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Modeling Surface and Subsurface Pesticide Transport Under Three Field Conditions Using PRZM-3 and GLEAMS

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ABSTRACT. *Contaminant transport models should be evaluated over a wide range of conditions to determine their limitations. The models PRZM and GLEAMS have been evaluated many times, but few studies are available in which predicted movement in runoff and percolate were simultaneously evaluated against field data. Studies of this type are essential because pesticide leaching and runoff are mutually dependent processes. For this reason, PRZM-3 and GLEAMS were evaluated for their ability to predict metribuzin concentrations in runoff, sediment, subsurface soil, and pan lysimeters under three field conditions (yard waste compost amended, no-till, and conventional-till) on a Lowell silt loam soil. Sensitive input parameters were either site specific (climatic, soil, and chemical) or calibrated (K-factor, C-factor, curve number). In general, both models under-predicted metribuzin concentration in runoff water, runoff sediment, subplow layer soil (15-75 cm), and pan lysimeter water (75 cm). Contrary to field data, both models predicted that a large percentage (> 50%) of metribuzin would move below the "mixing zone" (top 1 cm) during the first rainfall event after application. Relatively little metribuzin was predicted to move beyond the plow layer (top 15 cm) into the pan lysimeters or subsurface soil throughout the simulation period, possibly due to the lack of a macropore component in the models. High metribuzin concentrations in sediment (field data) indicated that relatively little metribuzin moved below the "mixing zone", possibly because of hysteresis but much of the metribuzin that did move was quickly transported into the pan lysimeters, probably due to macropore flow. GLEAMS more accurately predicted pesticide concentration in sediment and PRZM predicted subsurface soil concentration somewhat more accurately than GLEAMS. Little difference in accuracy was detected between models on metribuzin concentration in runoff or metribuzin concentration in percolate. Although both models generally under-predicted metribuzin concentration in runoff, runoff transport (mass of metribuzin in runoff) for the study period was over-predicted by both models which emphasizes the importance of accurately predicting herbicide concentration and runoff volume soon after application when the surface pesticide concentrations are highest.*

Keywords. *Metribuzin, Contaminant transport, Leaching, Runoff, No-till, Compost.*

Non-point source contaminant transport models have been developed to assess pesticide transport over a large range of topographies, soil types, climatic conditions, and management conditions because site specific field studies are often prohibitively expensive. Two of the most commonly utilized pesticide transport models are PRZM (Carsel et al., 1985) and GLEAMS (Leonard et al., 1987). To determine which conditions are appropriate for using these models and to develop user confidence, these models should be assessed over a large range of conditions.

PRZM and GLEAMS have been evaluated in several studies but leaching and runoff are mutually dependent processes and few studies are available in which pesticide runoff and leaching are simultaneously compared (Flury, 1996). Most PRZM and GLEAMS assessments focused upon soil pesticide distribution or pesticide leaching (Zacharias and Heatwole, 1994; Pennell et al., 1990; Smith et al., 1991a; Mueller et al., 1992; Sauer et al., 1990; Parrish et al., 1992; Melancon et al., 1986; Banton and Villeneuve, 1989; Truman et al., 1998; Smith et al., 1991b). The few GLEAMS and PRZM assessments that considered surface pesticide transport include: the original GLEAMS article where surface pesticide transport was briefly addressed (Leonard et al., 1987); a study that assessed only the surface pesticide transport component of GLEAMS (Leonard et al., 1996); and a study that compared the observed and GLEAMS predicted runoff of sulfometuron and cyanaine (Wauchope et al., 1990). Also, many of the existing field assessments of PRZM and GLEAMS used soil cores to determine actual subsurface pesticide movement, but Shipitalo et al. (1990) indicated that percolate water samples may be necessary to accurately assess subsurface pesticide movement when macropores are present.

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Therefore, an independent field assessment of PRZM and GLEAMS including both the surface pesticide component (metribuzin concentration in sediment and water) and subsurface pesticide component (metribuzin concentration in percolate water and subsurface soil) is needed. A comprehensive assessment of this type is lacking in the literature and it will add to the database of PRZM and GLEAMS assessments under different conditions.

The objective of this research was to perform a comprehensive assessment of the pesticide component of PRZM-3 (beta version) and GLEAMS (version 2.10.2) on three field conditions (yard waste compost amended, no-till, and conventional-till) including: (1) surface metribuzin concentration in runoff; (2) surface pesticide concentration in sediment; and (3) subsurface pesticide concentration in percolation and soil. The hydrology and pesticide transport (the combination of hydrology and pesticide concentration) components of the models are briefly addressed but the main focus of this article is pesticide concentrations.

PRZM and GLEAMS have been described in detail by Leonard et al. (1987), Knisel et al. (1993), Mullins et al. (1993), and Carsel et al. (1985) and have been summarized by Pennell et al. (1990), Zacharias and Heatwole (1994), and Smith et al. (1991a). Therefore, model descriptions will only be discussed in the results section as needed. PRZM-3 has various revisions compared to previous versions including a revised algorithm to predict runoff pesticide concentration (Carsel, 1996, USEPA, Athens, Georgia, personal communication). Other enhancements to release 3.0 include algorithms for modeling nitrogen cycle soil kinetic processes with the ability to track nitrogen discharges from a septic tank into the soil environment and movement to groundwater; better simulation of physiochemical processes; increased flexibility in representing agronomic practices; and improved post-processing and data interpretation aids (Carsel et al., 1998).

Background and Procedures

Description of Field Data

Field plots (22.0 m × 7.3 m; 10% slope) were installed at the Kentucky State University research farm near Frankfort, Kentucky, in May 1994 to research the fate of metribuzin on three field conditions: compost-amended, no-till, and rototilled bare soil. The soil was a Lowell silt loam (fine, mixed mesic *Typic Hapludalf*). The compost-amended plot was amended with 212.2 Mg/ha of yard waste compost (YWC) in May 1994 and 115.7 Mg/ha of YWC in April 1995 by incorporating with a rototiller to a depth of 15 cm. An additional 20.9 Mg/ha of YWC was added to the soil surface of the compost-amended plot to reduce erosion in April 1995. The no-till plot was sowed with rye in 1994 then 4.6 L/ha of Roundup was applied to kill the rye cover in April 1995. The bare soil field condition was rototilled to 15 cm in April 1995. Tomatoes were planted on all plots in 1994, but nothing was planted in 1995 to simplify the processes and analysis. Therefore, the surface conditions of the three plots were compost-covered, rye residue, and bare soil.

Two zero-tension pan lysimeters (61 cm × 61 cm) were horizontally tunnel installed near the down gradient edge of each plot in 1994. The lysimeters were installed 75 cm below the soil surface to collect percolating water and designed to prevent edge effects. Pre-calibrated tipping buckets were installed to measure total runoff and collect a flow proportional runoff sample for pesticide and sediment analysis. Soil cores were obtained immediately after pesticide application and then weekly thereafter to 75 cm, composited by horizon, and frozen until analyzed (Malone et al., 1996b).

Metribuzin was extracted from soil and sediment using supercritical fluid extraction (SFE) and from water using solid phase extraction (SPE). Using 50 ppb spiked soil, 2 ppb spiked water and 0.25 ppb spiked water, recovery was 92 ± 14% (n = 48 replications), 91 ± 1% (n = 2 replications), and 115 ± 3% (n = 2 replications), respectively. Metribuzin analysis was performed using gas liquid chromatography (GC, Hewlett Packard Co., Model 5890 Series II, Palo Alto, Calif.). Details of the extractions and analytical methods were discussed in Malone et al. (1997).

Table 1. Site specific model input parameters

		Field Condition		
Parameter	Depth (cm)	Compost	No-till	Bare Soil
Bulk density (g/cm^3)	0–15	0.9	1.1	1.0
	15–75	1.55	1.55	1.55
Clay (%)*	0–15	13.6	12.7	10.3
	20–30	29.0	29.0	29.0
	30–55	30.0	30.0	30.0
	55–75	35.0	35.0	35.0
Silt (%)*	0–15	73.7	75.9	78.5
	20–30	59.0	59.0	59.0
	30–55	66.0	66.0	66.0
	55–75	52.0	52.0	52.0
K_{sat} (cm/h)	0–15	144	144	144
	20–30	12.6	12.6	12.6
	30–55	3.7	3.7	3.7
	55–75	1.2	1.2	1.2
Porosity (cm/cm)	0–15	0.66	0.58	0.6
	15–75	0.44	0.44	0.44
Field capacity (cm/cm)†	0–15	0.36	0.35	0.32
	20–30	0.35	0.35	0.35
	30–55	0.37	0.37	0.37
	55–75	0.35	0.35	0.35
Wilting point (cm/cm)†	0–15	0.21	0.21	0.15
	20–30	0.21	0.21	0.21
	30–55	0.25	0.25	0.25
	55–75	0.30	0.30	0.30
K_{oc} (mL/g)	0–15	36	46	46
	15–75	46	46	46
oc (%)	0–15	4.5	1.3	1.3
	20–55	0.3	0.3	0.3
	55–75	0.27	0.27	0.27
$t_{1/2}$ (days)	0–75	5.33	5.33	5.33
a.r. 1 (kg/ha)‡	na	0.83	0.82	0.79
a.r. 2 (kg/ha)‡	na	0.71	0.63	0.71

* Micro-pipette method (Miller and Miller, 1987).
† Method described in Felton (1992).
‡ a.r. 1 and 2 indicate the first and second metribuzin application rate on day 128 and day 156.

Metribuzin (2.64 g/L H_2O) was applied to the three plots using a CO_2-pressurized backpack sprayer. Exact metribuzin application to each plot was determined by measuring mixture volume before and after application (table 1). Metribuzin drift off of plots was not directly measured but application was designed to minimize drift. Two applications were necessary to maintain detectable metribuzin concentrations in the soil.

The field experiments are described in more detail by Malone et al. (1996a,b). Note that data from the 1995 growing season were used to evaluate PRZM and GLEAMS. The 1994 data were used only for testing of equipment and analysis techniques.

Input Data for Models

The computer models PRZM-3 and GLEAMS were used to simulate metribuzin movement from and within the three field conditions. Relevant model input parameters found sensitive by Fontaine et al. (1992) and Smith et al. (1990) were field capacity, wilting point, bulk density, daily rainfall, temperature, curve number, evaporation, solar radiation, horizon depths, saturated hydraulic conductivity, soil texture, porosity, pesticide half-life, partition coefficient (K_d), percent organic carbon (% oc), and total pesticide applied. Various other input data found important by Smith et al. (1990) (e.g., humidity and plant uptake) were not applicable to this investigation because they were not input parameters for GLEAMS and PRZM (e.g., the ET component did not require humidity and no plants were present for the 1995 simulation). Most sensitive model input parameters were laboratory-determined for each field condition using site specific soil as described below (field capacity, wilting point, bulk density, saturated hydraulic conductivity, soil texture, porosity, pesticide half-life, partition coefficient, organic carbon, and total pesticide applied). Sensitive parameters that were not laboratory-determined were calibrated (curve number, USLE K-factor, USLE C-factor).

Climatic input parameters were measured at KSU research farm with the exception of pan evaporation and solar radiation data. Daily rainfall was measured from either an automated tipping bucket rain gauge or a manually read rain gauge and daily air temperature was obtained from a weather station. Daily pan evaporation and solar radiation values were obtained from the University of Kentucky's Spindletop farm located approximately 50 km from the KSU research farm. A pan factor of 0.76 and an evaporative depth of 15 cm were used in the simulations (Mullins et al., 1993). Average monthly solar radiation was calculated for use in GLEAMS along with a soil evaporative parameter of 4.5 $mm \cdot d^{-0.5}$ (Knisel et al., 1993; Richie, 1972).

The soil horizon depths were approximately as follows: 0-20 cm (A); 20-30 cm (B1); 30-55 (B2); and 55-75 cm (B3). The soil properties in table 1 were determined from triplicate core samples for each horizon. The model input concerning the plow layer (0-15 cm) was different for each field condition corresponding to the different measured soil properties. To avoid measuring the soil properties of the adjacent 5 cm depth of soil (15-20 cm), and adding another horizon, we used the same properties for the 15 to 20 cm soil as the 20 to 30 cm soil. This had negligible influence on water and pesticide transport. Field capacity was defined as the soil water content at a pressure of –10 kPa because field data showed subsoil samples remained at this pressure throughout the experiment; wilting point was defined as the soil water content at a pressure of –1500 kPa.

The curve number, the USLE K-factor, and the USLE C-factor were calibrated to obtain accurate simulated runoff and sediment yield. Our calibration goal was to force each predicted runoff event to be reasonably close to actual values so that the runoff quantity effect upon runoff and sediment metribuzin concentrations would be minimal. The calibrated curve numbers on bare soil were 84 for PRZM and 90 for GLEAMS and on compost were 60 for PRZM and 70 for GLEAMS. A large rainfall on day 138 washed much surface-applied compost off the compost amended plot, therefore the curve numbers were adjusted after this day to 85 and 90 for PRZM and GLEAMS, respectively. The C-factors on bare soil were set to 1 for both PRZM and GLEAMS and on compost were calibrated to 0.3 for PRZM and 0.03 for GLEAMS. The K-factors on bare soil and compost were calibrated to 0.18 for PRZM and 0.16 for GLEAMS. Zacharias and Heatwole (1994) also found that the calibrated curve number was less for PRZM than GLEAMS. More detail on hydrology and erosion model input was discussed in Malone (1996).

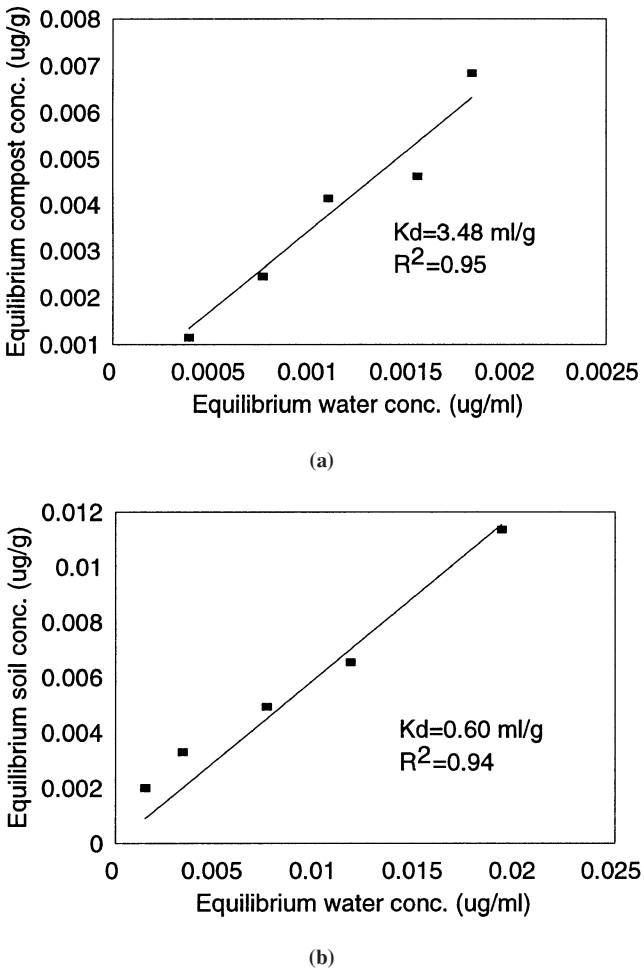

Figure 1–Determination of partition coefficient (K_d) for (a) compost, and (b) soil using batch type procedures.

The soil and compost partition coefficients were determined using batch type tests adapted from the method described by Roy et al. (1990) (fig. 1). Compost and soil batch test mass were 70 and 200 g, respectively, and water volumes were 700 mL and 400 mL, respectively. Approximately 24 h were allowed for equilibrium to occur.

Research shows that pesticide sorption from water is primarily due to the organic carbon content of the soil or $K_{oc} = K_d/oc$ where oc is the carbon mass divided by the total soil mass (Karickhoff et al., 1979). The organic carbon content was determined for each field condition and each horizon using a LECO CR12 carbon determinator (table 1). The K_{oc} of the soils are shown in table 1. The K_{oc} of the compost amended soil was computed from the K_d of the soil and the compost and the carbon content of the compost and soil. These K_{oc} values (36-46 mL/g) are similar to the USDA-ARS recommended value of 52 for metribuzin and well within the range found by other researchers (Hornsby et al., 1996).

The metribuzin half-life listed in table 1 was determined for each field condition (Malone et al., 1996b) by taking weekly surface soil cores to 15 cm and using the first order rate equation described by Nash (1980). Little difference was found between field conditions, therefore the average of the three field conditions was used as model input. Although metribuzin degradation is dependent upon soil depth (Locke and Harper, 1991; Jones et al., 1990), Mullins et al. (1993) recommended using a constant value for all depths due to lack of information regarding degradation as a function of depth. The field-determined half-life (5.33 days) was less than the reported range of one to two months (Tomlin, 1994) but within the field determined range found by Sorenson et al. (1991). Also, a metribuzin field half-life of five days is not uncommon for Kentucky soils (Dr. William Witt, 1996, Weed Scientist, University of Kentucky, personal communication). Metribuzin lost through leaching and runoff would not have significantly influenced the dissipation rate because less than 1.0% of metribuzin was lost through leaching and runoff on each field condition (Malone et al., 1996b).

Model Comparison

Model comparisons to actual pesticide concentrations and comparisons between models were performed on an event basis when applicable. Also, comparison between PRZM and GLEAMS model accuracy was performed using the root mean square error (RMSE) as discussed by Zacharias and Heatwole (1994). The RMSE was calculated for each field condition (compost, no-till, bare soil) and for each transport mechanism (runoff, sediment, percolation, subsurface soil) using each event from the entire simulation period (day 129 through day 206)

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n}} \qquad (1)$$

where P_i are predicted values, O_i are observed values, i is the event (runoff or percolation event 1, 2, etc.), and n is the number of observations (events). The RMSE is an objective method to evaluate model results. For metribuzin concentration, the only events used to compute the RMSE were events that percolation, runoff, or sediment were predicted by both models and where metribuzin was actually detected from the field samples. All events were used to compute the RMSE for metribuzin transport (metribuzin concentration multiplied by runoff volume, sediment transport, or percolate volume).

Results and Discussion

Simulated versus Field Hydrology and the Implications for Pesticide Transport

A complete assessment of the pesticide component of a contaminant transport model includes assessing transport in runoff, in sediment, and in percolate. Transport includes both pesticide concentration and hydrology (water movement) because hydrology affects the quantity of chemical reaching either surface water or groundwater. To limit the scope of this article and thus make it more focused, transport (the combination of concentration and hydrology) will only be briefly addressed. Discussion will primarily focus on the ability of the models to predict metribuzin concentration in runoff, in sediment, in percolate, and in subsurface soil. Hydrologic analysis that affects pesticide transport will be summarized. Detailed hydrologic discussion, including tables and figures of data, is available in Malone (1996).

Runoff was not assessed for the no-till plot because only negligible runoff was observed (Malone et al., 1996a; Malone 1996). Subsurface metribuzin movement (pan lysimeter and subsurface soil) will be discussed for all three field conditions.

Both models were calibrated for runoff and sediment transport (USLE K-factor, USLE C-factor, and curve number). Therefore, the model predicted runoff, sediment concentration, and percolation were reasonably close to the actual quantities (table 2). The notable difference was for percolation on the compost-amended plot which may be due partially to the added water storage capacity of the erosion control surface applied compost. The differences between predicted and actual total runoff and total sediment transport over the simulation period were mainly due to two reasons: (1) the models were calibrated to achieve the lowest RMSE rather than calibrating to equate the total predicted and actual values over the simulation period; and (2) extreme events (outliers) were not included in the calibration process but were used to compute the values in table 2.

Both models underpredicted runoff during dry conditions partially because neither model simulated upward water movement. Runoff quantity is a function of the surface soil water and both models underpredicted surface soil water during dry periods. While underpredicting surface soil water (0-15 cm) during dry periods, the models overpredicted

Table 2. Hydrology for entire simulation period*

Hydrologic Component†	Compost			No-till			Bare Soil		
	PRZM	GLMS	Actual	PRZM	GLMS	Actual	PRZM	GLMS	Actual
RAIN (cm)	28.69	28.69	28.69	28.69	28.69	28.69	28.69	28.69	28.69
ET (cm)	18.15	19.49	NM‡	17.94	17.64	NM	19.05	22.07	NM
RO (cm)	0.95	1.14	1.40	0.00	0.00	0.07	2.53	2.99	4.46
PERC (cm)	9.25	8.44	2.37	11.10	11.10	10.37	6.88	3.83	7.16
SED (t/ha)	0.79	0.85	1.45	0.00	0.00	0.06	2.96	3.22	6.27

* A large, intense runoff event (6.76 cm rainfall) was missed due to equipment failure on day 138; therefore, this event was not included in this article.

† ET = evapotranspiration, RO = runoff, PERC = percolation, SED = sediment transport.

‡ NM indicates not measured.

subsurface soil water (15-75 cm). The combination of underpredicting runoff and overpredicting subsurface soil water during dry periods led to the models overpredicting percolation during dry periods.

The most notable differences between the models were the calibrated curve number and the evaporative differences. The calibrated GLEAMS curve number (90 for bare soil) was similar to the published value and was much greater than the calibrated PRZM curve number (84 for bare soil). Zacharias and Heatwole (1994) also found that the calibrated GLEAMS curve number was greater than the calibrated PRZM curve number. This was mostly due to the different methods that the models used to calculate runoff as a function of soil water content. Therefore, without calibration, PRZM would over-predict runoff and thereby over-predict pesticide transport if pesticide concentration were accurately predicted.

Under dry conditions (stage II evaporation), PRZM predicted greater evaporation than GLEAMS due to the different algorithms used to compute evaporation as a function of potential evaporation. This led to less PRZM simulated water content in the surface soil (0-15 cm) compared to GLEAMS during dry conditions. Because PRZM predicted surface water content (0-15 cm) was less than GLEAMS during dry conditions, PRZM predicted less runoff than GLEAMS during these conditions. Another evaporative difference between the models is that GLEAMS computes potential evaporation as a function of the USLE C-factor. As the C-factor decreased, GLEAMS simulated potential evaporation also decreased. Also, GLEAMS generally simulated greater potential evaporation than PRZM on bare soil. The combination of GLEAMS nearly always predicting more potential evaporation than PRZM and more runoff during dry conditions, contributed to GLEAMS under-predicting percolation compared to actual and PRZM values (table 2). The PRZM predicted potential ET was most likely more accurate than GLEAMS because it used pan evaporation. The GLEAMS predicted ET may have been improved by calibrating input parameters that affect potential ET but this would not be attempted in most modeling scenarios.

The most obvious way hydrology affects pesticide transport is that increased runoff results in increased pesticide mass transported to surface water. Also, a single variable sensitivity analysis on GLEAMS indicated that runoff quantity directly affected both predicted runoff metribuzin concentration and predicted sediment metribuzin concentration (table 3). This indicates that predicted pesticide mass transport to surface waters is affected by hydrology in at least two ways: (1) increased runoff volume results in increased pesticide mass transported to surface water; and (2) increased runoff volume results in increased pesticide concentrations in runoff and sediment transport (table 3). Therefore, if a model such as GLEAMS excessively overpredicts or underpredicts runoff soon after pesticide application when the pesticide concentrations are highest, it could have a large effect on accurate pesticide transport predictions.

Table 3. Single variable sensitivity analysis on GLEAMS for runoff metribuzin as affected by runoff volume and sediment yield for various runoff events*

Day of Year	Runoff (cm)	Metribuzin Concentration (μg/L)	Sediment Yield (kg/ha)	Runoff Sediment Metribuzin Concentration (μg/kg)
129	0.24	307.6	348	183.0
	0.58	406.6	568	241.8
	1.21	675.0	1071	400.0
137	0.54	10.7	604	6.4
	1.00	16.5	958	9.8
	1.75	32.0	1628	19.2
152	0.06	1.9	155	1.1
	0.23	2.4	239	1.4
	0.63	4.1	503	2.4
163	0.17	81.0	245	48.2
	0.43	106.2	403	63.2
	0.93	171.3	777	101.9

* The field condition was bare soil. The runoff was adjusted by changing the curve number. Note that sediment load was affected only by changing runoff volume; erosion input parameters were not adjusted (K-factor, C-factor, etc.).

Pesticide Concentration in Runoff Water

Metribuzin runoff concentrations were underpredicted by both GLEAMS and PRZM for all events on compost and most events on bare soil, especially a few days after metribuzin application (fig. 2). This may be due to model underprediction of the soil metribuzin concentration in the upper 1 cm soil (mixing zone). Smith et al. (1991b) found that PRZM and LEACHMP underpredicted soil pesticide concentration in the 0-1 cm soil depth at the end of a 60-day column experiment which was attributed to an under estimation of the partition coefficient. The partition coefficient was not underestimated in this research because it was batch-determined using site specific soil. Others have also observed that PRZM and GLEAMS underpredict pesticide concentration in the 0-1 cm of soil (Zacharias and Heatwole, 1994), or metribuzin concentration in the soil surface (0-10 cm) compared to deeper soil depths (Mueller et al., 1992) after time elapsed. Mueller et al. (1992) attributed this to the inequalities of herbicide adsorption:desorption (hysteresis).

Often pesticides desorb less than a simple partition coefficient would predict; this is known as hysteresis (e.g., Koskinen et al., 1979). The PRZM and GLEAMS models use a simple partition coefficient and thus may over-predict metribuzin mobility shortly after application. For the same reason, after a few rainfalls the actual metribuzin remaining in the soil mixing zone would be greater than predicted by the models. Therefore, more pesticides would be available for runoff (after a few rainfalls) than predicted and the actual runoff concentrations would be greater than predicted (Dr. Don Wauchope, 1998, Research Chemist, USDA-ARS, Tifton, Georgia, personal communication).

Research concerning metribuzin hysteresis is mixed. Xue and Selim (1995) found alachlor adsorption-desorption to show extensive hysteretic behavior. Karickhoff (1984) indicated that organic contaminant desorption rates (mass desorped per unit time) may be less than the sorption rates. In addition, Harris and Warren (1964) reported, using the pesticides atrazine, 2, 4 D, simazine, and amiben, that desorption from muck (organic soil) was less than from bentonite (mineral soil). Graham

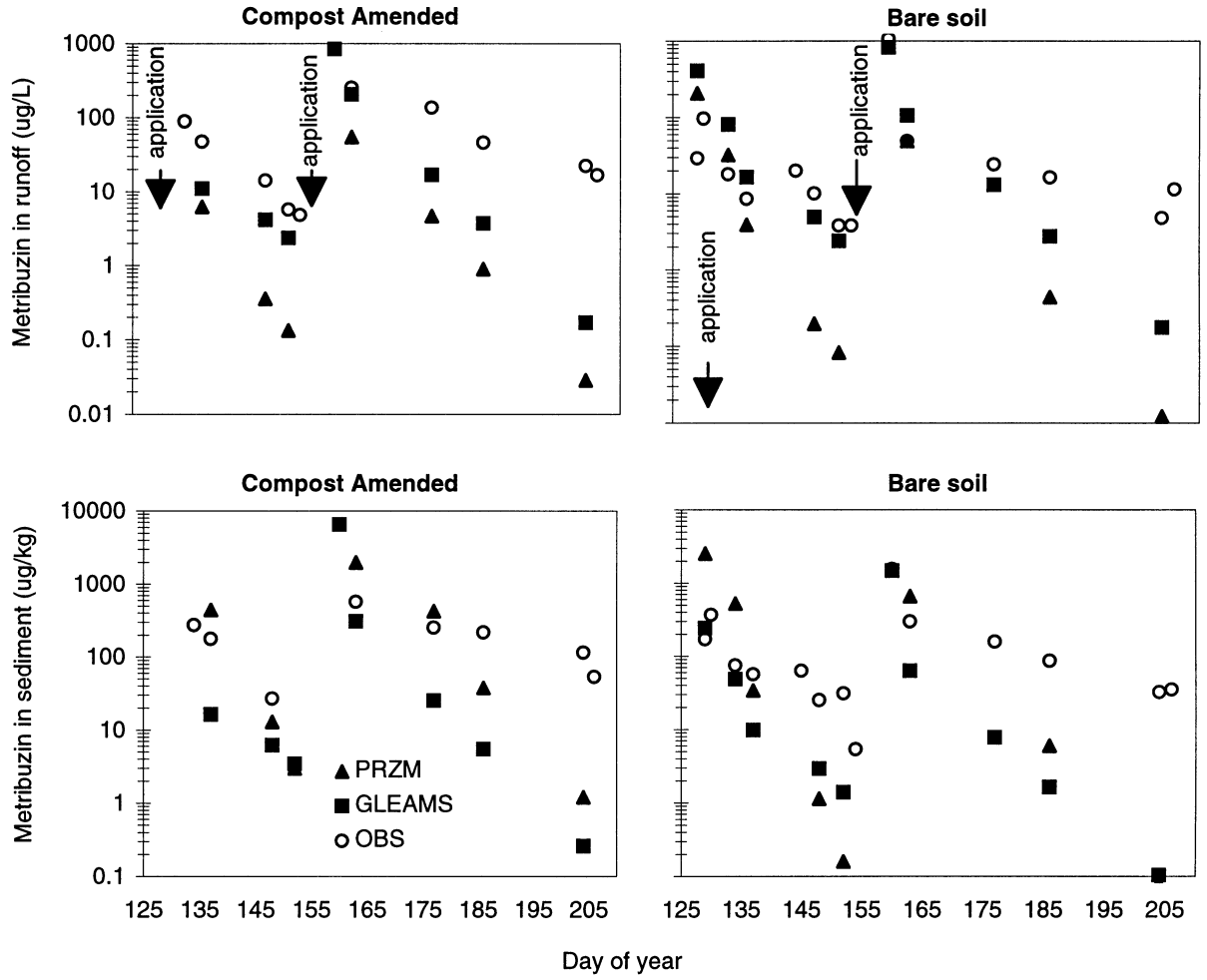

Figure 2–Metribuzin concentration in runoff and in sediment.

and Conn (1992) reported metribuzin hysteresis on Tanana silt loam (oc = 3.8%, pH = 6.5) and cited other research that supports metribuzin hysteresis. In contrast, Boesten and van der Pas (1988) reported no metribuzin hysteresis and desorption kinetics were as fast as adsorption on a loamy sand (organic matter fraction = 0.018, pH = 7.4). Boesten and van der Pas (1988) asserted that higher surface metribuzin concentration found in field studies than expected from adsorption isotherms may be due to a sorption process that equilibrates on a time scale of weeks or months.

Metribuzin runoff concentrations shortly after application (day 129 bare soil, 134 bare soil, 137 bare soil GLEAMS only, and 163 bare soil) may have been overpredicted partially because these runoff events were all within 10 days of metribuzin application, and the application rates input into the models were greater than the actual field determined rate (fig. 3, first day of each application). The field values were probably less than predicted because of a combination of three factors: drift, rapid dissipation (e.g., volatilization), and unextractable pesticide quantity. In addition, it is expected that the actual runoff metribuzin concentrations would be less than predicted shortly after application because of hysteresis. Also, the models overpredicted runoff volume on days 129 and 137 (by a factor of about 8 and 1.9, respectively; both models simulated similar runoff volumes) and, as previously mentioned, GLEAMS predicted greater runoff metribuzin concentration with increased runoff volume.

GLEAMS more accurately simulated runoff concentration for the compost field condition than PRZM while PRZM more accurately simulated runoff concentration on bare soil than GLEAMS based on the root mean square error method (table 4). This corresponds with GLEAMS predicting higher runoff metribuzin concentration than PRZM and the runoff metribuzin concentration on the compost plot being higher than on the bare soil (fig. 2). GLEAMS predicted higher runoff metribuzin concentration than PRZM on each runoff occurrence. Initially, 1 cm soil concentrations predicted by the models were nearly equal, but the GLEAMS predicted soil metribuzin concentration was greater than PRZM later in the simulation (fig. 4) partly due to upward pesticide movement during evaporation (Leonard et al., 1987). This effect may be observed in figure 4 (e.g., days 132, 135, 165).

Pesticide Concentration in Sediment

GLEAMS underpredicted the metribuzin concentration in sediment on each runoff event except day 129 bare soil (fig. 2). The underprediction may be partly due to hysteresis during the early runoff events as explained above. Also, GLEAMS predicted an enrichment ratio of

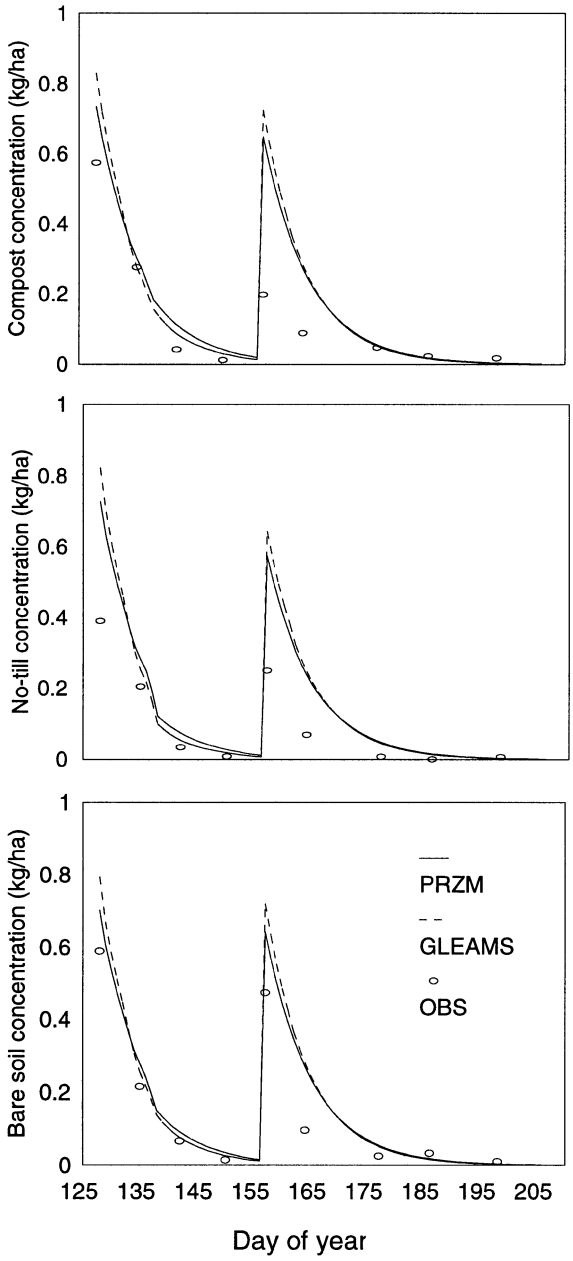

Figure 3–Simulated and measured plow layer (0-15 cm) metribuzin concentration for each field condition.

Table 4. Root mean square error (RMSE) from observed and predicted metribuzin concentrations

Transport Process	Compost		No-till		Bare Soil	
	PRZM	GLEAMS	PRZM	GLEAMS	PRZM	GLEAMS
Runoff (µg/L)	93.2	53.5	NA	NA	63.7	136.9
Sediment (µg/kg)	597.5	184.5	NA	NA	866.7	94.7
Percolation (µg/kg)	6.5	6.5	11.2	11.1	1.8	1.8

1.0; whereas, Massey and Jackson (1952) found that eroded soil had a higher organic carbon content than the upper soil horizon. Enrichment indicates that runoff sediment has greater organic carbon than the surface soil. Day 129 runoff concentration was overpredicted partially

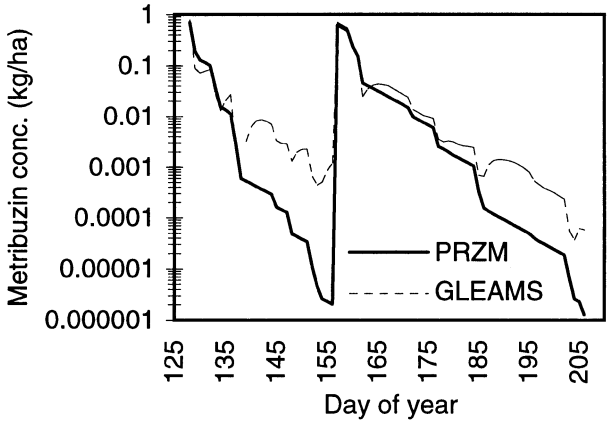

Figure 4–Predicted metribuzin soil concentration in the mixing zone (0-1 cm) of the bare soil plot.

because the runoff was overpredicted by a factor of about eight and GLEAMS predicted higher concentration with higher runoff volume. Also, the application rate input into the models was greater than the actual rate as previously discussed.

Sediment metribuzin concentrations later in the GLEAMS simulation were underpredicted to a greater degree than earlier predictions, possibly reflecting the cumulative effect of hysteresis. In fact, the actual metribuzin concentration in sediment for the bare soil plot closely followed a first order rate equation (fig. 5) with an average half-life between the two applications of approximately eight days. This was a slightly greater half-life than found in the surface soil ($t_{1/2}$ = 5.33 days) indicating that little metribuzin was transported beyond the mixing zone (0-1 cm). A similar result was observed on the compost field condition (results not shown). In contrast, both models predicted that greater than half of the remaining metribuzin that did not degrade or runoff on day 129 (the first runoff event) was transported below the mixing zone into the 1- to 15-cm soil depth (sub-mixing zone plow layer soil).

The runoff sediment metribuzin half-life may have been greater than the upper soil horizon (0-15 cm depth) due to slower pesticide degradation on the high organic carbon

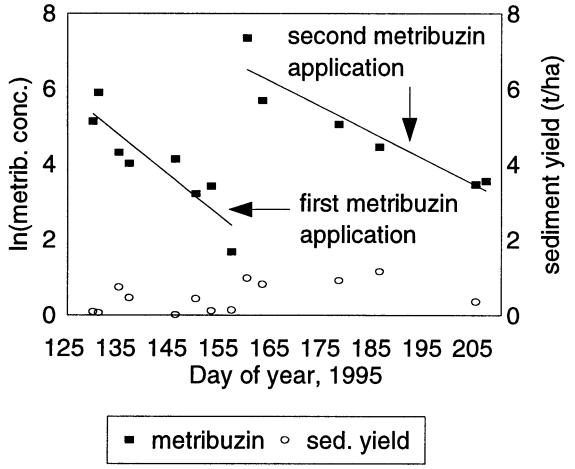

Figure 5–Metribuzin dissipation in sediment using first-order rate equation (bare soil).

content and smaller particle size sediment. Manilal and Alexander (1991) reported that sorption by soil organic matter slows the biodegradation of polycyclic aromatic hydrocarbons and Goetz et al. (1990) found that imazethapyr was more persistent in soil with greater clay and greater organic matter content.

Massey and Jackson (1952) found an inverse relationship between enrichment ratio and sediment load which was consistent with this research. Figure 5 shows that the metribuzin concentration in sediment on the bare soil was higher than predicted by first-order decay (days 130, 145, 152, 160, 206) when the sediment yield was lower than average (average sediment yield was 0.257 t/ha for first metribuzin application, 0.705 for second metribuzin application). In contrast, the sediment metribuzin concentration on bare soil was lower than predicted by first-order decay on higher than average sediment runoff events (days 134, 137, 163, 177, 186). An inverse relationship between sediment metribuzin concentration and sediment load was not applicable on only two runoff events (days 129 and 154); the remaining two runoff events (days 148 and 204) nearly equaled the first order rate equation predicted values. This all helps to explain why the sediment metribuzin half-life was greater than the upper soil horizon; it is possible that the metribuzin degraded slower on the organically enriched sediment and the larger sediment runoff events were likely less enriched than the smaller events. The actual organic content of the sediment was not measured because all collected sediment was used for pesticide analysis.

Figure 6 also supports the assertion that a significant inverse relationship existed between sediment yield and metribuzin concentration. The y-axis is the difference between the natural log of the actual metribuzin concentration and the best line fit value for the two applications shown in figure 5. The x-axis is the difference between the actual sediment yield and the average sediment yield for the two applications. These differences are labeled residuals in figure 6.

Leonard et al. (1996) also found that GLEAMS (version 2.10) underpredicted pesticide concentration in runoff sediment. They improved the accuracy of GLEAMS by varying the degradation rate with time, water content, and temperature and representing the partition coefficient as a function of time. They called this modified model GLEAMS-TC.

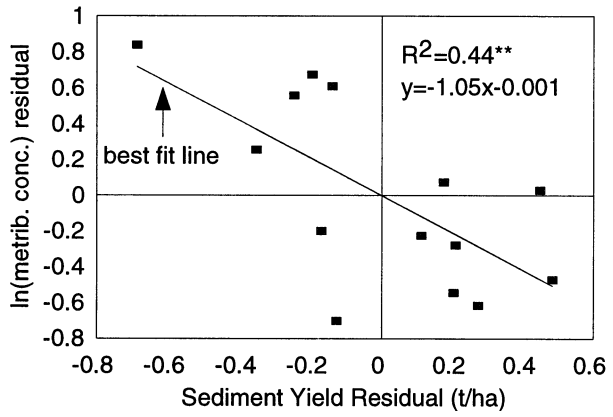

Figure 6–Relationship between sediment yield residual and natural log of metribuzin concentration residual. The symbol ** indicates that a highly significant relationship exists ($p < 0.01$).

Soon after metribuzin application (applications were on days 128 and 156) PRZM overpredicted sediment metribuzin concentration (fig. 2; days 137 compost, 163 compost, 177 compost, 129 bare soil, 134 bare soil, 163 bare soil). As time elapsed, PRZM underestimated sediment metribuzin concentration (days 148 compost, 186 compost, 204 compost, 137 bare soil, 148 bare soil, 152 bare soil, 186 bare soil, 204 bare soil). PRZM may have overpredicted sediment metribuzin concentration soon after application because it does not consider the extraction ratio as described by Leonard and Wauchope (1980) which has the effect of reducing sediment pesticide concentration. PRZM underpredicted sediment metribuzin concentration later in the simulation partly due to overpredicted metribuzin transport from the soil mixing zone into the sub-mixing zone plow layer soil (1-15 cm). It was previously described that a large percentage of metribuzin was predicted to move below the mixing zone but sediment analysis on field runoff samples indicated that little metribuzin moved below the mixing zone.

The sediment metribuzin concentration was predicted with greater accuracy by GLEAMS than PRZM based on the root mean square error (table 4). Shortly after pesticide application, PRZM overpredicted metribuzin concentration in sediment compared to GLEAMS which was not due to a difference in the 1-cm metribuzin concentration (fig. 4). This was mainly attributed to two factors: (1) GLEAMS, unlike PRZM, predicts sediment pesticide concentration as a function of an extraction ratio which reduces pesticide concentration in sediment (Leonard and Wauchope, 1980); and (2) GLEAMS predicted an enrichment factor of one throughout the simulation; whereas, PRZM predicted an enrichment factor of approximately two throughout the simulation. GLEAMS calculates the organic matter enrichment to be the same as the clay fraction (Leonard et al., 1987) and the eroded particle size distribution was calculated as described in Foster et al. (1980) and Foster et al. (1985). On the other hand, PRZM calculates organic matter enrichment as a function of soil loss per unit area (Mullins et al., 1993). After a period of time elapsed, the models predicted similar pesticide concentrations in sediment (days 152 compost, day 148 bare soil, and 204 bare soil).

Subsurface Pesticide Concentration

Both models consistently under-predicted pan lysimeter metribuzin concentration except for days 152 no-till and 154 no-till (fig. 7), possibly due to macropore transport which neither model simulates. Kladivko et al. (1991) found pesticides in subsurface drains sooner than predicted by convective-dispersive transport most likely because of preferential flow. Kladivko et al. (1991) suggested that about 7% of the pore volume was active in rapid transport which was consistent with research on Kentucky soils where an effective porosity of less than 0.10% of the total soil volume was determined (Dunn and Phillips, 1991). The more soil that is effective in transporting water, the less metribuzin that would move into deeper soil due to partitioning. Smith et al. (1991b) also found that PRZM and LEACHMP underpredicted pesticide percolation on intact soil columns.

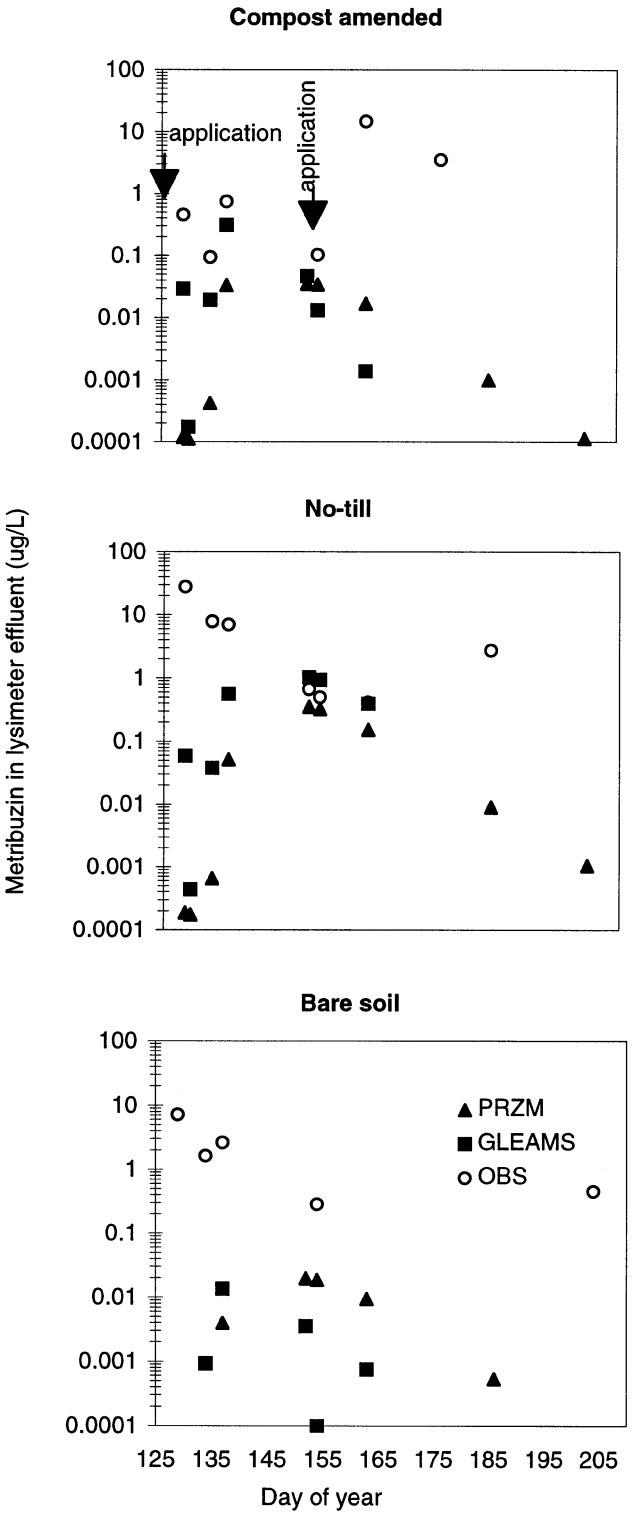

Figure 7–Metribuzin concentration in lysimeter effluent.

The lysimeter metribuzin concentration on day 129 was much higher than on day 163. These were the first percolate observed after the first and second application, respectively, and it has been argued that these concentrations should be similar. The reason for the large difference may be due to the day 160 rainfall event that did not produce percolation but moved the metribuzin into the soil matrix reducing the potential for macropore transport (Shipitalo et al., 1990). Also, approximately a week elapsed between the second metribuzin application (day 156) and day 163 percolate, allowing degradation to occur. Day 129 percolation occurred less than one day after application and no small rainfall event occurred before percolate was observed.

The actual sub-plow layer (15-75 cm) soil metribuzin concentration was greater than predicted on each field condition and each date that metribuzin was detected (table 5). This would be unexpected if strictly convective-dispersive transport were occurring because the predicted plow layer soil concentration was initially higher on each field condition than observed (fig. 3). An overestimated partition coefficient as a reason for an underpredicted sub-plow layer pesticide concentration was unlikely because the K_{oc} was determined on site specific soil and compost, and the sediment pesticide concentrations indicated that little metribuzin moved below the mixing zone. Hysteresis and nonequilibrium transport, as discussed above, would tend to reduce the pesticide movement from the surface to the subsurface horizons. These assertions support preferential flow. Another possible reason for the models underpredicting sub-plow layer soil metribuzin concentration was that the same half-life was input for all soil horizons (Mullins et al., 1993). Research indicates that metribuzin subsurface half-life may be greater than surface half-life (Jones et al. 1990; Locke and Harper, 1991).

GLEAMS predicted a higher lysimeter metribuzin concentration than PRZM on all field conditions early in the simulation (pre-day 138; fig. 7). This was due to a higher GLEAMS predicted soil concentration than PRZM in the bottom soil layer (65-75 cm) on each field condition prior to day 138 (fig. 8). Post-day 138 comparisons of predicted lysimeter metribuzin concentration were mixed reflecting the model predicted 65 to 75 cm soil metribuzin concentration (fig. 8). The differences may be attributed to the pesticide transport mechanisms used in the models; PRZM numerically solves the advective-dispersive equation while GLEAMS simply considers advective transport between soil layers.

Little difference in predicted percolation concentration accuracy was detected between models based on the root

Table 5. Subplow layer soil metribuzin concentration

			Concentration (µg/kg)		
Day	Horizon	Field Condition	Actual*	GLEAMS	PRZM
157	2	Compost	8.84	0.55	1.61
157	2	No-till	5.89	1.16	3.11
157	2	Bare soil	10.89	0.75	3.22
157	3	Compost	3.53	0.19	0.56
157	3	No-till	3.43	0.57	1.65
157	3	Bare soil	2.08	0.11	0.88
157	4	No-till	4.77	0.28	0.16
157	4	Bare soil	3.00	0.00†	0.02
164	4	Compost	2.30	0.00	0.01
177	2	Compost	3.53	0.13	0.44
177	2	Bare soil	1.98	0.26	1.24
177	3	Compost	2.49	0.00	0.06
177	4	Compost	2.15	0.00	0.00
RMSE‡				4.6	3.8

* The approximate detection limit was 4.0 (µg/kg). Lower soil concentrations were occasionally detected due to GC variance.

† 0.00 indicates that the simulated concentration was less than 0.01 (µg/kg).

‡ RMSE is root mean square error.

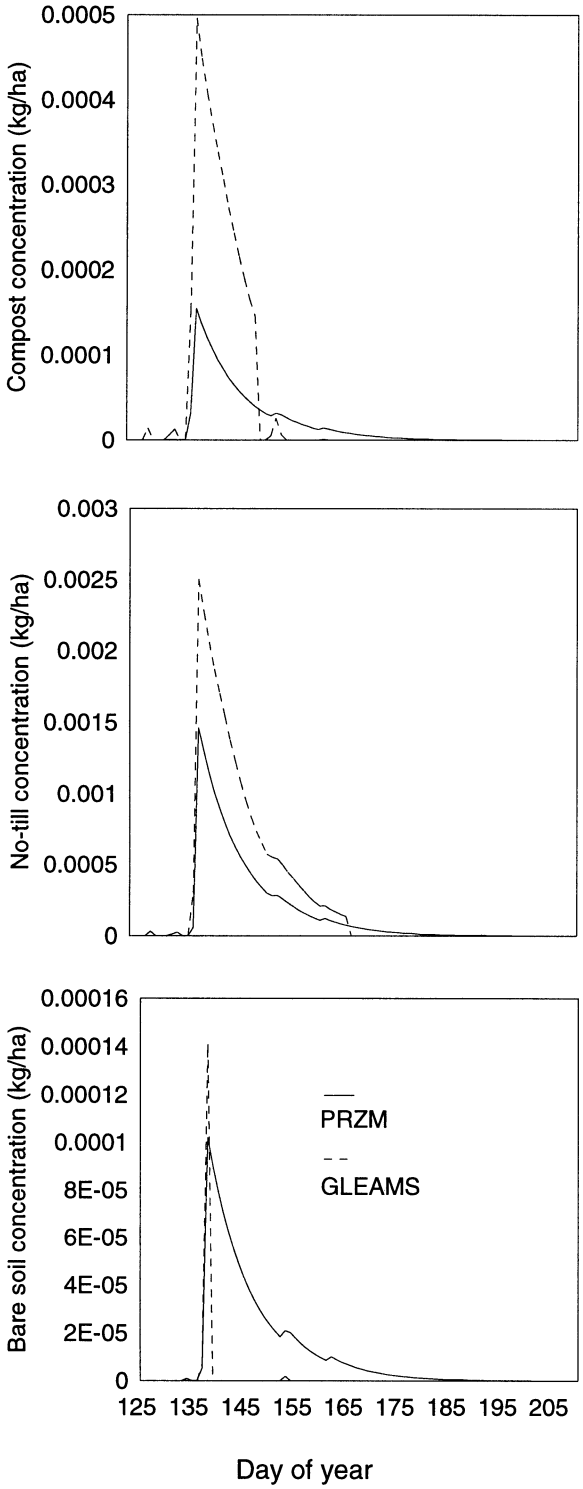

Figure 8–Simulated lower soil horizon metribuzin concentration (65-75 cm) for the three field conditions.

mean square error (table 4) but PRZM predicted soil concentration somewhat better than GLEAMS on days when metribuzin was detected (table 5). Note that metribuzin was detected in only 13 subsurface soil composite samples (table 5) while over 80 subsurface soil composite samples were analyzed (9 sample dates × 3 subsurface horizons × 3 field conditions).

Metribuzin Transport and the Interdependence between Surface and Subsurface Pesticide Movement

One of the most interesting findings of this research was that the models generally underpredicted runoff, sediment, and subsurface (both subsurface soil and lysimeter percolation) pesticide concentration. This is because very little pesticide actually moved out of the mixing zone as indicated by the sediment pesticide concentration, yet what did move was quickly transported to the pan lysimeters and subsurface soil likely due to macropore flow as indicated by the relatively large concentrations found in the percolate and soil (fig. 7 and table 5). Both models, on the other hand, predicted that after the first rainfall (day 129) more than 50% of the metribuzin remaining in the bare soil plot had moved below the soil mixing zone. Yet relatively little metribuzin was predicted to move below the surface horizon (1-15 cm), probably due to the lack of a macropore component in the models. More metribuzin than predicted remained in the mixing zone (surface 1 cm) possibly because of hysteresis.

One of the more helpful aspects of determining both surface and subsurface pesticide concentrations, was that it increased our confidence in each independent aspect of the assessment: pesticide runoff component, sediment pesticide component, and subsurface pesticide component. By analyzing all metribuzin transport mechanisms (sediment, runoff, and percolate), we were prevented from making false conclusions such as: (1) a greatly overpredicted surface transport contributed to the underpredicted percolate concentrations; or (2) an overestimated partition coefficient was partially responsible for underpredicted percolate pesticide concentration. For example, by having field data on surface metribuzin transport, we realized that the partition coefficient was not overpredicted. If a lower partition coefficient were input into the models, more pesticide would have moved into the sub-mixing zone soil reducing the mixing zone metribuzin concentration further and thereby reducing the predicted sediment metribuzin concentration. Also, determining sensitive pesticide transport parameters such as half-life and partition coefficient on site specific soil, as opposed to using literature determined values, provides confidence in these input values.

Table 6 shows total metribuzin transport (g/ha) for each of the transport mechanisms. Items of interest are that the models predicted greater than actual metribuzin runoff transport on the bare soil plot compared to actual metribuzin runoff primarily due to the relatively large simulated runoff event immediately after the first application (day 129). Also, PRZM predicted sediment metribuzin transport was more than actual (table 6) because the metribuzin concentration was greatly overpredicted soon after application possibly due to not considering the extraction ratio as described above. Metribuzin transported in runoff on bare soil was overpredicted by both models in spite of the models underpredicting concentration on most events. Also, PRZM overpredicted sediment metribuzin transport in spite of underpredicting concentration on most events. This indicates that a model must accurately predict runoff quantity and pesticide concentration soon after application to successfully predict sediment and runoff pesticide transport to surface waters.

Table 6. Metribuzin transport (g/ha) during first and second application*

Appli-cation	Transport Process	Compost			No-till			Bare Soil		
		PRZM	GLMS	Actual	PRZM	GLMS	Actual	PRZM	GLMS	Actual
1st	Runoff	0.01	0.10	0.24	0.00	0.00	0.13	12.81	26.79	2.21
2nd		2.11	8.62	12.11	0.00	0.00	0.06	1.66	4.81	7.98
Total		2.13	8.72	12.35	0.00	0.00	0.19	14.47	31.60	10.19
RMSE		1.80	1.29					3.80	7.41	
1st	Sediment	0.00	0.00	0.00	0.00	0.00	0.00	1.84	0.16	0.13
2nd		0.61	0.08	0.29	0.00	0.00	0.00	0.26	0.03	0.57
Total		0.62	0.08	0.29	0.00	0.00	0.00	2.09	0.19	0.71
RMSE		0.18	0.05					0.53	0.11	
1st	Perc.	0.01	0.10	0.10	0.06	0.39	8.95	0.00	0.00	1.76
2nd		0.00	0.00	0.20	0.02	0.06	0.09	0.00	0.00	0.00
Total		0.01	0.10	0.30	0.08	0.45	9.04	0.00	0.00	1.76
RMSE		0.065	0.062		1.69	1.66		0.334	0.334	
Grand Total		2.76	8.91	12.94	0.08	0.45	9.23	16.57	31.80	12.65

* A large, intense runoff event (6.76 cm rainfall) was missed due to equipment failure on day 138; therefore, this event was not included in the analysis. The RMSE is the computed root mean square error considering all events.

Table 6 also shows the RMSE considering all events. It is noteworthy that the RMSE trend is the same for transport (table 6) as for concentration (table 4); if the RMSE indicated that a model performed better for concentration, it indicated that the same model performed better for transport.

Summary and Conclusions

Both models underpredicted metribuzin runoff concentration, especially a few days after metribuzin application. This may be because the models overpredicted metribuzin emanating from the mixing zone (top 1 cm) into the 1-15 cm soil due to hysteresis which the models do not simulate. There was no clear evidence as to which model predicted runoff concentration more accurately.

GLEAMS underpredicted metribuzin concentration in sediment partially due to underpredicting organic enrichment of the runoff sediment. PRZM overpredicted sediment metribuzin concentration soon after application partially because it does not consider sediment pesticide concentration as a function of the extraction ratio which has the effect of reducing sediment pesticide concentration. PRZM underpredicted sediment metribuzin concentration on most runoff events. Both PRZM and GLEAMS underpredicted sediment metribuzin concentration partially due to overpredicting metribuzin transport from the mixing zone into the sub-mixing zone plow layer soil (1-15 cm). Actual field observations indicated that little metribuzin moved beyond the mixing zone of the soil because the metribuzin half-life determined from the runoff sediment was greater than the half-life determined from the upper soil horizon (0-15 cm). This may be due to hysteresis. Sediment metribuzin concentration was predicted with greater accuracy by GLEAMS than PRZM based on the root mean square error.

Both models underpredicted subsurface metribuzin transport compared to actual data probably due to macropore transport which neither model simulated. Predicted lysimeter concentration accuracy did not differ much between models, but PRZM predicted subplow (15-75 cm) soil concentration somewhat better than GLEAMS based on the root mean square error.

Although both models generally underpredicted metribuzin concentration in runoff, sediment, percolation, and subsurface soil, runoff transport was overpredicted by both models and sediment transport was overpredicted by PRZM. This emphasizes the importance of accurately simulating runoff volume and pesticide concentration soon after application when the herbicide concentrations are highest.

Two potential improvements to the versions of PRZM and GLEAMS used in this research and under the conditions of this study would be the addition of a macropore component and the reduction of the pesticide transport out of mixing zone into sub-mixing zone soil on the first few rainfall events. Predicted sediment pesticide concentration in PRZM would likely be improved by calculating sediment pesticide concentration as a function of an extraction ratio. Predicted sediment pesticide concentration in GLEAMS may be improved by changing the sediment organic enrichment calculation. GLEAMS and PRZM predicted metribuzin movement could be improved by adjusting model input (e.g., metribuzin half-life and partition coefficient), but sensitive model input were determined from site-specific data or input as suggested by the user manual (Mullins et al., 1993; Knisel et al., 1993).

These results must be viewed considering that this evaluation was based upon one growing season, which is similar to Zacharias and Heatwole (1994). According to Zacharias and Heatwole (1994), studies of this type have limitations but are useful due to the scarcity of detailed field studies of longer duration in different regions.

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REFERENCES

Banton, O., and J. P. Villeneuve. 1989. Evaluation of groundwater vulnerability to pesticides: A comparison between the pesticide drastic index and the PRZM leaching quantities. *J. Contaminant Hydrol.* 4(3): 285-296.

Boesten, J. J. T. I., and C. J. T. Van Der Pas. 1988. Modeling adsorption/desorption kinetics of pesticides in a soil suspension. *Soil Science* 146(4): 221-231.

Carsel, R. F., J. C. Imhoff, P. R. Hummel, J. M. Cheplick, and A. S. Donigian Jr. 1998 (draft). *PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0*. Athens, Ga.: USEPA.

Carsel, R. F., L. A. Mulkey, M. N. Lorber, and L. B. Baskin. 1985. The Pesticide Root Zone Model (PRZM): A procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling* 30(1/2): 49-69.

Dunn, G. H., and R. E. Phillips. 1991. Macroporosity of a well-drained soil under no-till and conventional tillage. *Soil Sci. Soc. Am. J.* 55(3): 817-823.

Felton, G. K. 1992. Soil hydraulic properties of reclaimed prime farmland. *Transactions of the ASAE* 35(3): 871-877.

Flury, M. 1996. Experimental evidence of transport of pesticides through field soils-a review. *J. Environ. Qual.* 25(1): 25-45.

Fontaine, D. D., P. L. Havens, G. E. Blau, and P. M. Tillotson. 1992. The role of sensitivity analysis in groundwater risk modeling for pesticides. *Weed Technology* 6(3): 716-724.

Foster, G. R., L. J. Lane, and J. D. Nowlin. 1980. A model to estimate sediment yield from field sized areas: Selection of parameter values. In *CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems,* 36-64, ed. W. G. Knisel. Conservation Research Report 26. Washington, D.C.: USDA.

Foster, G. R., R. A. Young, and W. H. Neibling. 1985. Sediment composition for nonpoint source pollution analysis. *Transactions of the ASAE* 28(1): 133-139, 146.

Goetz, A. J., T. L. Lavy, and E. E. Gbur. 1990. Degradation and field persistence of imazethpyr. *Weed Science* 38(4/5): 421-428.

Graham, J. S., and J. S. Conn. 1992. Sorption of metribuzin and metolachlor in Alaskan subarctic agricultural soils. *Weed Science* 40(1): 155-160.

Harris, C. I., and G. F. Warren. 1964. Adsorption and desorption of herbicides by soil. *Weeds* 12(2): 120-126.

Hornsby, A. G., R. D. Wauchope, and A. E. Herner. 1996. *Pesticide Properties in the Environment*. New York, N.Y.: Springer Verlag.

Jones, R. E., P. A. Banks, and D. E. Radcliffe. 1990. Alachlor and metribuzin movement and dissipation in a soil profile as influenced by soil surface condition. *Weed Science* 38(6): 589-597.

Karickhoff, S. W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydr. Engng.* 110(6): 707-735.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research* 13(3): 241-248.

Kladivko, E. J., G. E. Van Scoyoc, E. J. Monke, K. M. Oates, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *J. Environ. Qual.* 20(1): 264-270.

Knisel, W. G., F. M. Davis, R. A. Leonard, and A. D. Nicks. 1993. GLEAMS Version 2.10 Part III: Users Manual. In *GLEAMS Groundwater Loading Effects of Agricultural Management Systems,* ver. 2.10, ed. W. G. Knisel. Tifton, Ga.: USDA-ARS Southeast Watershed Research Laboratory.

Koskinen, W. C., G. A. O'Conner, and H. H. Cheng. 1979. Characterization of hysteresis in the desorption of 2,4,5-T from soils. *Soil Sci. Soc. Am. J.* 43(5): 871-874.

Leonard, R. A., F. M. Davis, and C. C. Truman. 1996. A two-compartment model for simulating pesticide fate and transport. ASAE Paper No. 96-2024. St. Joseph, Mich.: ASAE.

Leonard, R. A., W. G. Knisel, and D. A. Still. 1987. GLEAMS: Groundwater loading effects of agricultural management systems. *Transactions of the ASAE* 30(5): 1403-1418.

Leonard, R. A., and R. D. Wauchope. 1980. The pesticide submodel. In *CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems,* 88-112, ed. W. G. Knisel. Conservation Research Report 26. Washington, D.C.: USDA.

Locke, M. A., and S. S. Harper. 1991. Metribuzin degradation in soil. I. Effects of soybean residue amendment, metribuzin level, and soil depth. *Pesticide Sci.* 31(2): 221-237.

Malone, R. W., R. C. Warner, and M. Byers. 1997. Extraction of metribuzin from soil using supercritical CO_2 (SFE). *Bulletin of Environ. Contam. & Toxicol.* 58(1): 46-52.

Malone, R. W., R. C. Warner, and M. Byers. 1996a. Runoff losses of surface-applied metribuzin as influenced by yard waste compost amendments, no-tillage and, conventional-tillage. *Bulletin of Environ. Contam. & Toxicol.* 57(4): 536-543.

_____. 1996b. Subsurface losses of surface-applied metribuzin as influenced by yard waste compost amendments, no-tillage and, conventional-tillage. *Bulletin of Environ. Contam. & Toxicol.* 57(5): 751-758.

Malone, R. W. 1996. Field assessment and modeling surface and subsurface metribuzin transport under three treatments: Yard waste compost amended, no-till, and conventional-till. Ph.D. diss. Lexington, Ky.: Dept. of Biosystems and Agricultural Engineering, University of Kentucky.

Manilal, V. B., and M. Alexander. 1991. Factors affecting the microbial degradation of phenanthrene in soil. *Appl-microbiol-Biotech* 35(3): 401-405.

Massey, H. F., and M. L. Jackson. 1952. Selective erosion of soil fertility constituents. *Soil Sci. Soc. Am. Proc.* 16: 353-356.

Melancon, S. M., J. E. Pollard, and S. C. Hern. 1986. Evaluation of SESOIL, PRZM and PESTAN in a laboratory column leaching experiment. *Environ. Toxicol. & Chem.* 5(10): 865-878.

Miller, W. P., and D. M. Miller.1987. A micro-pipette method for soil mechanical analysis. *Communica. in Soil & Plant Analysis* 18(1): 1-15.

Mueller, T. C., R. E. Jones, P. B. Bush, and P. A. Banks. 1992. Comparison of PRZM and GLEAMS computer model predictions with field data for alachlor, metribuzin and norflurazon leaching. *Environ. Toxicol. & Chem.* 11(3): 427-436.

Mullins, J. A., R. F. Carsel, J. E. Scarbrough, and A. M. Ivery. 1993. *PRZM-2, A model for Predicting Pesticide Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 2.0*. EPA/600/R-93/046. Athens, Ga.: USEPA.

Nash, R. G. 1980 Dissipation rate of pesticides from soil. In *CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems,* 560-594, ed. W. G. Knisel. Conservation Research Report 26. Washington, D.C.: USDA.

Parrish, R. S., C. N. Smith, and F. K. Fong. 1992. Tests of the Pesticide Root Zone Model and the aggregate model for transport and transformation of aldicarb, metolachlor, and Bromide. *J. Environ. Qual.* 21(4): 685-697.

Pennell, K. D., A. G. Hornsby, R. E. Jessup, and P. S. C. Rao. 1990. Evaluation of five simulation models for predicting aldicarb and bromide behavior under field conditions. *Water Resour. Res.* 26(11): 2679-2693.

Richie, J. T. 1972. Model for predicting evaporation from a row crop with incomplete cover. *Water Resour. Res.* 8(5): 1204-1213.

Roy, W. R., I. G. Krapac, S. F. J. Chou, and R. A. Griffin. Submitted 1990. Batch-type procedures for estimating soil adsorption of chemicals. EPA/530-SW-87-006-F. Cincinnati, Ohio: USEPA.

Sauer, T. J., K. J. Fermanich, and T. C. Daniel. 1990. Comparison of the Pesticide Root Zone Model simulated and measured pesticide mobility under two tillage systems. *J. Environ. Qual.* 19(4): 727-734.

Shipitalo, M. J., W. M. Edwards, W. A. Dick, and L. B. Owens. 1990. Initial storm effects on macropore transport of surface-applied chemicals in no-till soil. *Soil Sci. Soc. Am. J.* 54(6): 1530-1536.

Smith, C. N., R. S. Parrish, and D. S. Brown. 1990. Conducting field studies for testing pesticide leaching models. *Intern. J. Environ. Anal. Chem.* 39(1): 3-21.

Smith, M. C., A. B. Bottcher, K. L. Campbell, D. L. Thomas. 1991a. Field testing and comparison of the PRZM and GLEAMS models. *Transactions of the ASAE* 34(3): 838-847.

Smith, W. N., S. O. Prasher, S. F. Barrington. 1991b. Evaluation of PRZM and LEACHMP on intact soil columns. *Transactions of the ASAE* 34(6): 2413-2420.

Sorenson, B. A., P. J. Shea, and F. W. Roeth. 1991. Effects of tillage, application time and rate on metribuzin dissipation. *Weed Research* 31(6): 333-345.

Tomlin, C., ed. 1994. 10th Ed. *The Pesticide Manual*. Cambridge, UK: British Crop Protection Council.

Truman, C. C., R. A. Leonard, and A. W. Johnson. 1998. Fenamiphos transport, transformation, and degradation in a highly weathered soil. *Transactions of the ASAE* 41(3): 663-671.

Wauchope, R. D., R. G. Williams, and L. R. Marti. 1990. Runoff of sulfometuron-methyl and cyanazine from small plots: Effects of formulation and grass cover. *J. Environ. Qual.* 19(1): 119-125.

Xue, S. K., and H. M. Selim. 1995. Modeling adsorption-desorption kinetics of alachlor in a Typic Fragiudalf. *J. Environ. Qual.* 24(5): 896-903.

Zacharias, S., and C. D. Heatwole. 1994. Evaluation of GLEAMS and PRZM for predicting pesticide leaching under field conditions. *Transactions of the ASAE* 37(2): 439-451.