is calculated as the difference between rainfall and the infiltration in each computational time step. Chemical transport within the soil matrix is calculated using a sequential partial displacement and mixing approach in 10 mm depth increments during infiltration process.

For chemical transport, the soil matrix is divided into mesopore (mobile) and micropore (immobile) regions. Initially, soil water and chemical in both regions are assumed to be in equilibrium. During successive infiltration steps, the displacement of solution in saturated soil layers occurs only in the mobile regions following a piston displacement approach, but diffusion continues between the two regions. Mixing also occurs within the mobile region after each displacement step. For a soil−adsorbed chemical, either a linear isotherm and instantaneous equilibrium adsorption or a first−order reversible kinetic adsorption−desorption is assumed to occur between the solution and the adsorbed phases in both regions (Ahuja et al., 1996). At the end of an infiltration event, both regions reach equilibrium conditions within each depth increment. Chemicals in the top−mixing zone (20 mm) are subjected to nonuniform mixing by raindrops during precipitation and transfer to runoff. The degree of mixing (B) between rainwater and soil solution is assumed to be complete at the soil surface (z = 0) and decreases exponentially with depth (z), as described by Ahuja (1986):

$$B = e^{-bz} \tag{1}$$

where b is a parameter that is a function of soil type, surface roughness, and cover conditions, and z is the depth below the soil surface. Pesticide processes simulate the transformation and metabolism of a pesticide in different compartments of the soil−water−plant environment. Pesticides applied on plant and plant residues are subjected to degradation and wash−off losses. Pesticide degradation in the soil matrix is assumed to follow the first−order dissipation equation (Ahuja et al., 1996):

$$\frac{dC}{dt} = -kC \tag{2}$$

where C is pesticide concentration, k is a degradation rate constant (k = 0.693/half−life), and t is the time elapsed since pesticide application. This equation works well for initial degradation, but often not at later stages. The RZWQM provides four options for pesticide degradation modeling. These include: lumped dissipation, consisting of a one−compartment model (eq. 2) and a two−compartment model (two k values); individual dissipation; and the daughter products dissipation. The equilibrium process of sorption is assumed to be linear and instantaneous, as given below (Ahuja et al., 1996):

$$C_s = \mathrm{K}_d C_l \tag{3}$$

where C_s (µg g^{-1}) and C_l (µg mm^{-3}) are pesticide concentrations on the soil solid phase and in solution, respectively, and K_d is the overall partitioning coefficient, which is estimated from soil organic carbon coefficient (K_{oc}):

$$\mathrm{K}_d = \mathrm{K}_{oc} f_{oc} \tag{4}$$

where f_{oc} is the fractional soil organic carbon content in the soil, which can be calculated from the soil organic matter.

Table 1. Soil horizon properties of the study field used as model input (source: USDA, 1994).

Horizon	Depth (m)	Bulk Density[a] (Mg m^{-3})	Porosity	Field Capacity[a]	Hydraulic Conductivity[a] (mm h^{-1})	Soil Texture (%) Sand	Silt	Clay
1	0.16	1.20	0.55	0.28	35	25	42	33
2	0.27	1.24	0.53	0.28	35	24	40	36
3	0.66	1.30	0.51	0.28	35	26	39	35
4	0.92	1.32	0.50	0.27	35	26	40	34
5	1.12	1.41	0.47	0.24	35	26	41	33
6	1.48	1.65	0.38	0.13	35	44	36	20
7	2.50	1.78	0.33	0.16	6	39	42	19
8	2.94	1.78	0.33	0.14	6	52	32	16

[a] Adjustments were made during calibration.

More details on the pesticide component of RZWQM can be found in Ahuja et al. (1999).

MATERIALS AND METHODS

A 44.5 ha field within the Walnut Creek watershed near Ames, Iowa (41° 55' N, 93° 40' W) was selected as part of the Management System Evaluation Areas (MSEA) project. This site was extensively monitored for subsurface drainage flows and herbicide losses with subsurface drainage water from 1992 through 1997. The field was owned and managed by a farmer−cooperator and located in Major Land Resource Area 103, highly suitable for row crop production. Soils in the Walnut Creek watershed were formed in calcareous glacial till deposited within the Des Moines lobe during the Wisconsin glaciation. The topography is relatively level with minor variations in relief around depressional areas. The field is poorly drained and has high seasonally water table and, therefore, benefits from a subsurface drainage system (Hatfield et al., 1999).

This field is comprised of Canisteo (fine−loamy, mixed (calcareous), mesic typic haplaquolls), Clarion (fine−loamy, mixed, mesic typic hapludolls), Harps (fine−loamy, mesic typic calciaquolls), Nicollet (fine−loamy, mixed, mesic aquic hapludolls), Okoboji (fine, montmorillonitic, mesic cumulic haplaquolls), and Webster soils with a major portion (34%) of Webster soil (fine−loamy, mixed, mesic typic haplaquolls) in the field. Soil physical properties of Webster soil (USDA, 1994) were used as input values to the model (table 1). The field had been under long−term corn−soybean rotation with chisel plowing in the fall after corn harvest and spring cultivation before planting and field cultivation during the growing season to control weeds. Corn (*Zea mays* L.) was planted in 750 mm rows in 1993, 1995, and 1997. Soybean (*Glycine max* L.) was planted in 350 mm rows in 1992, 1994, and 1996. Nitrogen fertilizer at the rate of 90 kg ha^{-1} was applied to corn as NH_3 injected one week before planting, and no N−fertilizer was applied to soybean (table 2). The commonly used herbicides in the corn−belt regions of the Midwest are atrazine and metolachlor, which were applied to corn. Metribuzin was used during soybean growing seasons at the standard rates used in Iowa (Hatfield et al., 1999). The amount, method, and application times for herbicide applications are given in table 2.

The Walnut Creek watershed is mostly drained by a system of subsurface field drains (tiles) that feed into a network of large subsurface drains maintained by county drainage districts (Jaynes et al., 1999). The rapid delivery of groundwater by subsurface drains into stream ditches is a defining characteristic of the watershed; therefore, subsurface drains were monitored on a field basis within the watershed. The study field was drained by a single subsurface drain installed at approximately 1.2 m depth below the ground surface. The setup for monitoring subsurface drainage flow included a FLO−TOTE system (Marsh−McBirney, Inc., Frederick, Md.) to collect and record within−pipe flow data. Water samples were collected for chemical analysis by an auto−sampler (model 3700, ISCO, Lincoln, Neb.) programmed to collect samples based on volume of water discharged. These units were checked weekly for proper operation and correct performance. Herbicide concentrations (mg L^{-1}) in subsurface drainage water samples were analyzed following the procedure described by Hatfield et al. (1999). The herbicide load in subsurface drainage water (kg ha^{-1}) was calculated on a daily basis by multiplying the herbicide concentrations (mg L^{-1}) by the subsurface drainage (mm) and dividing it by 100 (conversion factor). The daily herbicide loads were added to calculate the total amount of herbicide leached annually with subsurface drainage water.

MODEL PARAMETERIZATION AND CALIBRATION

The model parameterization and calibration process was followed as described in Ahuja et al. (1999) and Bakhsh et al. (2001b). Soil properties data were grouped into eight soil layers depending on the texture of the soil profile (table 1). A deep soil profile of 2.94 m was modeled, which was required for simulating water table fluctuations and subsurface drainage flows. The drainable porosity (difference between porosity and field capacity) and hydraulic conductivity were the key parameters in calibrating subsurface

Table 2. Schedule of management activities for the study field.

Year	Crop	Planting Date	Harvesting Date	Fertilizer[a]
1992	Soybean	15 May	15 Oct.	None
1993	Corn	1 May	30 Oct.	90 kg/ha
1994	Soybean	1 May	25 Oct.	None
1995	Corn	15 May	20 Oct.	90 kg/ha
1996	Soybean	15 May	25 Oct.	None
1997	Corn	5 May	1 Nov.	90 kg/ha

[a] NH_3 injected 1 week before planting using spoke injector, chisel plow in fall one week after corn harvest, and field cultivation 1 week before planting and 3 weeks post−emergence for weed control.
Atrazine applied to corn during planting as broadcast (0.68 kg ha^{-1}), metolachlor applied to corn 30 days before planting as broadcast (1.81 kg ha^{-1}), and metribuzin applied to soybean during planting as broadcast (0.56 kg ha^{-1}).

drainage flow simulations. Meteorological data that were used in the model input file, such as wind speed, total radiation, actual and saturated vapor pressures, and air temperature, were measured every minute and averaged every 60 min at a location less than 2 km from the site. On−site measured rainfall data were used to prepare the breakpoint data file (Jaynes and Miller, 1999). Further details on the model initialization and hydrologic calibration can be found in Bakhsh et al. (2001b). After the calibration of the subsurface drainage module, the pesticide component of the model was calibrated to simulate the herbicide losses with subsurface drainage water.

The model was run for the 10−year period (1981 to 1991) prior to the simulation period of 1992 through 1997 to initialize the herbicide concentrations in the soil profile. The output herbicide concentrations in the soil profile, at the end of 10−year continuous simulations for a corn−soybean rotation system, were used directly as the initial values for the calibration year (1992). The model was calibrated using 1992 data of atrazine, metolachlor, and metribuzin losses in subsurface drainage water, and validated using 1993 to 1997 data. After the calibration of the pesticide module, simulations were made with a single continuous run from 1992 through 1997, and no parameter was changed for the validation period. In addition to many other herbicide characteristics responsible for its degradation, only two parameters, i.e., herbicide half−life and the partitioning coefficient based on soil organic carbon (K_{oc}), were used to calibrate the pesticide module.

Using K_{oc} has an advantage over using K_d (the overall partitioning coefficient) because it is associated with the soil organic carbon, which can vary from soil layer to layer and the model takes care of this effect during K_d computation for each computational layer. The K_{oc} values, however, may vary by a factor of 1 to 3, with the average value determined in the laboratory under controlled conditions (Knisel and Turtola, 2000). K_{oc} is a sensitive parameter in herbicide simulations; therefore, its site−specific value and range of spatial variation in the field are desirable for adequate simulation results.

The second most important parameter, used during pesticide calibration module, is the pesticide half−life in the soil. It determines the pesticide persistence in the soil profile and affected pesticide loss in subsurface drainage water, which percolates through the soil profile to reach the subsurface drainage tile lines. A specific half−life describes the degradation rate of the pesticide residing at a specific place. The RZWQM simulates pesticide fate using data from four compartments, i.e., foliar, residue, soil surface, and soil layers, and provides the option to assign half−life value for each compartment. Within each compartment, the user can assign a lumped soil layer half−life in addition to aerobic and anaerobic half−life values. The model also provides the option to adjust the half−life value according to the soil depth. This study, however, made use of the aerobic half−life option in the soil layer system because pesticide persistence is greatly affected by soil moisture and soil temperature values (Walker, 1991). Herbicide leaching losses in drainage water were adjusted by changing the half−life parameter. The herbicide leaching losses decreased with decrease in half−life and increased with increasing half−life.

Initially, calibration was started with default values and changes were made in half−life as well as in the K_{oc} values to minimize the difference between measured and predicted data and to match the temporal distribution of the herbicide leaching losses. After calibration, a single model run was made from 1992 through 1997, but validation was performed using data from 1993 to 1997. The following model evaluation criteria were used.

Percentage of Difference (%D)

The goodness of fit statistic was %D, which represents the percentage of difference between the predicted (*P*) and observed (*O*) data (Ahuja et al., 1999):

$$\%\,D = \frac{P - O}{O} \times 100 \tag{5}$$

The standard way of validating a model, however, is to apply certain tests to assess the goodness of fit of the model predictions. Loague and Green (1991) and Vinten et al. (1991) applied the following measures to judge the model's prediction capability:

Root Mean Square Error (RMSE)

The value of RMSE should be equal to zero for a model showing perfect fit between the observed and predicted data:

$$RMSE = \frac{\left[\sum_{i=1}^{n} (P_i - O_i)^2 / n\right]^{0.5}}{\overline{O}} \times 100 \tag{6}$$

Model Efficiency (EF)

EF is a measure of the deviation between model predictions and measurements relative to the scattering of the observed data. This parameter is calculated using the Nash and Sutcliffe (1970) relationship, and its value is 1.0 for a perfect fit:

$$EF = 1 - \frac{\sum_{i=1}^{n} (P_i - O_i)^2}{\sum_{i=1}^{n} (O_i - \overline{O})^2} \tag{7}$$

Coefficient of Residual Mass (CRM)

This indicator shows the difference in observed and predicted data relative to the observed data and is similar to the percentage of difference discussed above when multiplied by 100:

$$CRM = \frac{\left(\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i\right)}{\sum_{i=1}^{n} O_i} \tag{8}$$

where P_i and O_i are the predicted and observed values, respectively, $\overline{O}$ is the average of the observed data, and *i* is the number of observations ranging from 1 to *n*.

PARAMETER SENSITIVITY ANALYSIS

The partitioning coefficient based on soil organic carbon (K_{oc}) and the half−life parameters were found to be sensitive in adjusting herbicide leaching losses in subsurface drainage water. Therefore, sensitivity analysis of these two parameters was carried out to assess their effects on herbicide leaching losses. The calibrated and validated model was used for

Table 3. List of selected herbicide parameters.

Parameters	Atrazine	Metolachlor	Metribuzin
Aerobic half−life in soil layer (days)[a]	32	70	13
Soil organic carbon sorption coefficient (K_{oc}) (cc g^{-1})[a]	80	230	120
Water solubility (mg L^{-1})	33	530	1220
Vapor pressure (mm Hg)	2.89×10^{-7}	3.14×10^{-5}	1×10^{-5}

[a] Adjustments were made during calibration.

sensitivity analysis. The K_{oc} values were changed from 50 to 250 cc g^{-1} with an increment of 50 cc g^{-1} for atrazine, metolachlor, and metribuzin. During sensitivity analysis, all herbicides were assumed to be applied during planting at their standard application rates (table 3). All other parameters were kept constant, and only K_{oc} effects on herbicide leaching losses were simulated. Similarly, half−life effects on herbicide leaching in subsurface drainage water were simulated by changing the half−life values of all herbicides from 20 to 100 days, in increments of 20 days, while no other parameter was changed.

RESULTS AND DISCUSSION

MODEL CALIBRATION PARAMETERS

The hydrology module was calibrated first, and the partitioning of precipitation was checked to account for the amount of surface runoff, evapotranspiration, and subsurface drainage flows that were simulated, using literature data (Hatfield et al., 1999; Jaynes and Miller, 1999). This partitioning should be acceptable in addition to comparison of the measured data. This means that if measured data for all of the water balance components are not available, which is the common case for most of the sites, then the values of various hydrologic components should be within the range for the study area. This analysis also shows which water balance components are being overestimated or underestimated. From here, fine−tuning of the variables starts according to the required output variables (Hanson et al., 1999).

In this study, subsurface drainage flow data were available; therefore, the drainable porosity (DP) was the main parameter used to control the accuracy in the predictions of subsurface drainage flows. Porosity calculations are also implicit in bulk density values. Moreover, infiltration into the soil profile is enhanced if bulk density for the top layer is decreased. For example, if the model is simulating more runoff, then decreasing the bulk density value for the top soil layer will increase infiltration and accordingly decrease the runoff. Similarly, percolation from layer to layer is controlled by the DP and hydraulic conductivity values. If more water is retained in the top layer, it will also allow more evapotranspiration. Therefore, calibration of the subsurface drainage flow involves adjustment of the DP and hydraulic conductivity for the entire soil profile so that acceptable subsurface drainage flows can be simulated. The adjustment in the values of these properties incorporates the spatial variability effects and enables the single soil profile to simulate integrated effects of soil properties on subsurface drainage simulation for the entire field (Bakhsh and Kanwar, 2001). The calibration criteria in this study were to minimize the difference between predicted and measured data and match the predicted and measured drainage flow hydrographs. DP values ranged from 0.19 for the bottom soil horizon to 0.27 for the top soil horizon, which can be associated with the change in bulk density values and the retention of water in the soil profile. After calibrating the model for 1992 data, a continuous simulation was conducted from January 1, 1992, through December 31, 1997. This single−run model simulation overcomes the problems of initializing the input data when models are run for several growing seasons. More details on model calibration can be found in Bakhsh et al. (2001b), Ahuja et al. (1999), and Ma et al. (1998).

The year 1992 was selected as the calibration year because it had an annual precipitation of 800 mm, which is close to the 30−year normal precipitation of 818 mm at this site (Hatfield et al., 1999). The study period experienced variability in precipitation, ranging from a wet year in 1993 (1290 mm) to a dry year in 1994 (560 mm), and near−average precipitation in 1995 (723 mm), 1996 (895 mm), and 1997 (671 mm). About 25% of the average annual precipitation contributed as subsurface drainage flow for this experimental field.

Leaching of herbicides also depends on its adsorption characteristics. The potential for leaching losses of herbicides in subsurface drainage water increased as K_{oc} values decreased. The fraction of the pesticide loss with pore water is determined by K_d, as given by equations 3 and 4. In addition, K_{oc} sensitivity also depends on soil organic carbon; therefore, pesticide leaching is most sensitive to K_{oc} values. The K_{oc} affected herbicide transport with subsurface drainage water. K_{oc} values ranged from 80 cc/g for atrazine to 120 cc g^{-1} for metribuzin and 230 cc g^{-1} for metolachlor. A wide range of K_{oc} values has been reported in the literature. These values vary according to the soil organic matter and soil moisture contents (Gaynor et al., 2000; Kladivko et al., 1999; Jaynes and Miller, 1999).

Herbicide degradation or persistence in the soil was affected by half−life, which also affected the temporal distribution of herbicide leaching in subsurface drainage water. The persistence of herbicides in the soil−water environment applied in this study increased in the order of metribuzin < atrazine < metolachlor (table 3). The calibrated values of half−life for metribuzin, atrazine, and metolachlor were 13, 32, and 70 days, respectively. These values are close to those reported by Gaynor et al. (2000) studying the same herbicides in Brookston soil. Metribuzin had the shortest half−life and resulted in the minimum leaching losses, whereas metolachlor had the longest half−life and gave the maximum leaching losses with subsurface drainage water (table 4). Further details of K_{oc} and half−life effects on herbicide leaching will be discussed in the Sensitivity Analysis section.

HERBICIDE LEACHING LOSSES WITH SUBSURFACE DRAINAGE WATER

The rainfall variability over the years affected the subsurface drainage volume, which ranged from a low of 68 mm in 1994 to a high of 600 mm in 1993 because of the significant relationship ($P < 0.05$) between annual precipitation and the annual subsurface drainage volume for the study

Table 4. RZWQM simulations of herbicide loss in subsurface drainage water from 1992 to 1997 with various model performance indicators.

	All Years[a]						Validation Years (1993 to 1997)[b]				
Variable	1992	1993	1994	1995	1996	1997	Average	%D	RMSE	EF	CRM
Annual precipitation (mm)											
	800	1290	560	723	895	671	823				
Subsurface drainage (mm)											
Observed	117.0	606.3	67.8	124.7	207.1	106.6	222.5				
Predicted	108.6	585.3	57.6	152.3	206.7	118.0	223.9	0.7	7.6	0.99	0.0
Atrazine leaching loss via subsurface drainage flow (mg ha^{-1})											
Observed	237.3	974.8	62.0	11.2	233.7	8.9	258.1				
Predicted	230.4	133.1	101.3	68.8	25.5	16.5	249.1	−3.5	39.4	0.92	0.04
Metolachlor leaching loss via subsurface drainage flow (mg ha^{-1})											
Observed	152.1	2441	2.9	13.9	123.4	37.1	523.7				
Predicted	136.6	1974	107.4	348.2	231.2	133.3	558.7	6.7	51.4	0.92	−0.06
Metribuzin leaching loss via subsurface drainage flow (mg ha^{-1})											
Observed	10.8	14.6	0.0	0.0	0.0	0.0	2.9				
Predicted	10.1	14.3	1.1	0.1	0.1	0.0	3.1	6.9	18.4	0.99	−0.07

[a] 1992 = calibration year; 1993 to 1997 = validation years.

[b] %D = percent difference between predicted and observed data; RMSE = root mean square error in percent. EF = model efficiency; CRM = coefficient of residual mass.

area ($R^2 = 0.93$). The model predicted subsurface drainage flows satisfactorily, showing a close agreement with the measured data, and also satisfied the evaluation criteria. When averaged across the validation years (1993 to 1997), the model achieved percent difference (%D), root mean square error (RMSE), and model efficiency (EF) values of 0.7, 8, and 0.99, respectively. The temporal evaluation of the model response was compared with the measured data on a daily basis (figs. 1 and 2). The subsurface drainage simulations followed the trend of the measured data in response to rainfall events. The model, however, underpredicted the peaks of subsurface drainage flows after crop harvest in 1992 and during early spring in 1993, which can be attributed to the preferential flow paths rather than the soil matrix flow as simulated by the model. The simulated subsurface drainage flows were in close agreement with the measured data for other years (table 4). In a normal structured soil, however, preferential flow may become critical for chemical transport processes (Kanwar and Bakhsh, 2001).

Herbicide leaching losses were sensitive to subsurface drainage flows. A significant ($P < 0.05$) correlation was observed between herbicide leaching and subsurface drainage flows with $R^2 = 0.94$ for atrazine and $R^2 = 0.96$ for metolachlor. Atrazine and metolachlor were applied to corn in 1993, 1995, and 1997, and metribuzin was applied to soybean in 1992, 1994, and 1996. The herbicide leaching losses, however, were observed during the entire simulation period whether or not the herbicide was applied in those particular years (table 4). This shows the persistence of these herbicides and the effect of drainage flow on herbicide leaching losses.

Atrazine simulations were compared with the measured data (figs. 3 and 4; table 4). The model simulated atrazine in close agreement with the measured data for 1992 and 1993, overestimated for 1994, 1995, and 1997, and underestimated for 1996. The model simulated atrazine well for 1992 but underestimated the peaks for 1993 (figs. 3 and 4). However, when averaged across the validation years and based on performance indictors of %D = −4, RMSE = 39, and EF = 0.92 (table 4), the model simulations were within the same order of magnitude as the measured data. The model was able to predict the atrazine leaching losses in those years when

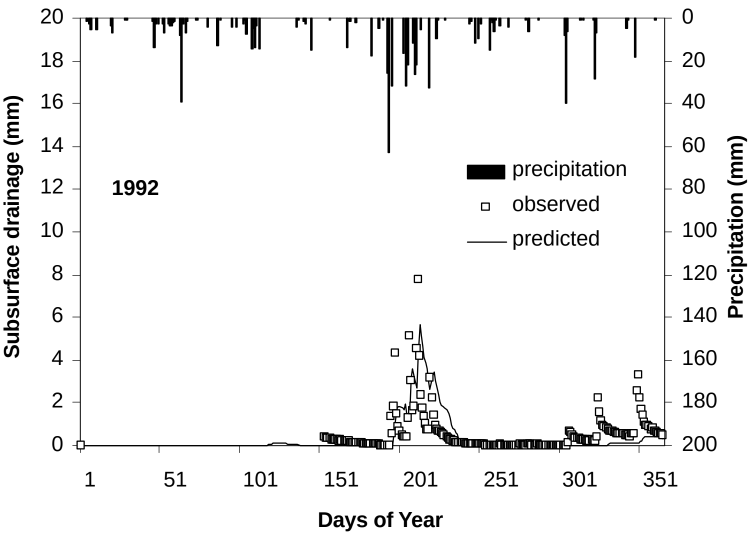

Figure 1. Subsurface drainage simulations in relation to precipitation for 1992.

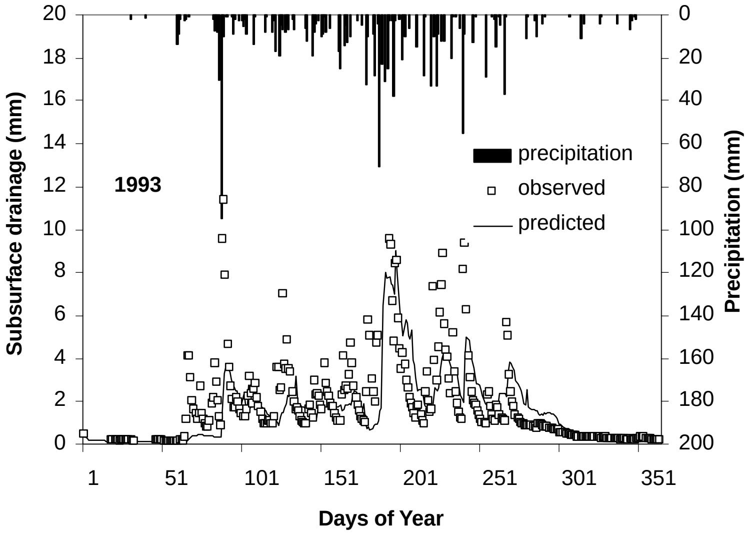

Figure 2. Subsurface drainage simulations in relation to precipitation for 1993.

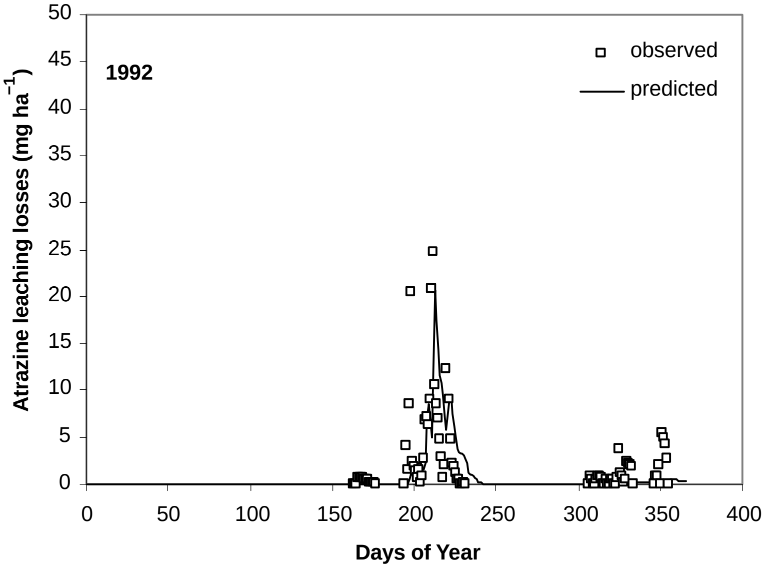

Figure 3. RZWQM simulations of atrazine leaching losses with subsurface drainage water for 1992.

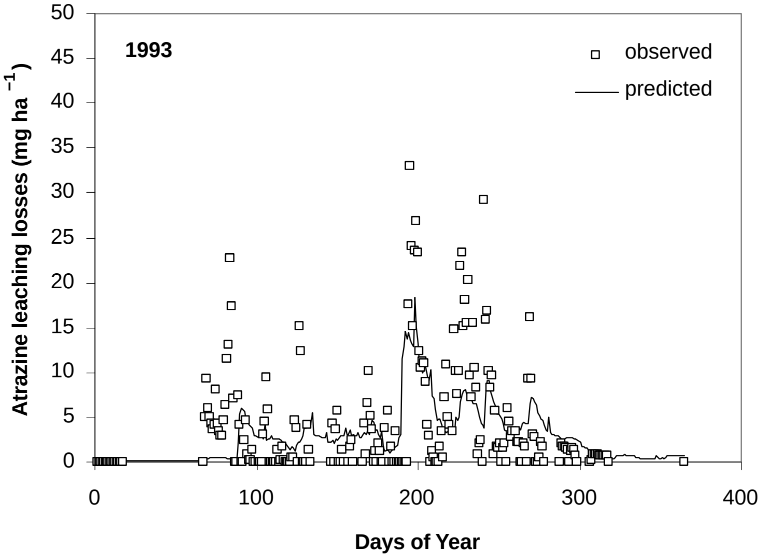

Figure 4. RZWQM simulations of atrazine leaching losses with subsurface drainage water for 1993.

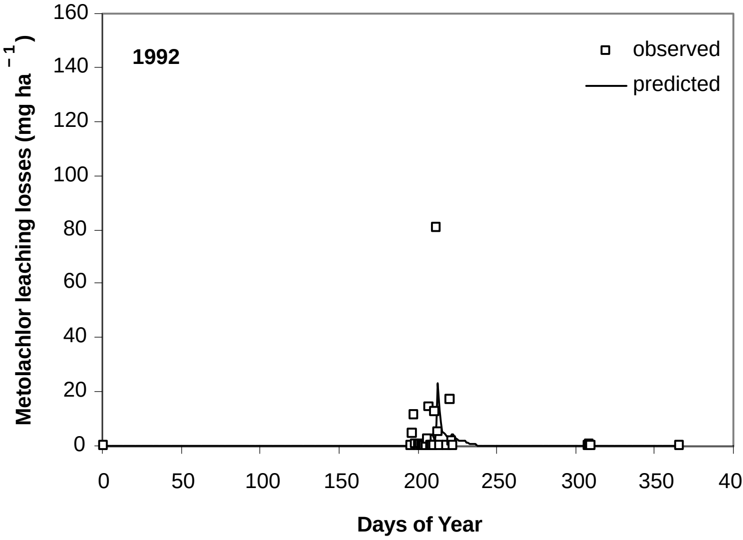

Figure 5. RZWQM simulations of metolachlor leaching losses with subsurface drainage water for 1992.

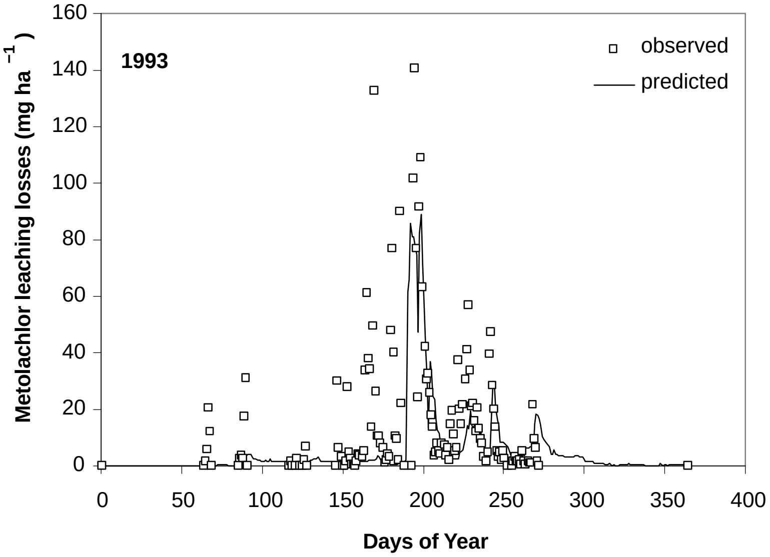

Figure 6. RZWQM simulations of metolachlor leaching losses with subsurface drainage water for 1993.

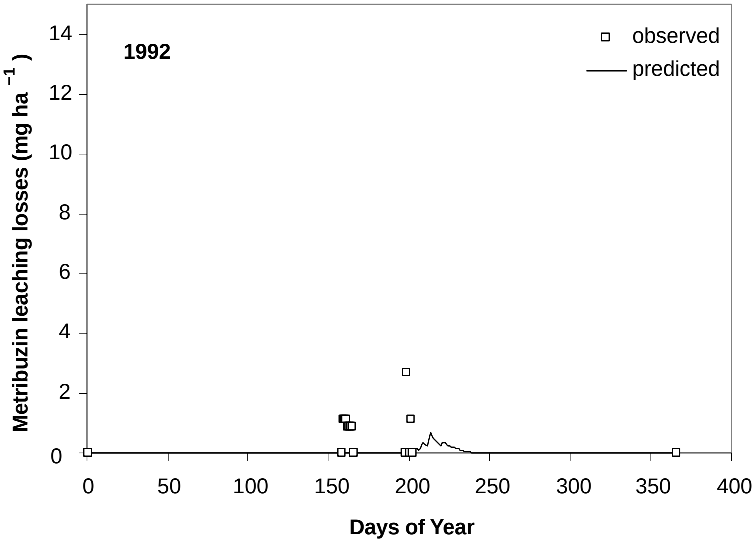

Figure 7. RZWQM simulations of metribuzin leaching losses with subsurface drainage water for 1992.

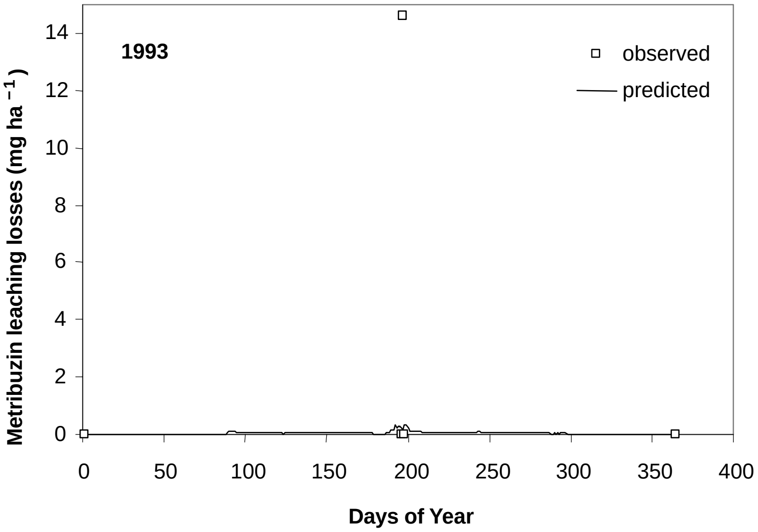

Figure 8. RZWQM simulations of metribuzin leaching losses with subsurface drainage water for 1993.

atrazine was not applied, as shown in the observed data. This shows that the model was able to predict the time lag effects on herbicide leaching due to atrazine persistence in the soil profile, as reported by Yuan et al. (2000). Similar predictions for atrazine were reported by Jaynes and Miller (1999) when they simulated another field in the same watershed. The overall average of the simulated values for the validation years was close to the observed data (258 vs. 249 mg ha^{-1}) (table 4).

Metolachlor resulted in the maximum leaching losses with subsurface drainage water due to its greater persistence in the soil profile. Metolachlor was detected in all years, although it was only applied to corn in 1993, 1995, and 1997. Metolachlor losses were greatly affected by the drainage volume of the particular years. A significant correlation (R^2 = 0.96) was observed between subsurface drainage volume and metolachlor leaching losses in subsurface drainage water. The model predictions of metolachlor losses matched with the observed data, (figs. 5 and 6). The model underestimated the peaks of the herbicide leaching losses after crop harvest in 1992 and during early spring of 1993. The model overpredicted in 1994, 1995, 1996, and 1997, probably because of the greater time lag effects simulated by the model. The maximum leaching loss was observed in 1993 due to greater drainage volume for that year. When averaged across the validation years (1993 to 1997), the average values were in close agreement with the observed data, showing evaluation indicators of %D = 7, RMSE = 51, and EF = 0.92.

Metribuzin showed minimum leaching losses with subsurface drainage water due to its shortest half−life and lower persistence in the soil profile. The model was able to predict closely the pattern of metribuzin leaching losses when compared with measured data (figs. 7 and 8). When averaged across the validation years, the average predicted values were very close to the measured data (2.9 vs. 3.1 mg ha^{-1}). The evaluation indicators of %D = 7, RMSE = 18, and EF = 0.99 were also found to be satisfactory (table 4).

The discrepancies in the model simulations, especially underestimating the peaks of herbicide leaching losses, can be attributed to preferential flow paths developed during the growing season and spring period. Preferential flow has been reported to be an active mechanism for transporting the herbicide in the soil profile and to the subsurface drains (Kanwar and Bakhsh, 2001; Kladivko et al., 1999; Jayachandran et al., 1994). The peak herbicide leaching losses at the start of the rainfall event can also be attributed to herbicide transport from the soil matrix to preferential flow paths between rainfall intervals, which increased the measured herbicide losses at the start of rainfall events (Kladivko et al., 1991). The preferential flow option was not invoked in this study because data on macropores were not available for the experimental site. Using the macropore option with default values, however, did not improve herbicide leaching losses in subsurface drainage water.

FRACTIONAL LEACHING LOSSES

The total amount of atrazine applied to corn in 1993, 1995, and 1997 was 2.04 kg ha^{-1}, at the rate of 0.68 kg ha^{-1} (a.i.) each year. The total measured and predicted leaching losses of atrazine from 1993 to 1997 were 1290 and 1245 mg ha^{-1}, respectively, which were found to be 0.06% of the herbicide amount applied over a period of 1993 to 1997 (table 4). The metribuzin leaching losses were less than 0.002% of the amount applied to soybean from 1992 through 1997. These fractional leaching losses are within the range of those reported by Kladivko et al. (1999), Jaynes and Miller, (1999), and Yuan et al. (2000).

SENSITIVITY ANALYSIS FOR K_{oc} AND HALF-LIFE EFFECTS ON HERBICIDE LEACHING LOSSES

The K_{oc} values were changed from 50 to 250 cc g^{-1} with an increment of 50 cc g^{-1} for atrazine, metolachlor, and metribuzin, and the corresponding effects on herbicide leaching losses were studied (fig. 9). The increase in K_{oc} values of atrazine, metolachlor, and metribuzin from 50 to 100 cc g^{-1} decreased the leaching losses by 66%, 81%, and 84%, respectively. Similarly, the increase in K_{oc} values from 200 to 250 cc g^{-1} decreased the leaching losses for atrazine, metolachlor, and metribuzin by 26%, 39%, and 17%, respectively. Overall, the increase in K_{oc} values from 50 to 250 cc g^{-1} resulted in decrease of leaching losses of atrazine, metolachlor, and metribuzin by 90%, 98%, and 94%, respectively. The absolute increase in rank order of the herbicide leaching losses was metribuzin < atrazine < metolachlor (fig. 9), depending on their adsorption, K_{oc}, and

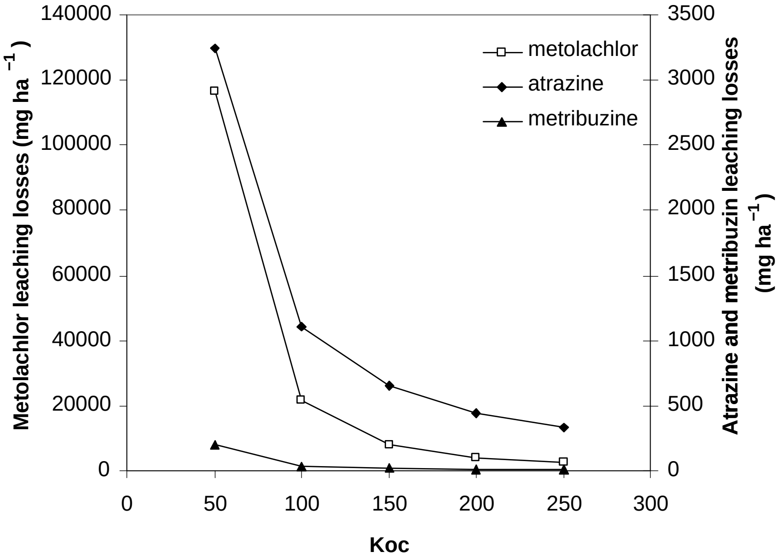

Figure 9. Sensitivity analysis for soil organic carbon based partitioning coefficient (K_{oc}).

half−life characteristics. These simulations showed that the herbicide leaching losses decreased as K_{oc} values increased in subsurface drainage water.

Half−life was the second most sensitive parameter affecting the herbicide leaching losses with subsurface drainage water. The increase in half−life value from 20 to 40 days increased the leaching losses by a factor of 4, 4.5, and 5 for atrazine, metolachlor, and metribuzin, respectively (fig. 10). Overall, the increase in half−life from 20 to 100 days increased the leaching losses by a factor of 18, 17, and 32 for atrazine, metolachlor, and metribuzin, respectively. The order of increase in leaching losses as a function of increase in the half−life values was metribuzin < metolachlor < atrazine. Maximum increase in leaching losses was observed for atrazine, which ranged from 531 to 9337 mg ha^{-1} as half−life increased from 20 to 100 days (fig. 10).

CONCLUSIONS

The improved version of the RZWQM model was calibrated and validated to simulate the herbicide leaching losses with subsurface drainage water using six years (1992 to 1997) of data from a field in the Walnut Creek watershed. The study included sensitivity analysis of the calibrated parameters of the pesticide component of the model to ascertain their effects on the herbicide leaching losses with subsurface drainage water. The following conclusions were drawn:

- The predicted subsurface drainage volumes, when averaged across the validation years (1993 to 1997), showed very close agreement with the measured data and satisfied the evaluation criteria of percent difference between measured and predicted data (%D) = 1, root mean square error (RMSE) = 8, and model efficiency (EF) = 0.99.
- The overall averages of the predicted atrazine, metolachlor, and metribuzin leaching losses with subsurface drainage water were within the same order of magnitude as the measured data. The model was able to simulate the time lag effects on herbicide leaching losses as found in the observed data. Discrepancies were noticed in predicting the herbicide leaching losses for some of the years.
- The partitioning coefficient (K_{oc}) and half−life were found to be the most sensitive parameters in the calibration of the pesticide component of the model, and

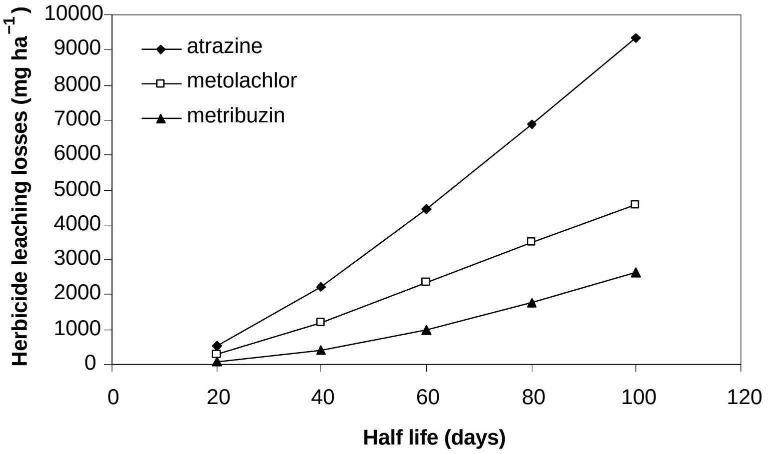

Figure 10. Sensitivity analysis for half−life effects on herbicide leaching losses.

changes in these parameters were helpful in adjusting the herbicide leaching losses with subsurface drainage water.

- The model, however, needs to include the development of preferential flow paths during the growing season in cultivated soils in order to improve the prediction of herbicide leaching losses with subsurface drainage water, especially after crop harvest and during the early spring season.

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