

Mobility and Dissipation of ^{14}C -Labeled Atrazine, Metolachlor, and Primisulfuron in Undisturbed Field Lysimeters of a Coastal Plain Soil

Kyle E. Keller* and Jerome B. Weber

Crop Science Department, North Carolina State University, Raleigh, North Carolina 27695-7620

Mobility and dissipation of ^{14}C -labeled atrazine, metolachlor, and primisulfuron were evaluated for 1 year when applied preemergence to fallow loamy sand soil column field lysimeters. The relative mobility of the herbicides and/or metabolites in field lysimeters over the 1 year period in descending order was metolachlor > atrazine = primisulfuron. Thirty days after treatment, losses of ^{14}C due to apparent volatilization, with other loss mechanisms being involved, accounted for 57, 43, and 62% of the applied ^{14}C for atrazine, metolachlor, and primisulfuron, respectively. Chemical analysis of the 0–8 cm layer showed the presence of four metabolites for atrazine, two for metolachlor, and two for primisulfuron. Calculated half-lives were 4 days for atrazine, 7 days for metolachlor, and 5 days for primisulfuron.

Keywords: Degradation; volatilization; leaching; half-life

INTRODUCTION

Recent detections of atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N'*-(2-methoxy-1-methylethyl)acetamide] in our nation's groundwater have heightened interest in the fate and transport of these compounds in soil. Seventy-five percent of the atrazine and metolachlor is applied in the Midwest (Gianessi and Puffer, 1990). Understandably, most research focusing on groundwater contamination by these compounds occurs in Midwest soils.

Unlike soil in the Midwest, Coastal Plain soils in the southeastern United States are distinctly different in their physical and chemical properties and exposure to climatic conditions. These differences suggest dissimilar herbicide movement, dissipation, and potential for groundwater contamination. To our knowledge, the movement and dissipation of atrazine, metolachlor, and primisulfuron [2-[[[[[4,6-bis(di fluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoic acid] in a Coastal Plain soil and their potential of groundwater contamination have not been examined. Supportably, models such as DRASTIC (Aller et al., 1985), HLP/SLP (Weber, 1991), and PRZM (Carsel et al., 1984) indicate that the Coastal Plain soils are susceptible to groundwater contamination by herbicides.

Atrazine, a symmetrical triazine herbicide, is registered for use in corn (*Zea mays* L.) and controls many broadleaf and some grassy weeds (*Herbicide Handbook of the Weed Science Society of America*, 1989). Atrazine is a weakly basic compound with a pK_a of 1.68 (Gunther and Gunther, 1970), water solubility of 33 mg/L at pH 7 and 27 °C, and vapor pressure of 3.0×10^{-7} mmHg at 20 °C (*Herbicide Handbook of the Weed Science Society of America*, 1989). It is readily adsorbed by a variety of clay minerals and organic colloids (Gunther and Gunther, 1970). Sorption increases with decreasing pH (Talbert and Fletchall, 1965; McGlamery and Slife, 1966; Weber, 1970). Metolachlor, a chloroacetamide herbicide, is registered for use in corn, potato (*Solanum tuberosum* L.), peanut (*Arachis hypogaea* L.), and soybean [*Glycine max* (L.) Merr.] and is used to control annual grasses, certain broadleaf weeds, and yellow

nutsedge (*Cyperus esculentus* L.) (*Herbicide Handbook of the Weed Science Society of America*, 1989). Metolachlor is a nonionic compound, with a water solubility of 530 mg/L at 20 °C and a moderate vapor pressure of 1.3×10^{-5} mmHg at 20 °C (*Herbicide Handbook of the Weed Science Society of America*, 1989). Adsorption of metolachlor has been positively correlated with clay content (Peter and Weber, 1985; Braverman et al., 1986) and humic (Kozac et al., 1983) and organic matter content (Peter and Weber, 1985) of soils.

Primisulfuron, a recently registered sulfonylurea herbicide, is applied postemergence for control and/or suppression of certain grass and broadleaf weeds in corn (*Technical Data Sheet-Primisulfuron (BEACON)*, 1990). It is a weakly acidic compound with a pK_a of 5.1, a moderate water solubility of 70 mg/L at pH 7 and 20 °C, and a vapor pressure $<7.5 \times 10^{-12}$ mmHg at 20 °C (*Pesticide Fact Sheet*, 1990). Adsorption of the sulfonylurea herbicides occurs in soils high in organic matter (Harvey et al., 1985; Mersie and Foy, 1986) and of low pH (Harvey et al., 1985; Mersie and Foy, 1986; Shea, 1986).

The use of removed or intact lysimeters, whether utilizing disturbed or undisturbed soil, is well documented for studying the fate and behavior of pesticides in soil (Fuhr, 1985; Bowman, 1988; Kubiak et al., 1988; Bergstrom, 1990). Fallow undisturbed soil column field lysimeters were used in this study to determine the relative mobility and dissipation of atrazine, metolachlor, and primisulfuron in a Coastal Plain soil and their potential for groundwater contamination.

MATERIALS AND METHODS

Lysimeter Installation. Steel columns (20 cm i.d. and 98 cm in length) were driven 30 cm apart into a conventionally tilled Dothan loamy sand (Plinthic Kandiudult; fine-loamy, siliceous, thermic) by an inverted tractor-mounted postdriver in 1989 and 1990 at the Central Crops Research Station, Clayton, NC. Prior to insertion, a metal plate was placed atop each column which prevented damage to the column from the impact of the postdriver. To protect against runoff, 2 cm of the column remained above the soil surface.

Chemical Preparation and Application. On June 30, 1989, and May 30, 1990, ^{14}C -ring-labeled atrazine plus AAtrex

4L, ^{14}C -ring-labeled metolachlor plus Dual 8E, and ^{14}C -phenyl-labeled primisulfuron supplied by Ciba-Geigy Corp., Greensboro, NC, were applied in 20 mL of water by pipet in a cross-hatch pattern to the surface of each soil column. The atrazine solution included 4% methanol to ensure dissolution of the radiolabeled atrazine. The quantity of ^{14}C -labeled atrazine applied to each column was 15.4 μCi [specific activity (SA) = 19.5 $\mu\text{Ci}/\text{mg}$, 99%] for 1989 and 16.7 μCi (SA = 53.5 $\mu\text{Ci}/\text{mg}$, 94.1%) for 1990. The quantity of ^{14}C -labeled metolachlor applied to each column was 15.1 μCi (SA = 19.3 $\mu\text{Ci}/\text{mg}$, 98.9%) for 1989 and 15.9 μCi (SA = 71.5 $\mu\text{Ci}/\text{mg}$, 97%) for 1990. Each column of the primisulfuron treatment received 14.6 μCi (SA = 56.2 $\mu\text{Ci}/\text{mg}$, 97.7%) for 1989 and 10 μCi (SA = 52.4 $\mu\text{Ci}/\text{mg}$, 99.2%) for 1990. Application solutions were equivalent to 1.12 and 2.24 kg of ai/ha for atrazine and metolachlor, respectively. Primisulfuron was applied at 0.08 and 0.06 kg of ai/ha in 1989 and 1990, respectively.

Lysimeter Removal and Sectioning. For each year, duplicate columns were removed at 0, 30, 90, 180, and 360 days after treatment (DAT). After soil was removed from around the columns by the use of a post-hole auger, the columns were lifted by a winch to the soil surface. Column ends were secured with plastic and transported vertically to the laboratory. Columns were cut lengthwise, and the soil was removed in 12, 8 cm depth increments, weighed, mixed, placed in polyethylene bags, labeled, and sealed. Samples for herbicide/metabolite analysis were stored in polyethylene bags at -20°C . Due to limited space and time constraints, 0 day columns could not be removed from the field immediately following herbicide application. Instead, the ^{14}C -labeled herbicide application solutions and efficiency of the analytical procedures were verified by using the same rate of ^{14}C -labeled herbicides applied to field moist Dothan soil inside duplicate polyethylene bags. After herbicide application, soil comparable to the 0–8 cm zone was mixed inside each bag, equilibrated for 4 h, and then stored at -20°C .

Soil Analysis. For each 8 cm depth increment, soil properties including percent organic matter (chromic acid colorimetric method; Schulte, 1988), pH (1:1 soil/water; Eckert, 1988), and particle size distribution (hydrometer method; Gee and Bauder, 1986) were determined by A&L Agricultural Laboratories, Omaha, NE. Cation-exchange capacity (CEC) (Mehlich 3 method; Mehlich, 1984a) and percent soil humic matter (NaOH/DTPA-alcohol extraction method; Mehlich, 1984b) were determined by the North Carolina Department of Agriculture, Raleigh, NC. Organic C content was determined using a medium-temperature resistance furnace (Nelson and Sommers, 1982). Water content of soil samples from each section and sampling period was determined by gravimetric methods (Gardner, 1986).

^{14}C Determination. For total ^{14}C , four field moist 1 g samples from each section were combusted in a biological oxidizer (Model OX-300, R. J. Harvey Instrument Corp., Hillsdale, NJ) until the coefficient of variation was $<20\%$. The $^{14}\text{CO}_2$ evolved was trapped in 15 mL of Harvey ^{14}C scintillation cocktail and subsequently quantified in a liquid scintillation counter (Packard Model 2000 CA, Packard Instrument Co., Downers Grove, IL). Biological oxidizer efficiency was $>94\%$. The amount of ^{14}C for each soil section was converted to percent of applied ^{14}C .

In the 0–8 cm layer, metabolite and parent identification for each herbicide was performed for the 1990 study. One hundred grams of air-dry soil was extracted with 100 mL of methanol on a horizontal shaker for 1 and 4 h for the metolachlor and atrazine treatments, respectively. Air-dry soil was used since the removal of water hastened evaporation of methanol. Preliminary studies showed no loss of ^{14}C from the soil during air-drying. One hundred grams of field moist soil from the primisulfuron treatment was extracted with 100 mL of acetonitrile on a horizontal shaker for 1 h. Slurries were filtered through glass fiber filters under reduced pressure. Filtrates were transferred to 500 mL round-bottom flasks and evaporated to <2 mL at 34°C under reduced pressure. Extraction efficiencies of ^{14}C for the sampling dates varied from 79 to 86% for atrazine, from 74 to 92% for metolachlor, and from 88 to 97% for primisulfuron. Regardless of the herbicide,

extraction efficiencies did not increase when water was added to the extracting solution. Extracts were transferred to graduated centrifuge tubes and evaporated to 1 mL. A 0.1 mL aliquot of the extract was added to 15 mL of scintillation cocktail (Scintiverse E, Fisher Scientific Co., Springfield, NJ). Radioactivity was quantified by liquid scintillation spectrometry. Duplicate 1 g samples from the extracted soil were combusted to determine nonextractable ^{14}C . Biological oxidizer efficiency was $>94\%$. Recovery of extractable plus nonextractable ^{14}C was $>93\%$.

Concentrated extracts (150–500 μL ; >3000 dpm) plus standard (parent compound) were subjected to thin-layer chromatography (TLC) to determine degradates and parent compound (Miller, 1975). Solvent systems used were ethyl acetate/toluene (1:1 v/v) for atrazine, chloroform/methanol/formic acid/water (75:20:4:2 v/v/v/v) for metolachlor, and methylene chloride/ethyl acetate/acetic acid (50:50:1 v/v/v) for primisulfuron. To verify separations from primary solvent systems, randomly selected extracts were developed with secondary solvent systems. Radioactive zones, proportions, and corresponding R_f values were determined by scanning TLC plates (Whatman LK5F linear TLC plates, Whatman U.S.A., Hillsboro, OR) with an imaging TLC plate radiodensitometer (Bioscan System 400 imaging scanner, Bioscan Inc., Washington, DC). To verify proportions of radioactivity, zones were scraped from randomly selected TLC plates, combusted, and quantified by liquid scintillation spectrometry. All ^{14}C wastes were disposed of by the North Carolina State University Life Safety Services following proper procedures (*Manual For Chemical Waste Management*, 1991).

Climatic Conditions. Air temperature and rainfall were recorded daily by the Central Crops Research Station Weather Station (NOAA Site 31-1820-07). All columns were uncovered to receive rainfall. For the 1989 study, at the end of each week when rainfall was below the weekly 10 year average, irrigation (by graduated cylinder) was added to meet the deficit. For the 1990 study, irrigation was applied in the same manner but only during the first 150 days of the study. A U.S. Weather Bureau Class A-type evaporation pan was installed adjacent to the lysimeter site. Cumulative pan evaporation was recorded at least twice weekly. Soil temperature was obtained by inserting a 60 cm length dial thermometer (Omega Engineering, Inc., Stamford, CT) into a pit wall dug adjacent to the lysimeters. Soil temperatures were recorded weekly at 8, 15, 30, 45, 60, and 75 cm below a bare surface.

Experimental Design and Data Analysis. Herbicide treatments were arranged as a randomized complete block design with two replications, and the experiment was run once in each of two years. Analysis of variance was conducted to determine whether there were significant differences in years and herbicides for each depth and sampling date. Comparisons between depths and total recovery for each herbicide and sampling period were subjected to repeated measures using SAS procedures (*User's Guide: Statistics*, 1985). Regression analyses were used to predict herbicide longevity in the 0–8 cm depth.

RESULTS AND DISCUSSION

Soil Properties. Properties of the Dothan soil are shown in Table 1. Organic matter, humic matter, and organic C content decreased with depth. C content of the organic matter fraction ranged from 20% in 24–40 cm depth samples to 50% in 0–16 cm depth samples and 75% in 80–96 cm depth samples. Humic content of the organic matter fraction ranged from 0% in 88–96 cm depth samples to 20% in 32–88 cm depth samples and 50% in 0–32 cm depth samples. Clay content increased with depth, while silt content remained constant. Cation-exchange capacities were a function of the organic matter and clay contents. Soil pH ranged from slightly acid at the surface to extremely acid below 64 cm.

Climatic Conditions. Even though irrigation was applied to meet the weekly rainfall average, there were

Table 1. Soil Characteristics for the Dothan Soil Profile at Clayton, NC^a

depth, cm	OM, %	HM, %	OC, %	S, %	Si, %	C, %	CEC, mequiv/100 g	pH
0-8	1.1	0.4	0.5	84	10	6	2.3	6.1
8-16	0.9	0.4	0.5	85	8	7	2.0	5.7
16-24	0.8	0.4	0.3	83	9	8	1.6	5.2
24-32	0.5	0.3	0.1	82	9	9	1.3	5.1
32-40	0.5	0.1	0.1	82	9	9	1.4	5.1
40-48	0.5	0.1	0.2	80	9	11	1.9	5.0
48-56	0.5	0.1	0.2	76	9	15	2.0	5.0
56-64	0.5	0.1	0.2	73	8	19	2.5	4.6
64-72	0.5	0.1	0.3	70	9	21	3.0	4.4
72-80	0.5	0.1	0.3	67	9	24	3.0	4.3
80-88	0.4	0.1	0.3	65	9	26	3.1	4.4
88-96	0.4	0.0	0.3	60	11	29	3.9	4.4

^a Abbreviations: OM, organic matter; HM, humic matter; OC, organic carbon; S, sand; Si, silt; C, clay; CEC, cation-exchange capacity.

Table 2. Monthly and Cumulative Water Inputs and Monthly Pan Evaporation of Water for 1989 and 1990 Lysimeter Studies

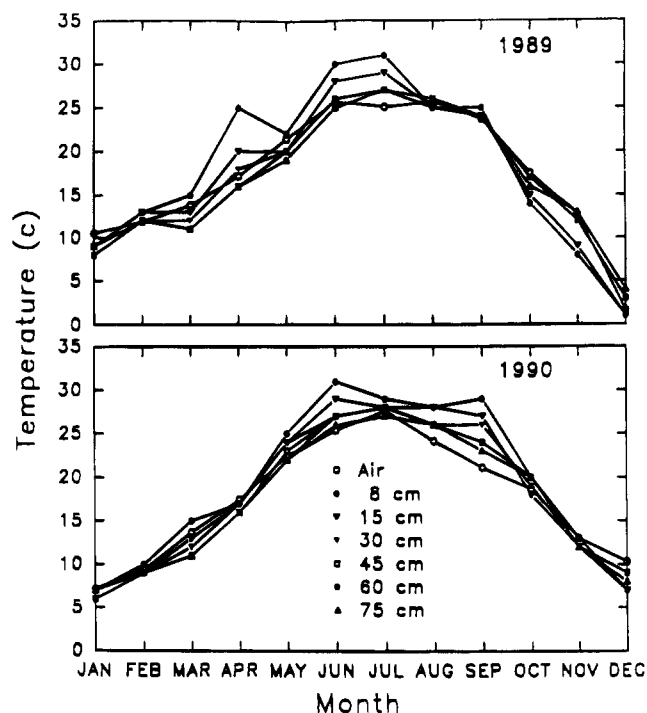
month	input, cm			pan evaporation, cm		
	1989	1990	10 year av ^a	1989	1990	10 year av ^b
January	10.4	10.4	11.0	3.9	3.4	ND ^c
February	8.7	1.1	10.5	5.3	4.5	ND
March	17.4	10.2	9.8	8.8	7.2	ND
April	9.7	3.8	8.9	12.5	9.2	13.7
May	14.6	7.9	10.1	11.2	10.9	16.8
June	8.4	10.6	9.1	15.8	15.8	18.6
July	18.5	17.0	11.5	13.2	16.6	19.1
August	11.1	22.1	10.7	8.2	10.0	17.1
September	15.5	11.9	8.4	8.3	11.1	13.2
October	15.4	15.3	5.9	6.6	9.7	9.4
November	9.3	4.4	8.6	5.2	5.6	6.6
December	11.5	9.1	7.8	1.4	6.7	ND
total	150.5	123.8	112.3	100.4	110.7	114.5
cumulative ^d			av			
30 DAT	16.8	8.6	12.7			
90 DAT	44.0	47.4	45.7			
180 DAT	81.3	81.3	81.3			
360 DAT	150.5	123.8	137.2			

^a 10 year period, 1978-1987; Central Crops Research Station, Clayton, NC (NOAA Station 31-1820-07). ^b 10 year period, 1978-1987; recorded 60 km NW of lysimeter site (NOAA Station 31-1677-03). ^c ND, not determined. ^d Cumulative DAT, days after treatment.

weeks within a month when rainfall exceeded the average. This occurrence resulted in only half of the monthly water inputs for both studies being similar to the 10 year average (Table 2). Cumulative water input for the first 30 days was twice as high for the 1989 season as for the 1990 season. Cumulative water inputs for 90 and 180 DAT were comparable for the 2 years. At the end of both studies, additive water inputs were 34 and 10% over the 10 year average for the 1989 and 1990 studies, respectively.

Monthly pan evaporations for the 1989 and 1990 studies were relatively similar and were in general agreement with the 10 year average (Table 2). Recorded pan evaporation generally followed evapotranspiration losses for the region (Van Bavel, 1961).

For both studies, fluctuating air temperatures were observed over the 12 month period (Figure 1). Excluding January and December, mean monthly air temperatures were within 3 °C for both studies. Mean monthly soil temperatures were within 3 °C for both studies except in December and at 8 cm in April and September through December. Considerable seasonal and monthly variations of soil temperature occurred, even at the lower depths. Soil temperatures at 8 and 15 cm were generally warmer than the air above, while tempera-

**Figure 1.** Average monthly air and soil temperatures for 1989 and 1990 studies.

tures at lower depths were below the monthly air temperature.

¹⁴C Recovery and Distribution. Even though both studies were initiated in different months and had some dissimilar water inputs and air and soil temperatures, ¹⁴C recovery and distribution were nonsignificantly different for both studies, regardless of the herbicide. Therefore, the 1989 and 1990 studies were combined.

Atrazine. Recovery of ¹⁴C from lysimeters treated with [¹⁴C]atrazine rapidly decreased to 30 DAT with minimal decrease occurring after this date (Figure 2). Total recovery of ¹⁴C was 43% at 30 DAT, 41% at 90 DAT, 38% at 180 DAT, and 36% at 360 DAT, which were nonsignificantly different from each adjacent sampling date (Table 3). Nonsignificant differences of the totals after 30 DAT indicated no further loss of atrazine and/or metabolites through volatilization, ¹⁴CO₂, or leaching below 96 cm. Since 43% of the applied ¹⁴C was recovered in the soil profile at 30 DAT and no radioactivity was present below 48 cm, 57% of the applied ¹⁴C was lost due to apparent volatilization of the herbicide, metabolites, or ¹⁴CO₂. This loss was much higher than expected on the basis of the literature. We examined other loss routes that may account for the loss.

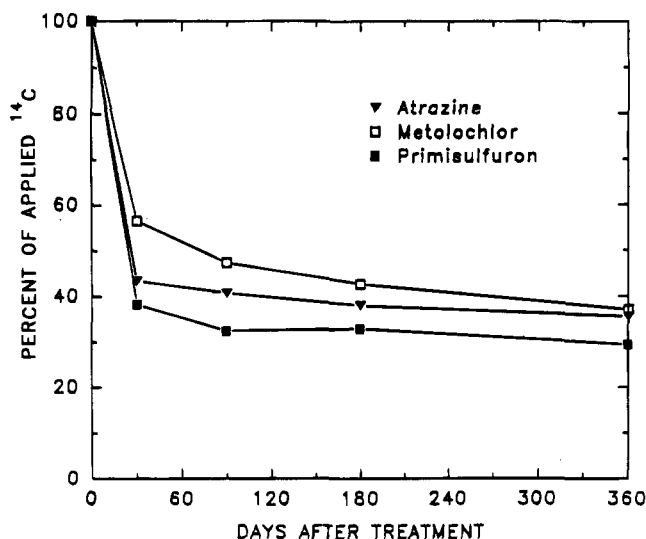


Figure 2. Total ¹⁴C recovery over time in lysimeters treated with ¹⁴C-labeled atrazine, metolachlor, and primisulfuron (mean of 1989 and 1990 studies).

Table 3. Percent of Applied ¹⁴C in Lysimeters Treated with ¹⁴C-Labeled Atrazine^a

depth, cm	days after treatment				
	0	30	90	180	360
0-8	100.0*+	30.5*	23.3*+	20.4*	19.7*
8-16	ND ^b	10.0	9.4*	9.2*	8.3*
16-24	ND+	2.3	4.2*	3.7	3.7*
24-32	ND	0.4+	1.5*	2.0*+	1.0*
32-40	ND	0.1	0.5	0.6	0.4
40-48	ND	0.1	0.4	0.5	0.4
48-56	ND	ND	0.3	0.3	0.3*
56-64	ND	ND	0.4	0.3	0.5
64-72	ND	ND	0.3	0.4	0.4
72-80	ND	ND	0.2	0.3	0.4
80-88	ND	ND	0.2	0.2	0.3*
88-96	ND	ND	0.1	0.1	0.2
total	100.0+	43.4	40.8	38.0	35.6

^a Mean of 1989 and 1990 studies; numbers followed by an asterisk are significantly different from the number immediately below, while numbers followed by a plus sign are significantly different from the number immediately to the right, as determined at the 0.05 level of probability. ^b ND, not detected.

In this study, there was no attempt to reduce losses due to volatilization or mineralization, nor were these processes measured. Other studies have shown that as much as 30-60% of atrazine applied to soil under laboratory conditions can be lost due to volatilization (Kearney et al., 1964), whereas in the field up to 13% may have been lost within the first month due to volatilization (Sorenson et al., 1993). Atrazine in rain-water further substantiates volatilization losses under field conditions (Nations and Hallberg, 1992; Richards et al., 1987). Nations and Hallberg (1992) suggest that volatilization may be the greatest pathway for pesticides to the atmosphere. They further state that pesticide volatilization is greatest a few days after application.

The evolution of ¹⁴CO₂ from ¹⁴C ring-labeled atrazine generally contributes a small percentage (<3%) of the applied ¹⁴C lost from the soil under laboratory conditions at 30 DAT (Best and Weber, 1974; Winkelmann and Klaine, 1991a; Miller, 1992) with as much as 28% (Winkelmann and Klaine, 1991a) and 36% (Miller, 1992) lost after 180 days. Furthermore, mineralization of the major radiolabeled atrazine metabolites applied to soil under laboratory conditions has contributed to as much as 16-59% of the applied ¹⁴C lost after 180 days

(Winkelmann and Klaine, 1991b). In our study, soil moisture and soil temperature conditions in the field, however, may have resulted in greater losses due to volatilization and mineralization than those observed under controlled laboratory conditions.

In a study at the same time, in the same field, and with the same water inputs as this study, Keller (1992) noted no ¹⁴C and <1% of the applied ³H₂O in cumulative leachate at 30 DAT from fallow lysimeters treated with [¹⁴C]metolachlor and ³H₂O. In the same study up to 120 DAT, the breakthrough curve for ³H₂O was symmetrical, indicating no preferential flow or immobile water, while the breakthrough curve for ¹⁴C was asymmetrical due to sorption-desorption processes. The absence of preferential flow and radioactivity in the leachate supports the lack of [¹⁴C]atrazine and/or metabolites beyond 48 cm and the remoteness of any rapid movement of radioactivity from the treatments beyond 96 cm prior to the first sampling in this study.

Overflow or splash erosion are other potential loss mechanisms of ¹⁴C. Even though these mechanisms were not measured, we feel loss of ¹⁴C from the atrazine treatment as well as the other two treatments was minimal and did not contribute to the large amount of radioactivity lost in the first 30 days. For the first 30 days in both years, daily rainfall events (not shown) were <2 cm, thus negating overflow of the 2 cm of column remaining above the soil surface. Also, the observed infiltration rate for this soil was rapid, such that ponding water was rare during daily observations, particularly after intense rains. Hardy and Weber (1994) at the same site on June 29, 1993, initiated a 21-day lysimeter study with [¹⁴C]atrazine and found measured losses due to runoff and splash erosion were <1% of the applied.

¹⁴C distributions of atrazine and/or metabolites remaining in the lysimeters for the various sampling periods are shown in Table 3. Even though lysimeters were subjected to an average of 13 cm of cumulative water inputs (Table 2), 98% of the remaining ¹⁴C was in the top 24 cm at 30 days after atrazine application (Table 3). Less than 0.5% of the applied ¹⁴C was detected below 24 cm, while no ¹⁴C was detected below 48 cm. After an additional 33 cm of water (Table 2), 91% of the ¹⁴C at 90 DAT remained in the top 24 cm (Table 3). Seven percent of the radioactivity detected for this time period was distributed below 24 cm, with <0.1% of the applied ¹⁴C observed beyond 88 cm. Even though 34 cm of water was added to the lysimeters between 90 and 180 DAT and 56 cm between 180 and 360 DAT (Table 2), >88% of the remaining ¹⁴C was present in the top three depths (Table 3). Below 32 cm, there were no significant differences in ¹⁴C within depths between 90 and 360 DAT. Reduction in movement of ¹⁴C after 90 DAT indicates that ¹⁴C was tightly sorbed.

Total ¹⁴C distribution is in general agreement with the results of Sorenson et al. (1993), who applied radiolabeled atrazine to sandy loam soil columns maintained under field conditions for 16 months. The large fraction of ¹⁴C in the upper 24 cm (Table 3) was probably a result of the high organic matter levels in this zone (Table 1) binding the ¹⁴C compounds to the soil by physical bonds, thus preventing rapid desorption and leaching of ¹⁴C through the lysimeters. Symmetrical triazines are physically and/or chemically adsorbed to soil organic matter depending on soil pH (Weed and Weber, 1974). Physical adsorption of atrazine in the

0–16 cm zone (Table 3) was probably more prevalent than chemical adsorption, because at pH 5.7–6.1 (Table 1) most of the herbicide is in the nonionized form. Blumhorst (1989) found that atrazine was equally desorbed from a Norfolk sandy loam (pH 5.7; 6, 1.0, and 0.1% clay, organic matter, and humic matter, respectively) with either deionized water or 0.1 M CaCl₂ indicating physical adsorption. Greater desorption with CaCl₂ would indicate chemical adsorption. Sorption of atrazine and its major metabolites has been correlated to increasing organic matter (Talbert and Fletchall, 1965; McGlamery and Slife, 1966; Brouwer et al., 1990).

Extraction of the 0–8 cm layer (discussed later) at 30 DAT showed that atrazine, hydroxyatrazine (HA), and deethylatrazine (DEA) constituted 49, 16, and 15% of the extractable radioactivity, respectively. Since HA is more tightly adsorbed than atrazine (Brouwer et al., 1990; Clay and Koskinen, 1990), the radioactivity present in the lower depths is likely DEA. In addition, HA has been found to be less mobile than atrazine, especially in acidic soils (Helling, 1971). DEA has a water solubility 13 times greater than that of atrazine (Beilstein et al., 1981) and, therefore, would be more mobile than atrazine and likely constitutes a large proportion of the radioactivity in the lower depths. The remaining portion of ¹⁴C may be parent atrazine since Miller (1992), using the same Dothan subsoil under laboratory conditions, reported no chemical or microbial degradation of atrazine.

The immobility of ¹⁴C in the acidic sandy clay loam subsoil is probably due to ionic adsorption of the protonated triazine molecules. Atrazine and atrazine transformed via chemical hydrolysis to HA (Armstrong et al., 1967; Skipper et al., 1967) in the acidic subsoil both possess basic tendencies (Weber, 1967; Vermeulen et al., 1982), and conceivably the other atrazine triazine degradates may become protonated in acidic soil, thus increasing the opportunity for ionic adsorption. Ionic adsorption signifies a strong binding mechanism which decreases the opportunity for desorption and subsequent mobility.

Metolachlor. Like the atrazine treatment, recovery of ¹⁴C from lysimeters treated with metolachlor rapidly decreased to 30 DAT, with minimal loss observed after 30 days (Figure 2). Total recoveries of ¹⁴C were 57% at 30 DAT, 48% at 90 DAT, 43% at 180 DAT, and 37% at 360 DAT, which were nonsignificantly different from each adjacent sampling date (Table 4). Nonsignificant differences of the totals indicate no further loss of metolachlor and/or metabolites through volatilization, ¹⁴CO₂, or leaching.

At 30 DAT, 43% of the applied ¹⁴C was lost through apparent volatilization of the herbicide and/or metabolites and/or less importantly by ¹⁴CO₂ that were not measured. In support of loss due to volatilization and to negate overflow or splash erosion contribution, Keller (1992) in a companion study at the same time (1990) and in the same field with no rainfall and 1.9 and 1.6 cm of irrigation (by graduated cylinder) at 2 and 9 days after treatment, respectively, recovered only 58% of the applied ¹⁴C at 14 DAT from fallow lysimeters treated with [¹⁴C]metolachlor. No radioactivity was detected below 24 cm in that study.

Review of the literature on alachlor, a related chloroacetamide herbicide that has a vapor pressure similar to that of metolachlor (*Herbicide Handbook of the Weed Science Society of America*, 1989), implies that metolachlor may be volatile under certain conditions. Glot-

Table 4. Percent of Applied ¹⁴C in Lysimeters Treated with ¹⁴C-Labeled Metolachlor^a

depth, cm	days after treatment				
	0	30	90	180	360
0–8	100.0*+	34.0*+	18.4*	15.2*	14.6*
8–16	ND ^b +	9.7	8.1*	6.9*	6.0*
16–24	ND+	5.3	3.7	3.8	2.7*
24–32	ND+	2.8	2.8*	2.6	1.9
32–40	ND	1.6	1.8	1.8	1.3
40–48	ND	1.2*	1.5	1.4	1.1
48–56	ND	0.8	1.7	1.9+	1.5
56–64	ND	0.9	2.1	3.1	2.7
64–72	ND	0.3+	2.3	2.4*	2.5*
72–80	ND	ND+	2.3	1.7	1.4
80–88	ND	ND+	1.9*+	1.2*+	0.8*
88–96	ND	ND+	1.0	0.8	0.5
total	100.0+	56.6	47.6	42.8	37.0

^a Mean of 1989 and 1990 studies; numbers followed by an asterisk are significantly different from the number immediately below, while numbers followed by a plus sign are significantly different from the number immediately to the right, as determined at the 0.05 level of probability. ^b ND, not detected.

felty et al. (1989) reported that 19% of the alachlor applied to a fallow soil volatilized within 24 DAT. Even higher losses were reported by Beestman and Deming (1974), who found under laboratory conditions that 50% of the applied alachlor volatilized from a wet soil (10% clay, 1% organic matter) within 12 DAT. Like atrazine, metolachlor and alachlor have been detected in rainwater (Richards et al., 1987) with concentrations reaching their maxima in events immediately following applications.

The amount of ¹⁴CO₂ produced from soil treated with [¹⁴C]metolachlor is generally very low. Laboratory studies show that after 4 weeks, <5% of [¹⁴C]metolachlor was released as ¹⁴CO₂ (Bailey and Coffey, 1986; LeBaron et al., 1988; Miller, 1992). As previously mentioned, soil moisture and soil temperature conditions in our study may have resulted in greater losses due to volatilization and mineralization than those observed under controlled laboratory conditions.

Distributions of ¹⁴C from metolachlor and/or metabolites remaining in the lysimeters for the various sampling dates are shown in Table 4. Like the atrazine treatment, ¹⁴C distribution was related to organic matter levels in the soil profile (Table 1). Organic matter is the most important soil property influencing metolachlor sorption (Jordan and Harvey, 1978; Obrigawitch et al., 1981; Peter and Weber, 1985) with physical bonding being proposed (Obrigawitch et al., 1981; Peter and Weber, 1985).

At 30 DAT, 86% of the ¹⁴C remaining was present in the top 24 cm (Table 4). After 13 cm of water (Table 2), <3% of the applied ¹⁴C was detected at any depth between 24 and 72 cm, with none being detected beyond 72 cm (Table 4). Between 30 and 90 DAT, significant amounts of ¹⁴C in the 0–8 cm layer were lost either by volatilization, ¹⁴CO₂, or leaching. This occurrence is not surprising since Wendt (1987) found that as much as 53% of the adsorbed metolachlor on a Norfolk soil was desorbed with water. The apparent desorption of ¹⁴C by 33 cm of water (Table 2) resulted in more radioactivity below 48 cm than what was present 60 days earlier (Table 4). At 90 DAT, 63% of the ¹⁴C resided in the upper 24 cm of the profile, with 1% of the applied ¹⁴C detected beyond 88 cm.

At 180 and 360 DAT, >60% of the remaining ¹⁴C was observed in the top three depths (Table 4). Distribu-

Table 5. Percent of Applied ^{14}C in Lysimeters Treated with ^{14}C -Labeled Primisulfuron^a

depth, cm	days after treatment				
	0	30	90	180	360
0-8	100.0* ⁺	23.9	11.0	12.0	11.5
8-16	ND ^b ⁺	8.6*	10.9	9.2	8.1*
16-24	ND	3.2	3.6	5.3	3.9
24-32	ND ⁺	0.9 ⁺	2.3*	2.4	1.9
32-40	ND	0.6	0.8	0.7	1.0
40-48	ND	0.4 ⁺	0.8	0.8	0.6
48-56	ND ⁺	0.2	0.5	0.7*	0.5
56-64	ND	0.1 ⁺	0.7*	0.5	0.4
64-72	ND	0.2	0.6	0.5	0.5
72-80	ND	0.1	0.6 ⁺	0.4	0.3
80-88	ND	0.1	0.6 ⁺	0.2	0.3
88-96	ND	0.1 ⁺	0.4	0.1	0.4
total	100.0 ⁺	38.4 ⁺	32.8	32.8	29.4

^a Mean of 1989 and 1990 studies; numbers followed by an asterisk are significantly different from the number immediately below, while numbers followed by a plus sign are significantly different from the number immediately to the right, as determined at the 0.05 level of probability. ^b ND, not detected.

tions of ^{14}C below 24 cm were similar at 90, 180, and 360 DAT. Noticeably, with 34 cm of water added between 90 and 180 DAT and 56 cm from 180 and 360 DAT (Table 2), there was no further movement of ^{14}C , indicating that the ^{14}C was tightly sorbed. Below 24 cm, low amounts of organic matter and high amounts of clay were present for sorptive processes (Table 1). Several investigators have reported that metolachlor adsorption has been correlated to clay content (Peter and Weber, 1985; Wood et al., 1987). In addition, the soil used in this study presents a maximum opportunity of sorption to occur in the nearly structureless B horizon. In a companion study, Keller (1992), using $^3\text{H}_2\text{O}$, observed no preferential flow or immobile water in the same soil.

^{14}C in the lower depths was presumably metabolites of metolachlor. Extraction and analysis of ^{14}C in the 0-8 cm layer (discussed later) showed that metolachlor constituted 90% of the extractable ^{14}C at 30 DAT, 83% at 90 DAT, 77% at 180 DAT, and 70% at 360 DAT. In addition, Keller (1992) reported that during a 360 day period, 10% of applied [^{14}C]metolachlor ended up in the leachate and that metabolites made up at least 68% of that detected.

Primisulfuron. Total ^{14}C in the primisulfuron columns rapidly declined to 30 DAT with a slight decline to 90 DAT and began to level off to 360 DAT (Figure 2). Total recovery of ^{14}C was 38% at 30 DAT, 33% at 90 and 180 DAT, and 29% at 360 DAT (Table 5). Total radioactivity at 30 DAT was significantly different from the totals at 90, 180, and 360 DAT, while the totals at 90, 180, and 360 DAT were not significantly different. Similar totals at 90, 180, and 360 DAT indicate no further loss of ^{14}C from the lysimeters.

As with atrazine and metolachlor, a large percent of the applied ^{14}C -labeled primisulfuron and/or degradates disappeared within 30 DAT (Table 5). Even though mineralization was not directly measured, the rapid loss of ^{14}C had to be due to mineralization of the radiolabeled phenyl ring. Since primisulfuron has a vapor pressure 40 000 times less than that of atrazine, losses due to volatilization were negligible. Furthermore, a review of the literature produced no reports of sulfonylurea volatilization.

Previous research has shown that 20% of two phenyl ^{14}C -labeled sulfonylurea herbicides applied to soil under

laboratory conditions was converted to $^{14}\text{CO}_2$ within 30 DAT (Anderson and Dulka, 1985; Fuesler and Hanafey, 1990), with as much as 50% being converted to $^{14}\text{CO}_2$ after 24 weeks (Anderson and Dulka, 1985). Anderson and Dulka (1985) concluded that in acid soils a nonbiological hydrolysis process predominates. After hydrolysis, microorganisms act on the ^{14}C -phenyl hydrolysis products to convert them eventually to $^{14}\text{CO}_2$. Dissimilarly, Miller (1992) found for the first 30 days <2% of the [^{14}C]primisulfuron applied to a Dothan soil under laboratory conditions was converted to $^{14}\text{CO}_2$. In our field study, particularly in the first 30 days, high surface soil temperatures (Figure 1) and soil moisture existed, which produced conditions conducive for enhanced microbial and chemical reactions. Supportably, a field study with a radiolabeled sulfonylurea herbicide applied to undisturbed soil columns near Raleigh, NC, showed that the loss of 45 and 65% of the applied ^{14}C at 60 and 120 DAT, respectively, was attributable to $^{14}\text{CO}_2$ (Anderson and Dulka, 1985).

Thirty days after application, 93% of the ^{14}C present was located in the upper 24 cm (Table 5). This is in agreement with the radiolabeled sulfonylurea herbicide field dissipation study performed by Anderson and Dulka (1985). The large retention of ^{14}C in this zone is related to the higher organic matter and the acidic conditions present (Table 1). Sulfonylurea sorption increases with increasing organic matter (Harvey et al., 1985; Mersie and Foy, 1986) and acidic soil conditions (Harvey et al., 1985; Mersie and Foy, 1986; Shea, 1986). In acid soils, the undissociated sulfonylurea molecules are more lipophilic; thus, sorption to organic matter increases.

After additions of 33 cm of cumulative water from 30 to 90 DAT, 34 cm from 90 to 180 DAT, and 56 cm from 180 to 360 DAT (Table 2), 78-81% of the ^{14}C remaining was located in the 0-24 cm zone, while <1% of the applied ^{14}C was noted at each depth below 32 cm (Table 5). Anderson and Dulka (1985) found similar results for a [^{14}C]sulfometuron methyl [2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid] field dissipation study. Radioactivity below 32 cm is likely in the form of the three metabolites commonly associated with sulfonylurea herbicides of similar structure to primisulfuron, those metabolites being saccharin (2,3-dihydro-1,2-benzisothiazol-3-one 1,1-dioxide), methyl 2-(aminosulfonyl)benzoate, and 2-(aminosulfonyl)benzoic acid (Harvey et al., 1985; Anderson and Dulka, 1985; *Primisulfuron Methyl*, 1992). Saccharin has been determined to be transient in soil (Anderson and Dulka, 1985).

Small fractions of the radioactivity in the lower depths may be primisulfuron in the anionic form. Ionization of primisulfuron results in increased water solubility and mobility. However, the anionic form of sulfonylurea herbicides is sorbed by aluminum and iron hydrous oxides commonly associated with soils in the southeastern United States (Shea, 1986; Goetz et al., 1989).

At 30 DAT, total ^{14}C in lysimeters in decreasing order was metolachlor > atrazine > primisulfuron (Tables 4, 3, and 5, respectively). This trend was maintained throughout the remaining sampling dates. Differences in total ^{14}C are primarily due to herbicide and/or metabolite volatilization and/or $^{14}\text{CO}_2$ losses.

Regardless of sampling time, the relative mobility of ^{14}C -labeled products through the Dothan soil, in decreasing order, was metolachlor > atrazine = primisulfuron (Tables 4, 3, and 5, respectively). Without know-

Table 6. Mass Balance Distribution as Percent of Applied ^{14}C in Lysimeters Treated with ^{14}C -Labeled Atrazine in 1990

distribution	days after treatment				
	0	30	90	180	360
volatilization ^a	ND ^b	54.1	55.5	60.6	62.1
surface (0–8 cm) ^c					
atrazine	73.7	5.3	0.6	0.3	0.3
metabolite 1 ^d	6.1	1.7	0.7	0.7	0.9
metabolite 2 ^d	0.4	1.2	0.2	0.1	0.1
metabolite 3 ^d	1.5	0.8	0.1	0.1	0.1
metabolite 4 ^d	3.2	1.6	0.2	0.1	0.1
unknown	0.6	0.2	0.2	0.2	0.2
unextracted	14.5	17.6	21.4	19.7	20.4
subsurface (8–96 cm)	ND	17.5	21.1	18.2	15.8
total	100.0	100.0	100.0	100.0	100.0

^a Vapor losses of parent herbicide, metabolites, or $^{14}\text{CO}_2$. ^b ND, not detected. ^c Extractable with methanol. ^d Identified by TLC: metabolite 1, hydroxyatrazine; metabolite 2, unidentified; metabolite 3, deisopropylatrazine; metabolite 4, deethylatrazine.

Table 7. Mass Balance Distribution as Percent of Applied ^{14}C in Lysimeters Treated with ^{14}C -Labeled Metolachlor in 1990

distribution	days after treatment				
	0	30	90	180	360
volatilization ^a	ND ^b	43.6	56.3	52.3	55.1
surface (0–8 cm) ^c					
metolachlor	88.8	7.7	0.9	0.5	0.4
metabolite 1	0.3	0.4	SA ^d	SA	SA
metabolite 2	0.6	0.3	SA	SA	SA
unknown	1.8	0.2	0.1	0.1	0.1
unextracted (bound)	8.5	25.9	17.1	13.3	13.2
subsurface (8–96 cm)	ND	21.9	24.2	26.2	21.6
leached ^e	ND	ND	1.4	7.6	9.6
total	100.0	100.0	100.0	100.0	100.0

^a Vapor losses of parent herbicide, metabolites, or $^{14}\text{CO}_2$. ^b ND, not detected. ^c Extractable with methanol. ^d SA, <0.05% of applied ^{14}C . ^e ^{14}C leached below 96 cm (Keller, 1992).

ing the structures of the ^{14}C -labeled products in the subsoil, one can only speculate the reasons for varying mobilities. Metolachlor and its metabolites are more water soluble and less sorbed than the other two herbicides and their byproducts, which would result in increased ^{14}C mobility of the former. Atrazine was less mobile due to its weakly basic character and tendency to be ionically bound to acidic soil colloids plus the relatively low water solubility of the molecular species. Primisulfuron was also low in mobility, probably due to its low water solubility under acidic conditions and its adsorptive tendency for organic matter.

Herbicide Dissipation. For the 1990 study, dissipation, as shown by a mass balance distribution, of atrazine, metolachlor, and primisulfuron in the lysimeters is shown in Tables 6, 7, and 8, respectively.

Atrazine. Over 50% of the applied ^{14}C -labeled atrazine and/or degradates was lost through apparent volatilization (Table 6). This conclusion was verified by the fact that ^{14}C was absent below 48 cm at 30 DAT (Table 3). At 360 DAT, even though total ^{14}C was nonsignificantly different from the previous sampling dates (Table 3), a trend suggests an additional 8% of the applied ^{14}C was lost to the atmosphere. This increase may be in part due to ^{14}C that leached below 96 cm. Beyond 90 DAT, consistent amounts of ^{14}C (bound plus extracted) in the 0–8 cm zone and decreasing ^{14}C in the subsurface (Table 6) suggest that a small portion of ^{14}C may have leached below 96 cm.

^{14}C in the 0–8 cm layer could not be completely

Table 8. Mass Balance Distribution as Percent of Applied ^{14}C in Lysimeters Treated with ^{14}C -Labeled Primisulfuron in 1990

distribution	days after treatment				
	0	30	90	180	360
volatilization ^a	ND ^b	71.4	76.7	78.5	78.4
surface (0–8 cm) ^c					
primisulfuron	95.0	1.1	0.3	0.2	0.3
metabolite 1	0.7	0.2	SA ^d	SA	SA
metabolite 2	ND	SA	SA	SA	SA
unknown	0.8	0.2	0.1	SA	0.1
unextracted (bound)	3.5	11.9	7.3	8.0	10.2
subsurface (8–96 cm)	ND	15.2	15.6	13.3	11.0
total	100.0	100.0	100.0	100.0	100.0

^a Vapor losses of parent herbicide, metabolites, or $^{14}\text{CO}_2$. ^b ND, not detected. ^c Extractable with acetonitrile. ^d SA, <0.05% of applied ^{14}C .

extracted with methanol (Table 6). On the day of application, 14% of the applied ^{14}C -labeled atrazine was bound. Other research has shown 5% of the applied [^{14}C]atrazine being unextractable on 0 day (Sorenson et al., 1993). In our study, the large bound fraction was probably due to the enclosure of adsorptive sites (primarily organic fraction) upon air-drying of the soil prior to extraction. For the other sampling dates, there was no influence of air-drying on ^{14}C extraction, and the lack of extractability was probably due to the inaccessibility of the herbicide and/or metabolites trapped in micropores within the soil colloids.

With time, the level of unextracted (bound) ^{14}C increased (Table 6). At 90, 180, and 360 DAT, bound ^{14}C accounted for >20% of the applied ^{14}C . These observations are not surprising. A steady decrease in the extractable fraction of ^{14}C compounds from soils treated with ^{14}C -labeled atrazine has frequently been observed (Best and Weber, 1974; Capriel et al., 1985; Winkelmann and Klaine, 1991a). Unextractable residues as determined by high-temperature distillation and supercritical methanol generally include atrazine, DEA, deisopropylatrazine (DIA), HA, and the dealkylated analogues of the latter (Capriel et al., 1985, 1986). In addition, Best and Weber (1974) found that it was more difficult to extract HA than atrazine from soil. Therefore, a greater fraction of the bound ^{14}C is expected to be HA.

The atrazine application solution was 94.1% pure; however, the 0 day soil extract contained 12% impurities (Table 6). Atrazine degradation could have taken place during the 4 h after application until the soil was frozen and when the samples were thawed and air-dried for extraction. Sorenson et al. (1993) noted a similar occurrence when applying ^{14}C -labeled atrazine to undisturbed soil columns.

Observed metabolites with corresponding R_f values as determined by thin-layer chromatography are shown in Table 9. Atrazine metabolite R_f values in this study correlate well with those determined by Blumhorst and Weber (1992) using a nearly identical chromatographic technique (Table 9). Since metabolite standards were not used in this study, speculation on the identity of these metabolites is obtained from Blumhorst and Weber (1992).

For the 0 day extraction, metabolite 1 was the most polar metabolite ($R_f = 0.03$; Table 9) and is probably HA. Metabolites 3 and 4 were identified as DIA and DEA, respectively. Metabolite 2 was not identified; however, on the basis of its polarity ($R_f = 0.13$), it is likely a HA analogue or dealkylatrazine. The unknown

Table 9. R_f Values of Atrazine, Metolachlor, Primisulfuron, and Metabolites on Silica TLC Plates Using Various Solvent Systems

compound	solvent systems ^a		
	A	B	C
atrazine	0.66 (0.61) ^c		
metabolite 1 ^b (HA)	0.03 (0.00) ^c		
metabolite 2 ^b	0.13		
metabolite 3 ^b (DIA)	0.34 (0.32) ^c		
metabolite 4 ^b (DEA)	0.44 (0.43) ^c		
metolachlor		0.81	
metabolite 1		0.30	
metabolite 2		0.43	
primisulfuron			0.72
metabolite 1			0.09
metabolite 2			0.41

^a Solvent systems: A, ethyl acetate:toluene (1:1 v/v); B, chloroform:methanol:formic acid:water (75:20:4:2 v/v/v/v); C, methylene chloride:ethyl acetate:acetic acid (50:50:1 v/v/v). ^b Metabolite 1, hydroxyatrazine; metabolite 2, unidentified; metabolite 3, deisopropylatrazine; metabolite 4, deethylatrazine. ^c Ethyl acetate:toluene (1:1 v/v) with silica GF TLC (Blumhorst and Weber, 1992).

fraction (Table 6) refers to radioactivity that did not chromatograph into distinct peaks.

Thirty days after atrazine application, 11% of the applied ¹⁴C was extractable (Table 6). Half of the extractable ¹⁴C was atrazine, while HA (metabolite 1), metabolite 2 (unidentified), and DEA (metabolite 4) constituted the majority of the remaining ¹⁴C. HA and DEA are commonly detected in greater concentrations than the other metabolites (Sironi et al., 1973; Muir and Baker, 1978; Winkelmann and Klaine, 1991a). Large amounts of HA would be expected as hydroxylation is considered to be a major route of atrazine degradation (Armstrong et al., 1967; Skipper et al., 1967).

At 90, 180, and 360 DAT, <2% of the applied [¹⁴C]-atrazine was extractable (Table 6). The decrease in extractable ¹⁴C was accompanied by increases in bound and subsurface (leached) ¹⁴C. The concentrations of extractable ¹⁴C beyond 90 DAT were HA > atrazine > DEA > metabolite 2 > DIA. The order of metabolite concentrations is similar to those found in the literature (Sironi et al., 1973; Winkelmann and Klaine, 1991a).

Metolachlor. After 30 DAT, 44% of ¹⁴C applied as metolachlor was lost through apparent volatilization (Table 7). The absence of ¹⁴C below 72 cm at 30 DAT confirms the loss of ¹⁴C through volatilization (Table 4). Even though total ¹⁴C at 30 and 90 DAT (Table 4) was nonsignificantly different, a trend suggests an additional 13% of the applied ¹⁴C was lost to the atmosphere after 30 DAT (Table 7). After this period, loss of ¹⁴C to the atmosphere was negligible and indicates that ¹⁴C-labeled metolachlor and/or degradates were sorbed to soil colloids and were no longer available for volatilization or mineralization.

Radioactivity in the subsurface was rather constant beyond 30 DAT (Table 7). These levels were maintained due to a reduction of ¹⁴C (extractable plus bound) in the surface layer and evidence of leached ¹⁴C beyond 96 cm (Keller, 1992). In a companion study, Keller (1992) found that cumulative leachate from lysimeters treated with ¹⁴C-labeled metolachlor contained 1% of the applied ¹⁴C at 90 DAT, 8% at 180 DAT, and 10% at 360 DAT. Corrections for radioactivity lost below 96 cm are shown in Table 7.

On the day of application, 8% of the ¹⁴C-labeled metolachlor (97% pure) was bound (Table 7). Like the atrazine treatment, this was probably due to the enclosure of adsorptive sites upon air-drying of the soil

prior to extraction. For the other sampling periods, there was no influence of air-drying on ¹⁴C extraction. Bound ¹⁴C accounted for 26% of the applied ¹⁴C at 30 DAT, 17% at 90 DAT, and 13% at 180 DAT, indicating that the bound portion was available for other dissipating processes. The bound fractions at 180 and 360 DAT were similar, indicating that the ¹⁴C was not available for further losses or that losses would be very low.

At 30 DAT, 9% of the applied ¹⁴C was extractable (Table 7). For this period, 90% of the extractable ¹⁴C was metolachlor with two polar metabolites (Tables 7 and 9), accounting for the majority of the remaining radioactivity. This is in agreement with the results of Miller (1992), who detected two metabolites in the same Dothan soil. TLC procedures used in this study (Table 9) made it impossible to correlate the metabolites produced in this study with the metabolites observed by other researchers (McGahen and Tiedje, 1978; Liu et al., 1988, 1991).

The amount of extractable parent and metabolites declined with time (Table 7). Extractable metolachlor accounted for 0.9% of the applied ¹⁴C at 90 DAT, 0.5% at 180 DAT, and 0.4% at 360 DAT. Accordingly, metabolites composed <0.05% of the applied ¹⁴C. Since bound ¹⁴C did not increase with time, low quantities of extractable metabolites indicate that metolachlor was not present to degrade and/or that metabolites leached from the 0–8 cm depth.

Primisulfuron. At 30 DAT in 1990, no radioactivity was detected below 56 cm (not shown); therefore, more than 70% of the applied ¹⁴C was lost to the atmosphere (Table 8). Primisulfuron and its major metabolite, saccharin (Anderson and Dulka, 1985; *Primisulfuron Methyl*, 1992), are considered to be nonvolatile; hence, the majority of ¹⁴C was lost as ¹⁴CO₂. The mechanism for ¹⁴CO₂ production from soil treated with a sulfonyl-urea herbicide was previously discussed.

For the four later sampling dates, radioactivity in the subsurface was rather constant and accounted for <16% of the applied ¹⁴C (Table 8). This occurrence suggests that ¹⁴C in the surface leached, contributing to a constant pool of ¹⁴C for the subsurface. On the other hand, radioactivity from 8 to 56 cm at 30 DAT may have been redistributed to deeper depths and sorbed. In this scenario, the reduction of ¹⁴C in the surface over time would be due to vapor losses.

Less than 4% of the primisulfuron application solution (99% pure) was bound on the day of application (Table 8). Thirty days after application and beyond, bound ¹⁴C made up 7–12% of the applied ¹⁴C. The slight reduction in the bound fraction after 30 days implies that fixed ¹⁴C was available for other dissipating processes.

Thirty days after application, <2% of the applied [¹⁴C]-primisulfuron was extractable (Table 8). For this sampling date, primisulfuron accounted for 73% of the extractable ¹⁴C, while two polar metabolites (Tables 8 and 9) made the difference. For the remaining sampling periods, <0.5% of the applied ¹⁴C was extractable (Table 8). At least three metabolites have been determined in soil treated with primisulfuron (*Primisulfuron Methyl*, 1992). These products include saccharin, methyl 2-(aminosulfonyl)benzoate, and 2-(aminosulfonyl)benzoic acid. Similarly, Anderson and Dulka (1985) used sulfometuron methyl, structurally comparable to primisulfuron, in a laboratory study and found the same three metabolites plus methyl 2-[[N-(aminocarbonyl)amino]sulfonyl]benzoate. For this study, concentrations of ex-

Table 10. Parameter Estimates, Coefficients of Determination (R^2), and Soil Half-Lives for Atrazine, Metolachlor, and Primisulfuron in the 0–8 cm Depth Calculated from the Square Root Weighted Exponential Regression Model $Y = \exp(A - BX) + C^a$

herbicide	parameter estimates ^b			R^2	half-life, days
	A	B	C		
atrazine	4.297 ± 0.034	-0.094 ± 0.002	0.460 ± 0.259	0.99	4
metolachlor	4.483 ± 0.041	-0.089 ± 0.002	0.701 ± 0.422	0.99	7
primisulfuron	4.544 ± 0.044	-0.135 ± 0.004	0.235 ± 0.254	0.99	5

^a Y, percent of herbicide; X, days. ^b Values ± standard errors.

tractable ¹⁴C throughout the remaining periods were primisulfuron > metabolite 1 > metabolite 2.

Herbicide Half-Life. Tables 6–8 indicate reduction of ¹⁴C-labeled herbicides in the 0–8 cm zone was the result of dissipating processes. These processes, in decreasing order, were apparent volatilization of herbicides, metabolites, and/or ¹⁴CO₂ > subsurface (leaching) ≥ bound (adsorption) > nonvolatile metabolites (degradation). As a result of these dissipating processes, regression analyses were used to predict herbicide longevity in the 0–8 cm depth.

A square root weighted exponential regression model was used to calculate herbicide half-life from parent compound listed in Tables 6–8. Half-life is defined here as the time in days for half of the “extractable” parent compound to disappear from the 0–8 cm zone. For this study, the half-life is dependent upon the previously mentioned dissipating processes. The regression model took the form $Y = \exp(A - BX) + C$, where Y is the percent of applied herbicide remaining, X is the time in days, and A, B, and C are the parameter estimates. The equation is only valid for the range of independent variables used in the study. Parameter estimates, coefficients of determination, and half-life values calculated from the regression model are presented in Table 10.

Atrazine. A soil half-life of 4 days for atrazine is strikingly less than the values obtained in fallow field studies performed in the southern United States. Half-life values of 14 days in Tennessee at 0–3 cm depth (Winklemann and Klaine, 1991a) and 23 days in Alabama at 0–15 cm depth (Sikka and Davis, 1966) were reported when formulated atrazine was applied. Similarly, researchers in Kentucky, after applying ¹⁴C-labeled atrazine to undisturbed cylinders, determined a half-life of 23 days in the 0–15 cm zone (Kells et al., 1980). The disparity in half-life values is likely due to differences in soil types, sampling depth, environmental conditions, vaporization rates of formulated and radiolabeled atrazine, definition of parent, and the method used to estimate half-life.

Metolachlor. The half-life for metolachlor was 7 days. This value is not in agreement with the 15–25 days reported for the southern United States (Skipper et al., 1976; *Herbicide Handbook of the Weed Science Society of America*, 1989). The disparity in the half-life values is probably due to the differences mentioned for atrazine.

Primisulfuron. A soil half-life of 5 days for primisulfuron compares with the 3–12 days reported in the literature (*Pesticide Fact Sheet*, 1990). Unlike atrazine and metolachlor, the sulfonylurea herbicides degrade rapidly by chemical hydrolysis and microbial breakdown and are accelerated under warm, moist, light-textured, low pH soils (Beyer et al., 1987). These conditions were maintained through the first 30 days.

Conclusions. Due to the short half-lives of these compounds, which are lost primarily by volatilization

and adsorption, atrazine and primisulfuron should not be of major concern to groundwater contamination in acid soils of the Coastal Plain. The threat of metolachlor contributing to groundwater contamination is of concern, however; this concern may be minimized by delaying application until crops have reduced the soil water content in the profile or by restricting use of the herbicide to less leachable soils as evaluated by stochastic models (Weber, 1991). Volatilization of atrazine and metolachlor or their metabolites was a major dissipation pathway and certainly warrants further research. In circumstances where volatilization is reduced, higher amounts of herbicide would be present, which in turn could be exposed to the other dissipation processes, most importantly, leaching, which could lead to groundwater quality concerns.

ABBREVIATIONS USED

SA, specific activity; DAT, days after treatment; HA, hydroxyatrazine, 6-hydroxy-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine; DEA, deethylatrazine, 6-chloro-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine; DIA, deisopropylatrazine, 6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine.

ACKNOWLEDGMENT

We acknowledge Ciba-Geigy Corp. for providing material and L. Swain, W. Baker, H. Marshall, G. Clark, D. Hill, R. Lee, J. VanKretschmar, R. Alexander, and D. Wilkins for technical assistance.

LITERATURE CITED

- Aller, L.; Bennett, T.; Lehr, J. H.; Petty, R. J. *DRASTIC: A standardized system for evaluating ground water pollution potential using hydrologic settings*; U.S. EPA, Office of Research and Development: Ada, OK, 1985; EPA 1600/2-851018.
- Anderson, J. J.; Dulka, J. J. Environmental fate of sulfometuron methyl in aerobic soils. *J. Agric. Food Chem.* **1985**, *33*, 596–602.
- Armstrong, D. E.; Chesters, G.; Harris, R. F. Atrazine hydrolysis in soil. *Soil Sci. Soc. Am. Proc.* **1967**, *31*, 61–66.
- Bailey, A. M.; Coffey, M. D. Characterization of microorganisms involved in accelerated biodegradation of metalaxyl and metolachlor in soils. *Can. J. Microbiol.* **1986**, *32*, 562–568.
- Beestman, G. B.; Deming, J. M. Dissipation of acetanilide herbicides from soils. *Agron. J.* **1974**, *66*, 308–311.
- Beilstein, P.; Cook, A. M.; Hutter, R. Determination of seventeen *s*-triazine herbicides and derivatives by high-pressure liquid chromatography. *J. Agric. Food Chem.* **1981**, *29*, 1132–1135.
- Bergstrom, L. Leaching of chlorsulfuron and metsulfuron methyl in three Swedish soils measured in field lysimeters. *J. Environ. Qual.* **1990**, *19*, 701–706.
- Best, J. A.; Weber, J. B. Disappearance of *s*-triazines as affected by soil pH using a balance-sheet approach. *Weed Sci.* **1974**, *22*, 364–373.

- Beyer, E. M.; Brown, H. M.; Duffy, M. J. Sulfonylurea herbicide soil relations. *Proc. Br. Crop Prot. Conf.-Weeds*. **1987**, 2, 531-540.
- Blumhorst, M. R. Behavior of Cyanazine in Soils. Ph.D. Thesis, Crop Science Department, North Carolina State University, Raleigh, NC, 1989.
- Blumhorst, M. R.; Weber, J. B. Cyanazine dissipation as influenced by soil properties. *J. Agric. Food Chem.* **1992**, 40, 894-897.
- Bowman, B. T. Mobility and persistence of metolachlor and aldicarb in field lysimeters. *J. Environ. Qual.* **1988**, 17, 689-694.
- Braverman, M. P.; Lavy, T. L.; Barnes, C. J. The degradation and bioactivity of metolachlor in the soil. *Weed Sci.* **1986**, 34, 479-484.
- Brouwer, W. W. M.; Boesten, J. J. T. I.; Siegers, W. G. Adsorption of transformation products of atrazine by soil. *Weed Res.* **1990**, 30, 123-128.
- Capriel, P.; Haisch, A.; Khan, S. U. Distribution and nature of bound (nonextractable) residues of atrazine in a mineral soil nine years after the herbicide application. *J. Agric. Food Chem.* **1985**, 33, 567-569.
- Capriel, P.; Haisch, A.; Khan, S. U. Supercritical methanol: An efficacious technique for the extraction of bound pesticide residues from soil and plant samples. *J. Agric. Food Chem.* **1986**, 34, 70-73.
- Carsel, R. F.; Smith, C. N.; Mulkey, L. A.; Dean, J. D.; Jowise, P. *User's manual for the pesticide root zone model (PRZM)*; U.S. EPA: Athens, GA, 1984.
- Clay, S. A.; Koskinen, W. C. Adsorption and desorption of atrazine, hydroxyatrazine, and s-glutathione atrazine in two soils. *Weed Sci.* **1990**, 38, 262-266.
- Eckert, D. J. Recommended pH and lime requirement tests. In *Recommended Chemical Soil Test Procedures for the North Central Region*; Dahnke, W. C., Ed.; North Central Regional Publication 221, revised ed.; North Dakota Agricultural Experiment Station Bulletin 499; 1988; pp 6-8.
- Fuesler, T. P.; Hanafey, M. K. Effect of moisture on chlorimuron degradation in soil. *Weed Sci.* **1990**, 38, 256-261.
- Fuhr, F. Application of ¹⁴C-labeled herbicides in lysimeter studies. *Weed Sci.* **1985**, 33 (Suppl. 2), 11-17.
- Gardner, W. H. Water content. In *Methods of Soil Analysis*; Klute, A., Ed.; Agronomic Series 9, Part 1, 2nd ed.; American Society of Agronomy: Madison, WI, 1986; pp 493-544.
- Gee, G. W.; Bauder, J. W. Particle-size analysis. In *Methods of Soil Analysis*; Klute, A., Ed.; Agronomic Series 9, Part 1, 2nd ed.; American Society of Agronomy: Madison, WI, 1986; pp 383-411.
- Gianessi, L. P.; Puffer, C. *Herbicide Use in the United States; Resources for the Future*; Washington, DC, 1990; pp 39, 93.
- Glotfelty, D. E.; Leech, M. M.; Jersey, J.; Taylor, A. W. Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor, and toxaphene. *J. Agric. Food Chem.* **1989**, 37, 546-551.
- Goetz, A. J.; Walker, R. H.; Wehtje, G.; Hajek, B. F. Sorption and mobility of chlorimuron in Alabama soils. *Weed Sci.* **1989**, 37, 428-433.
- Gunther, F. A.; Gunther, J. D. The triazine herbicides. *Residue Rev.* **1970**, 32, 19-354.
- Hardy, D. H.; Weber, J. B. Atrazine dissipation: A mass balance approach using field lysimeters. *Proc. South. Weed Sci. Soc.* **1994**, 47, 207-211.
- Harvey, J., Jr.; Dulka, J. J.; Anderson, J. J. Properties of sulfometuron methyl affecting its environmental fate: aqueous hydrolysis and photolysis, mobility and adsorption on soils, and bioaccumulation potential. *J. Agric. Food Chem.* **1985**, 33, 590-596.
- Helling, C. S. Pesticide mobility in soils. II. Applications of soil thin-layer chromatography. *Soil Sci. Soc. Am. Proc.* **1971**, 35, 737-743.
- Herbicide Handbook of the Weed Science Society of America*; Weed Science Society of America: Champaign, IL, 1989.
- Jordan, G. L.; Harvey, R. J. Adsorption of acetanilide herbicides in ten different Wisconsin soil types. *Abstracts of Papers*, 1978 National Meeting of the Weed Science Society of America, Dallas, TX; Weed Science Society of America: Champaign, IL, 1978; Paper 187.
- Kearney, P. C.; Sheets, T. J.; Smith, J. W. Volatility of seven s-triazines. *Weeds* **1964**, 12, 83-87.
- Keller, K. E. Movement and Dissipation of Atrazine, Metolachlor, and Primisulfuron in Field Lysimeters. Ph.D. Thesis, Crop Science Department, North Carolina State University, Raleigh, NC, 1992.
- Kells, J. J.; Rieck, C. E.; Blevins, R. L.; Muir, W. M. Atrazine dissipation as affected by surface pH and tillage. *Weed Sci.* **1980**, 28, 101-104.
- Kozac, J.; Weber, J. B.; Sheets, T. J. Adsorption of prometryn and metolachlor by selected soil organic matter fractions. *Soil Sci.* **1983**, 136, 94-101.
- Kubiak, R.; Fuhr, F.; Mittelstaedt, W.; Hansper, M.; Steffens, W. Transferability of lysimeter results to actual field situations. *Weed Sci.* **1988**, 36, 514-518.
- Lebaron, H. M.; McFarland, J. E.; Simoneaux, B. J. Metolachlor. In *Herbicides: Chemistry, Degradation, and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; Vol. 3, pp 336-382.
- Liu, S. Y.; Zhang, R.; Bollag, J. M. Biodegradation of metolachlor in a soil perfusion experiment. *Biol. Fertil. Soils.* **1988**, 5, 276-281.
- Liu, S. Y.; Freyer, A. J.; Bollag, J. M. Microbial dechlorination of the herbicide metolachlor. *J. Agric. Food Chem.* **1991**, 39, 631-636.
- Manual For Chemical Waste Management*; Department of Environmental Health and Hazardous Materials Management, Life Safety Services, North Carolina State University: Raleigh, NC, 1991.
- McGahen, L. L.; Tiedje, J. M. Metabolism of two new acylanilide herbicides, Antor herbicide (H-22234) and Dual (metolachlor) by the soil fungus *Chaetomium globosum*. *J. Agric. Food Chem.* **1978**, 26, 414-419.
- McGlamery, M. D.; Slife, F. W. The adsorption and desorption of atrazine as affected by pH, temperature, and concentration. *Weeds* **1966**, 14, 237-239.
- Mehlich, A. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **1984a**, 15, 1409-1416.
- Mehlich, A. Photometric determination of humic matter in soils, a proposed method. *Commun. Soil Sci. Plant Anal.* **1984b**, 15, 1417-1422.
- Mersie, W.; Foy, C. L. Adsorption, desorption, and mobility of chlorsulfuron in soils. *J. Agric. Food Chem.* **1986**, 34, 89-92.
- Miller, J. L. Degradation of Atrazine, Metolachlor, and Primisulfuron in Soil From Four Depths in a Dothan Loamy Sand. M.S. Thesis, Soil Science Department, North Carolina State University, Raleigh, NC, 1992.
- Miller, J. M. *Separation Methods in Chemical Analysis*; Wiley: New York, 1975.
- Muir, D. C. G.; Baker, B. E. The disappearance and movement of three triazine herbicides and several of their degradation products in soil under field conditions. *Weed Res.* **1978**, 18, 111-120.
- Nations, B. K.; Hallberg, G. R. Pesticides in Iowa precipitation. *J. Environ. Qual.* **1992**, 21, 486-492.
- Nelson, D. W.; Sommers, L. E. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; Agronomic Series 9, Part 2, 2nd ed.; American Society of Agronomy: Madison, WI, 1982; pp 539-579.
- Obrigawitch, T.; Hons, F. M.; Abernathy, J. R.; Gipson, J. R. Adsorption, desorption, and mobility of metolachlor in soils. *Weed Sci.* **1981**, 29, 332-336.
- Pesticide Fact Sheet*. Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency: Washington, DC, 1990.
- Peter, C. J.; Weber, J. B. Adsorption, mobility, and efficacy of alachlor and metolachlor as influenced by soil properties. *Weed Sci.* **1985**, 33, 874-881.
- Primisulfuron Methyl*. Special review technical support document; Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency: Washington, DC, 1992.

- Richards, R. P.; Kramer, J. W.; Baker, D. B.; Krieger, K. A. Pesticides in rainwater in the northeastern United States. *Nature* **1987**, *327*, 129–131.
- Schulte, E. E. Recommended soil organic matter tests. In *Recommended Chemical Soil Test Procedures for the North Central Region*; Dahnke, W. C., Ed.; North Central Regional Publication 221, revised ed.; North Dakota Agricultural Experiment Station Bulletin 499; 1988; pp 27–32.
- Shea, P. J. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Sci.* **1986**, *34*, 474–478.
- Sikka, H. C.; Davis, D. E. Dissipation of atrazine from soil by corn, sorghum, and johnsongrass. *Weeds* **1966**, *14*, 289–293.
- Sirons, G. J.; Frank, R.; Sawyer, T. Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam soil. *J. Agric. Food Chem.* **1973**, *21*, 1016–1020.
- Skipper, H. D.; Gilmour, C. M.; Furtick, W. R. Microbial versus chemical degradation of atrazine in soils. *Soil Sci. Soc. Am. Proc.* **1967**, *31*, 653–656.
- Skipper, H. D.; Gossett, B. J.; Smith, G. W. Field evaluation and soil residual characteristics of CGA-24705 and alachlor. *Proc. South. Weed Sci. Soc.* **1976**, *29*, 418–422.
- Sorenson, B. A.; Wyse, D. L.; Koskinen, W. C.; Buhler, D. D.; Lueschen, W. E.; Jorgenson, M. D. Formation and movement of ¹⁴C-atrazine degradation products in a sandy loam soil under field conditions. *Weed Sci.* **1993**, *41*, 239–245.
- Talbert, R. E.; Fletchall, O. H. The adsorption of some *s*-triazines in soils. *Weeds* **1965**, *13*, 46–52.
- Technical Data Sheet-Primisulfuron (BEACON)*. CIBA-Geigy: Greensboro, NC, 1990.
- User's Guide: Statistics*, version 5 ed.; SAS Institute: Cary, NC, 1985.
- Van Bavel, C. H. M. Lysimetric measurements of evapotranspiration rates in the Eastern United States. *Soil Sci. Soc. Am. Proc.* **1961**, *25*, 138–141.
- Vermeulen, N. M. J.; Apostolides, Z.; Potgieter, D. J. J.; Nel, P. C.; Smit, N. S. H. Separation of atrazine and some of its degradation products by high-performance liquid chromatography. *J. Chromatogr.* **1982**, *240*, 247–253.
- Weber, J. B. Spectrophotometrically determined ionization constants of 13 alkylamino-*s*-triazines and the relationships of molecular structure and basicity. *Spectrochim. Acta* **1967**, *23A*, 458–461.
- Weber, J. B. Adsorption of *s*-triazines by montmorillonite as a function of pH and molecular structure. *Soil Sci. Soc. Am. Proc.* **1970**, *34*, 401–404.
- Weber, J. B. Potential for ground water contamination from selected herbicides: A herbicide/soil ranking system. *Proc. South. Weed Sci. Soc.* **1991**, *44*, 45–57.
- Weed, S. B.; Weber, J. B. Pesticide-organic matter interactions. In *Pesticides in Soil and Water*; Guenze, W. D., Ed.; Soil Science Society of America: Madison, WI, 1974; pp 39–66.
- Wendt, D. R. The Behavior of Cinmethylin and Metolachlor in Soils and the Effects of Various Environmental and Edaphic Factors on Cinmethylin Activity. M.S. Thesis, Crop Science Department, North Carolina State University, Raleigh, NC, 1987.
- Winkelman, D. A.; Klaine, S. J. Degradation and bound residue formation of atrazine in a western Tennessee soil. *Environ. Toxicol. Chem.* **1991a**, *10*, 335–345.
- Winkelman, D. A.; Klaine, S. J. Degradation and bound residue formation of four atrazine metabolites, deethyl-atrazine, deisopropylatrazine, dealkylatrazine and hydroxy-atrazine, in a western Tennessee soil. *Environ. Toxicol. Chem.* **1991b**, *10*, 347–354.
- Wood, L. S.; Scott, H. D.; Marx, D. B.; Lavy, T. L. Variability in sorption coefficients of metolachlor on a Captina silt loam. *J. Environ. Qual.* **1987**, *16*, 251–256.

Received for review February 15, 1994. Revised manuscript received December 23, 1994. Accepted January 10, 1995.® We acknowledge the North Carolina Agricultural Foundation, American Cyanamid Co., PTRL East, Inc., Water Resources Research Institute, and U.S. Geological Survey (Grant 89-0496) for financial support. The use of trade names in this publication does not imply endorsement by the North Carolina Agricultural Research Service of the products named or criticism of similar ones not mentioned.

JF940079P

® Abstract published in *Advance ACS Abstracts*, March 1, 1995.