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FATE OF ¹⁴C-ATRAZINE IN A SILT LOAM SOIL

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Formation of ¹⁴C-atrazine degradation products and their distribution in the top 90 cm of a silt loam soil was determined during 16 months in the field. After 16 months, 68% of the applied ¹⁴C was still present in the soil. By 12 months after treatment (MAT), ¹⁴C leached to 70–80 cm. Atrazine accounted for 24% of the applied ¹⁴C remaining 16 MAT, and was the predominant ¹⁴C-compound below 10 cm through 16 MAT. Hydroxyatrazine (HA) was the major degradation product in the top 10 cm of soil comprising 13% of ¹⁴C present 1 MAT and increasing to 24% by 12 MAT. Predominant degradation products at depths greater than 10 cm were HA and deethylatrazine (DEA). Deisopropylatrazine (DIA) accounted for less than 6% of the radioactivity recovered at any soil depth. Deethyldeisopropylatrazine (DEDIA) was detected in soil extracts 2 MAT indicating further degradation of DIA and DEA. The proportion of DEA and DIA increased while the proportion of HA decreased at increasing soil depths indicating that DEA and DIA are more mobile in soil than HA. The large amount of ¹⁴C remaining in the soil 16 MAT, and the depth within the soil profile at which it is found, suggest that atrazine and its degradation products have the potential to persist and move deeper in the soil and possibly contaminate ground water supplies.

KEY WORDS: Leaching, ground water quality, ¹⁴C-herbicides.

INTRODUCTION

Detection of atrazine in ground and surface water supplies in the United States has raised concern about atrazine degradation products and their potential to contaminate water supplies^{1,2}. Atrazine degradation products in soil result from chemical and microbial processes. Chemical hydrolysis results in the formation of hydroxyatrazine (HA)³⁻⁵. Microbial degradation results in *N*-dealkylation⁶⁻¹⁰ to form deethylatrazine (DEA), deisopropylatrazine (DIA), and deethyldeisopropylatrazine (DEDIA)¹¹. Further degradation of dealkylated products results in formation of 4-amino-2-chloro-1,3,5-triazine¹². Hydroxylation of dealkylated products or dealkylation of hydroxylated products results in the formation of deethylhydroxylated products results in the formation products

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deisopropylhydroxyatrazine (DIHA) and deethyldeisopropylhydroxyatrazine (DEDIHA)^{6,8,9}. Complete degradation of atrazine to CO_2 has been observed through continued hydroxylation of the triazine ring to form ammiline, ammelide, and cyanuric acid prior to ring cleavage¹¹.

Atrazine residues appear to be very resistent to degradation following field application. Capriel and Haisch¹³ reported 83% of the initial radioactivity was present 8 years after application of ¹⁴C-atrazine to a sand. Following field application of ¹⁴C-atrazine to a sandy loam¹⁴, more than 75% of the radioactivity was still present 16 months after application. Such long-lived residues have a potential to leach through soil.

The extent of leaching is dependent on the nature of the residues and the physical and chemical properties of the soil. For instance, during a 16-month column leaching study in the field, ¹⁴C-residues were not detected in sandy loam soil deeper than 40 cm¹⁴, and no radioactivity was detected in leachate collected from a 1-m deep monitoring column. As the ¹⁴C-residues moved deeper in the soil, the proportion of HA decreased while the proportion of atrazine, DEA, and DIA increased, suggesting that atrazine, DEA, and DIA, were more mobile than HA. Several studies indicate that HA is strongly sorbed to the soil and does not leach^{15,16}. Schiavon¹⁷ reported only trace levels of radioactivity were detected in leachate following application of ¹⁴C-hydroxyatrazine of soil also indicating that HA is not mobile in soil. However, hydroxylated atrazine derivaties contributed as much as 21% of the radioactivity in leachate following ¹⁴C-atrazine application, suggesting hydroxylated products resulted from *in situ* degradation of previously leached residues and not from leaching through the soil. ¹⁴C-DEA-treated soil resulted in the most radioactivity collected in leachate and appeared to be the most persistent metabolite, indicating its potential to contaminate ground water by leaching through the soil¹⁷.

Generalizations regarding pesticide leaching with respect to soil type suggest that coarse textured soils have greater potential for pesticide leaching than fine textured soils. However, rapid water infiltration and short water residence time in coarse textured soil may result in less pesticide being leached than in finer textured soils. To evaluate pesticide movement in soil, factors such as water holding capacity, water infiltration rate, soil water content, and soil structure must be considered. For instance, atrazine moved deeper in a silt loam than in a sand following application to packed, field lysimeters even though OC content of the silt loam was nearly two times higher and had greater atrazine sorption than the sand¹⁸. Greater leaching in the silt loam was attributed to wetter soil conditions caused by the higher water holding capacity, and slower infiltration rate allowing atrazine more time to desorb and move with the water through the soil¹⁸.

To evaluate the effect of soil characteristics on formation and movement of atrazine residues in soil, studies were initiated to determine the amount of major atrazine degradation products in the top 90 cm of a silt loam soil over a 16-month period, and compare these data with those obtained from previous research on a sandy loam¹⁴ and a clay loam soil¹⁹.

MATERIALS AND METHODS

Chemicals and solvents

Atrazine (98.7% purity), DEA (99% purity), DIA (98% purity), DEDIA (90%, purity), HA (97% purity), DEHA (97% purity), and DIHA (95% purity) were obtained from

Ciba-Geigy Corporation* (Greensboro, NC 27419). ¹⁴C-uniformly ring-labeled atrazine (0.38 GBq mmol⁻¹) was purchased from Pathfinder Laboratories (St. Louis, MO 63178). Technical grade methanol, chloroform, ethyl acetate, dichloromethane, and scintillation grade toluene were used as received.

Field procedures

The experiment was conducted at the Olmstead Country Water Quality Research Plots at the Steve Lawler Farm, Rochester, MN 55901 on a Port Byron silt loam (Hapludoll) (Table 1). Sections of 0.3 m dia poly-vinyl chloride (PVC) pipe (wall thickness of 1.2 cm) 0.9 m long, with one end sharpened were coated with vegetable oil, and inserted into the soil with the front end loader of a 955L Caterpillar trackscavator in October 1987. Compression of the soil inside the columns following insertion was less than 5 cm. Additional columns 0.7 m deep were inserted into the soil at each location and equipped with a water collection device²⁰ to monitor movement of ¹⁴C from the bottom of the column. Water sampling was conducted following each rainfall or irrigation event and prior to each sampling.

After insertion, an additional 9 cm section of pipe was attached to the top of each column to prevent water from flowing across the treated soil. A fence was constructed to control access to the plots. ¹⁴C-atrazine (0.85 MBq) in 5 ml methanol was applied to the center 10 cm of the column, 2.5 cm below the soil surface on May 20, 1988 as previously described¹⁴. Maximum soil and air temperatures on the day of application were 24 and 27°C. Following application, three corn (*Zea mays* L.) seeds were planted in the center of each column. Corn was planted in the rest of the plot area at 60,000 seeds ha⁻¹, and atrazine, alachlor, and dicamba were applied as a tank mix to the entire plot area at 2.2, 3.4 and 0.7 kg ha⁻¹, respectively. After emergence, corn was thinned to 1 plant per column. Irrigation was applied to the columns in 2.5 cm increments as needed.

Soil		Organic	Clay	Silt	Sand
depin (cm)	pН	carbon %	(< 2 um) %	(2-50 um) %	(> 50 um) %
0 - 10	5.4	2.4	23	68	9
10 - 20	5.9	2.2	24	67	9
20 - 30	5.9	2.2	26	67	7
30 - 60	6.0	1.3	26	68	6
60 - 90	5.9	0.5	25	64	11

Table 1 Characteristics of Port Byron silt loam soil.

^{*} Mention of a trade name or company name is for information only and does not imply a recommendation or endorsement by USDA-ARS or University of Minnesota.

Columns were replicated three times in a completely randomized design. Soil columns were removed immediately following ¹⁴C-atrazine application, and 1, 2, 4, and 6 months after ¹⁴C-atrazine treatment (MAT). Prior to removing each column, the corn plants were removed and bagged. The column was capped with a PVC pipe cap. The columns were removed as previously described¹⁴, transported to a freezer, and stored at -15° C until processing.

During the second yr, columns were removed 12 and 16 MAT. Following the 12 MAT sampling, 3 corn seeds were planted into each of the remaining columns on May 22, 1989. After emergence, corn was thinned to 1 plant per column. Corn was planted in the plot area at 60,000 seeds ha⁻¹, the remaining columns were covered and a tank mix of atrazine, alachlor and dicamba was applied to the entire plot area, as done during the first year. At 16 MAT the plants and the columns were removed as previously described.

Laboratory procedures

Each column was sectioned into 10 cm depth increments¹⁴. Soil samples were weighed and mixed for 15 min in a jar mill type mixer. Separate subsamples were taken to determine soil moisture, total radioactivity, and degradation products. Soil moisture was determined by oven drying a 20 g subsample at 110°C for 24 hr. If the soil was too wet for mixing, samples were air dried for 24 hr and soil moisture content determined again. Corn plants were removed from the freezer and dried at 40°C for 48 hr. The samples were ground to pass a 6 mm screen using a Wiley type mill.

To determine total radioactivity in soil, three subsamples (0.3 to 0.5 g) from each soil depth sample, were combined with an equivalent weight of microcrystalline cellulose and oxidized using a Packard 306 sample oxidizer (Packard Instruments Co. Downers Grove, IL 60515). To determine total radioactivity in plants, three subsamples (2.0 g) were oxidized for 0.5 min as previously described¹⁴. Radioactivity was determined by liquid scintillation spectroscopy (LSS) using a Packard 1500 Tri-carb liquid scintillation analyzed (Packard Instruments Co. Downers Grove, IL 60515). ¹⁴CO₂ was trapped with 6 ml Carbosorb II and combined with 16 ml Permablend III scintillation cocktail for both soil and plant tissue. The efficiency of oxidation for both plant and soil samples was determined to be 0.90 ± 0.03 .

¹⁴C residues were extracted from soil as previously described¹⁴ by refluxing three times in methanol and water. ¹⁴C-compounds were separated and quantified using thin layer chromatography (TLC) with 20 × 20 cm 0.25 mm silica TLC plates¹⁴. Rf values of analytical standards following two elutions in 110:2:2 chloroform:methanol:formic acid (v:v:v) were 0.88, 0.66, 0.59, 0.23, and 0.03 for atrazine, DEA, DIA, DEDIA, and hydroxylated derivatives, respectively. To quantify the chlorinated products and total hydroxylated residues, plates were scanned for 10 min on a Berthold linear plate analyzer (Berthold Scientific Instruments Company, Pittsburg, PA). Peaks were integrated, backgrounds subtracted, and retention times compared to analytical standards. To isolate hydroxylated derivatives the plates were developed in a second solvent system (75:20:4:2, chloroform:methanol:water:formic acid v:v:v), Rf values of analytical standards were 0.98, 0.093, 0.90, 0.71, 0.62, 0.38, 0.32 for atrazine, DEA, DIA, DEDIA, HA, DEHA, and DIHA, respectively. Plates were rescanned, peaks integrated and retention times compared with those of analytical standards. Statistical analysis of the data was conducted by calculating the mean and standard error of the mean from the three replicates.

RESULTS

Total ¹⁴C

Recovery of total ¹⁴C from the soil 1 and 2 mo after ¹⁴C-atrazine application was 96 and 81% of that applied, respectively (Table 2). ¹⁴C remaining in the soil decreased to 64% of that applied 4 MAT and did not decrease further during the remainder of the study; 68% remained 16 MAT.

A small amount of ¹⁴C is presumeably lost due to volatilization and plant uptake. Potential volatilization losses were minimized by applying the ¹⁴C-atrazine below the soil surface. The maximum amount of applied ¹⁴C recovered in the corn plant was 5.2% 2 MAT. The rest of the ¹⁴C was assumed to be lost by mineralization to ¹⁴CO₂ rather than leaching out of the lysimeter, discussed below.

Leaching of ${}^{\prime\prime}C$

Between application and 1 MAT, the soil received 5.0 cm of irrigation water and 0.6 cm rainfall resulting in ¹⁴C leaching to 30- to 40-cm depth (Table 2). Between the 1- and 2-MAT sampling, 8.3 cm of rainfall was received and 10.0 cm of irrigation water was applied. During this time ¹⁴C in the 10- to 20-cm depth increased from 4.5 to 8.1%, but was not detected deeper than 40 to 50 cm. Between 2 and 4 MAT, 7 cm of rainfall was received in 7 rainfall events, all less than 2.5 cm, and 10 cm of irrigation water applied in four 2.5 cm applications, however no increase in ¹⁴C in the 10- to 20-cm depth or leaching beyond 40 to 50 cm was observed at 4 MAT.

¹⁴C was detected to the 60- to 70-cm sampling depth by 6 MAT (Table 2). ¹⁴C collected in leachate between the 4- and 6-MAT sampling indicated that some ¹⁴C (< 0.002% of applied) had moved through the soil with the water during this period. ¹⁴C was detected in leachate (700 ml) collected from the monitoring column between 6 and 12 MAT. Atrazine was the only compound detected in the leachate. ¹⁴C at the 10- to 20- cm depth increased to 12.5% of applied at 12 MAT and ¹⁴C was detected throughout the 80 cm deep soil column. From 6–12 MAT 18.2 cm precipitation was received as snow and rain. Distribution of ¹⁴C in the soil profile at 16 MAT was the same as at 12 MAT except ¹⁴C was only detected to 50–60 cm.

Atrazine degradation

Compounds detected in soil during the course of the study were atrazine, HA, DEA, DIA, DEDIA, an unidentified product (UP), possibly 4-amino-2-chloro-1,3,5-triazine¹², and some unidentified polar metabolites (Table 2). Each compound is represented as a percentage of radioactivity recovered at each depth to evaluate relative proportions of each compound at each depth over time.

Atrazine present in the top 10 cm of soil decreased from 88% of recovered immediately following application to 58 and 37% 1 and 2 MAT, respectively (Table 2). The proportion of ¹⁴C as atrazine decreased to an average 27% at 4 to 6 MAT. Decreased proportion of atrazine over time was accounted for primarily by increased levels of unextracted residues, HA, and DEA and to a lesser degree by DIA, DEDIA, and the UP.

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มกอกเ	יים קר אר	0.5 ± 0 0.5 ± 0 0.5 ± 0 0.5 ± 0 nd nd 1.1 ± 1 1.1 ± 1 1.1 ± 1 nd nd nd	2.3 ± 1 1.8 ± 1 1.8 ± 1 nd nd nd nd nd
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nu viv	0.5±0.74 nd 1.5±0.2 3.6±0.6 3.5 3.5 nd	2.2 ± 0.4 4.7 ± 1.0 3.8 ± 0.4 4.2 ± 1.3 nd nd 1.9 ± 1.0 1.8 ± 1.2 3.8 ± 0.4 nd nd	2.7 ± 0.6 3.3 ± 1.1 0.6 ± 0.9 2.8 ± 3.9 9.9 nd nd nd
ULA (% of recov	0.9± 1.3 nd 3.5± 0.4 11.0± 2.3 6.7± 6.7 2.6 nd	3.7 ± 1.0 11.3 ± 0.4 12.8 ± 1.5 14.5 ± 1.4 8.2 nd 5.2 ± 3.0 17.0 ± 5.2 15.6 ± 3.1 16.7 nd nd	7.4 ± 4.2 14.6 ± 7.5 10.8 ± 11.6 11.3 ± 10.8 14.4 20.0 nd nd
ĨĊ	87.5 ± 4.9 nd 58.5 ± 3.2 55.5 ± 4.7 74.9 ± 25.1 67.8 nd	36.7 ± 7.1 53.5 ± 0.3 62.9 ± 7.2 58.5 ± 5.2 79.6 nd 27.5 ± 7.6 48.0 ± 6.7 47.1 ± 7.6 89.3 nd	30.9± 4.4 33.2± 6.9 51.2± 9.9 57.1± 12.7 39.8 60.0 80.0 nd
M 1	1.5 ± 1.3 nd 8.0 ± 1.0 4.7 ± 3.7 nd nd	9.7 ± 2.6 10.3 ± 0.5 5.0 ± 5.0 9.0 ± 9.0 nd nd 10.0 ± 1.0 13.5 ± 2.5 9.7 ± 7.4 3.0 ± 4.2 nd nd	13.7 ± 3.9 16.7 ± 7.3 7.0 ± 9.9 nd nd nd nd nd
<i>טונאו</i> מרוכמ	4.0± 0.8 nd 16.0± 6.0 20.0± 3.7 15.0± 15.1 23.0 nd	32.7 ± 5.1 14.0 ± 1.4 9.5 ± 1.5 6.5 ± 6.5 nd 34.5 ± 5.5 13.5 ± 1.5 10.7 ± 10.5 nd nd nd	28.3 ± 10.8 23.7 ± 18.7 10.3 ± 10.1 15.7 ± 16.2 nd nd nd
(% of applied)	100.0± 4.4° nd ^e 90.7 ± 7.1 4.5 ± 2.6 0.3 ± 0.2 0.2 nd	69.9±14.0 8.1±1.6 2.1±0.8 0.8±0.7 0.1±0.2 nd 53.1±12.7 5.3±1.6 1.2±0.3 0.1±0.1 nd	56.2 ± 4.2 7.6 ± 2.6 1.6 ± 0.3 0.8 ± 0.5 0.1 ± 0.1 0.1 ± 0.1 0.1 ± 0.1 nd
(111-1)	0-10 10-20 0-10 20-30 30-40 40-90	0-10 10-20 30-40 50-90 10-20 10-20 10-20 50-30 50-30 50-30 50-30 50-30 50-30	0-10 10-20 20-30 30-40 50-60 50-60 70-80

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er	Soil				Π	Distribution of ¹⁴ C	per depth ^ª		
нон ((cm)	Total ¹⁴ C (% of applied)	Unextracted	МА	AT	DEA (% of recov	DIA ered)	ПЪ	DEDIA
	0-10	602+55	35.0+ 4.3	7.7 + 3.7	252+87	5.3 + 0.4	3.0+0.4	1.2 + 1.0	28+12
	10-20	12.5 ± 5.8	21.3 ± 10.3	14.7 ± 0.5	25.7 ± 1.3	17.3 ± 0.9	5.8 ± 1.2	pu	3.4 ± 0.4
	20-30	2.9 ± 1.0	38.7 ± 5.0	3.3 ± 4.7	29.0 ± 6.5	14.5 ± 1.4	2.7 ± 1.9	pu	4.4 ± 3.2
	30-40	1.8 ± 1.0	34.0 ± 9.0	nď	34.9 ± 7.4	20.7 ± 3.1	5.1 ± 1.6	pu	pu
	40-50	1.2 ± 0.5	33.5 ± 8.5	pu	43.3 ± 8.8	6.9 ± 6.9	2.1 ± 2.1	ри	pu
	50-60	0.9 ± 0.4	30.0 ± 5.0	pu	41.8 ± 10.7	4.6 ± 4.6	1.8 ± 1.8	ри	pu
	60-70	0.1	pu	pu	44.2	9.0	1.7	pu	pu
	70-80	0.1	pu	pu	44.2	9.3	1.7	pu	pu
	0-10	50.1 ± 4.7	34.7 ± 14.6	10.7 ± 1.7	24.0 ± 2.3	5.9 ± 0.9	2.2 ± 0.3	1.7 ± 0.3	3.0 ± 0.6
	10-20	12.1 ± 2.3	17.7 ± 3.8	16.7 ± 4.5	18.0 ± 3.0	16.8 ± 2.1	2.4 ± 0.7	0.2 ± 0.3	3.5 ± 1.4
	20-30	2.7 ± 0.2	30.3 ± 9.3	6.3 ± 9.0	37.0 ± 4.5	3.9 ± 3.3	0.6 ± 0.9	0.6 ± 0.8	1.1 ± 1.6
	30-40	1.2 ± 0.2	30.3 ± 3.5	pu	20.3 ± 0.2	12.6 ± 0.7	1.8 ± 1.8	pu	pu
	40-50	0.9 ± 0.8	22.5 ± 22.5	pu	26.1 ± 0.3	18.9 ± 3.0	3.0 ± 3.0	pu	pu
	50-60	0.5 ± 0.8	pu	pu	25.8 ± 2.3	12.0 ± 2.8	pu	pu	ри
	06-09	pu	nd	pu	pu	pu	pu	pu	pu

(cont.) Distribution of ¹⁴C following May 1988 application of 0.85 MBq ¹⁴C-atrazine to Port Byron silt loam.

xolar metabolites, AT = atrazine, DEA = deethylatrazine, DIA = deisopropylatrazine, DEDIA = deethyldeisopropylatrazine, UP = unidentified pr atrazine t standard error of the mean ot detected

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Unextractable residues in the top 10 cm of soil increased from 4% of total ¹⁴C measured immediately following application to 33% at 2 MAT and remained constant through the remainder of the study. The proportion of HA in the top 10 cm increased from 5.6% immediately following application to a high of 26%, 12 MAT. The maximum proportion of microbially dealkylated metabolites DEA, DIA, and DEDIA in the top 10 cm were 7, 3, and 3%, respectively, throughout the 16 mo incubation period. The maximum proportion of ¹⁴C present as an UP in the top 10 cm of soil was 1.7% at 16 MAT.

At depths greater than 10 cm, the proportion of atrazine decreased with time indicating the potential for degradation of atrazine in the soil below the plow layer. For instance, the proportion of atrazine present in the 10- to 20-, 20- to 30-, and 30- to 40- cm depths was 56, 75 and 68%, respectively, 1 MAT (Table 2). The proportion of atrazine decreased to 18, 37, and 20% for the same depth increments, 16 MAT. The decreased proportion of atrazine at depths greater than 10 cm was associated with increased proportion of DEA, HA, and unextracted residues.

DISCUSSION

Leachate collected from monitoring columns in the silt loam in this study and a clay loam¹⁹ and sandy loam¹⁴ indicated that water moved through the soils and was available for leaching ¹⁴C-compounds. Radioactivity was detected throughout the columns and in leachate collected from the silt loam and clay loam¹⁹, but not deeper than 40 cm or in leachate from the sandy loam¹⁴. It is interesting that more leaching occurred in the silt loam and clay loam¹⁹ soils than in the sandy loam¹⁴. Generalizations regarding the leaching potential of a specific soil based on its sand content may not be very good predictors of the potential for leaching to occur in a given soil and climate. Many factors determine the mobility of a specific pesticide in soil, which preclude making generalizations based on one soil factor.

Greater leaching of ¹⁴C in the silt loam and clay loam appears to be a function of the greater water holding capacity of these soils. Greater clay and silt contents in the silt loam and clay loam¹⁹ soils compared to the sandy loam¹⁴ maintained higher soil moisture longer, allowing more time for desorption of atrazine residues to occur and leach with the water. Rapid water movement in the sandy loam did not allow sufficient time for residues to desorb from soil and move with water. Previous results¹⁸ also showing greater atrazine leaching from columns packed with silt loam than sand may be to similar reasons.

In the silt loam, initial leaching resulted in greater concentrations of residues in the 10- to 20-cm depth, but leaching was limited to the top 40 cm. In contrast, initial leaching in the clay loam¹⁹ was rapid and characteristic of macroporous flow as observed in previous research²¹⁻²⁴.

In appears that soil factors such as texture, OC, and pH also affected availability of ¹⁴C-atrazine residues in these soils. Greater plant uptake of ¹⁴C from the silt loam than from the clay loam may have been due to lower OC and clay levels allowing atrazine residues to be more available to the corn plants. Research conducted on the affect of OC¹⁵ and soil pH^{15,16} indicate that sorption of atrazine and selected degradation products increased as OC increased and soil pH decreased.

Atrazine residues were degraded more rapidly in the silt loam than in the clay loam or sandy loam soil during the first 4 MAT. Radioactivity in the silt loam decreased to 64% of applied 4 MAT, compared to 75 and 80% in the sandy loam¹⁴ and clay loam¹⁹ soils,

respectively. A greater capacity for the silt loam to degrade the atrazine residues is evident by higher levels of unextracted products, PM, and more rapid decrease in atrazine concentration than in the sandy loam¹⁴ or clay loam¹⁹. Higher levels of unextracted radioactivity may be due to formation of secondary degradation products not extracted from the soil. Higher levels of PM suggests continued degradation of residues to more polar products not extracted from the aqueous soil extract. Total radioactivity in the silt loam and sandy loam¹⁴ soils did not decrease after the 4-MAT sampling and was 68 and 78%, respectively, 16 MAT. In the clay loam¹⁹, total radioactivity decreased from 81 to 64% between the 12- and 16-MAT sampling. During this time, HA in the top 10 cm of the clay loam decreased from 20 to 11%, PM increased from 5 to 18% and DEA increased from 6 to 12%.

HA was the major degradation product in the upper 10 cm of soil at all three locations. Microbial degradation resulted in the formation of DEA, DIA, DEDIA, and UP. As residues leached below the top 10 cm of soil, the proportion of HA decreased while the proportion of DEA increased. This suggested that DEA was more mobile in soil or degradation of atrazine at depths greater than 10 cm favored formation of dealkylated products over hydroxylated products. Increased levels of DEA suggest that microbial breakdown was occurring and microbial *N*-dealkylation of hydroxylated residues to more polar compounds and ¹⁴CO₂ may be occurring. These data are supported by Bowman¹⁸ who also observed greater DEA production with increasing soil moisture. Other research also indicates lower adsorption and greater mobility of DEA than atrazine and other degradation products²³⁻²⁷.

Detection of DEDIA and an UP in the silt loam and clay loam¹⁹ soils but not in the sandy loam¹⁴ indicates a greater capacity of silt loam and clay loam soils to degrade atrazine residues than the sandy loam. Detection of DEDIA and UP also indicates continued microbial degradation of atrazine residues because both compounds appear to be chlorinated derivaties and did not undergo chemical hydrolysis of the 2-chloro group.

In conclusion, significant levels of atrazine residues remained 16 MAT. Persistence of these residues in soil for a long time provides a pool of residues for potential contamination of ground water supplies. Detection of these residues in leachate collected from 70 cm deep monitoring columns indicates leaching did occur. Even though the amount leaching is extremely small, it appears that contamination of water supplies may occur by leaching through the soil. The extremely low atrazine levels detected in ground water supplies would require leaching of only < 0.1% of applied atrazine. It appears that contamination of ground water by atrazine and DEA can occur in silt loam soils.

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References

- 1. H. B. Pionke and D. W. Glotfelty. Chemosphere, 21, 813-822 (1990).
- 2. W. F. Ritter. J. Environ. Sci. Health Part B, 25, 1-29 (1990).
- 3. D. E. Armstrong, G. Chesters and R. F. Harris. Soil Sci. Soc. Am. Proc., 31, 61-66 (1967).
- D. E. Armstrong and G. Chesters. Environ. Sci. Tech., 9, 683–689 (1968).
- 5. H. D. Skipper, C. M. Gilmour and W. R. Furtick. Soil Sci. Soc. Am. Proc., 31, 653-656 (1967).
- 6. R. M. Behki and S. U. Khan. J. Agric. Food Chem., 34, 746-749 (1986).

- 7. M. C. Giardina, M. T. Giardi and G. Filacchioni. Agric. Biol. Chem., 46, 1439-1445 (1982).
- 8. M. T. Giardi, M. C. Giardina and G. Filacchioni. Agric. Biol. Chem., 49, 1551-1558 (1985).
- 9. D. D. Kaufman and J. Blake. Soil Biol. Biochem., 2, 73-80 (1970).
- 10. D. C. Wolf and J. P. Martin. J. Environ. Qual., 4, 134-139 (1975).
- 11. A. M. Cook and R. Hutter. J. Agric. Food Chem., 29, 1135-1143 (1981).
- 12. M. C. Giardina, M. T. Giardi and G. Filacchioni. Agric. Biol. Chem., 44, 2067-2072 (1980).
- 13. P. Capriel and A. Haisch. Weed Res., 30, 123-128 (1983).
- B. A. Sorenson, D. L. Wyse, W. C. Koskinen, D. D. Buhler, W. E. Lueschen and M. D. Jorgenson. Weed Sci., 41, 239–245 (1993).
- 15. W. W. M. Brouwer, J. J. T. I. Boesten and W. G. Siegers. Weed Res., 30, 123-128 (1980).
- 16. S. A. Clay and W. C. Koskinen. Weed Sci., 38, 262-266 (1990).
- 17. M. Schiavon. Ecotoxicol. Environ. Saf., 15, 46-54 (1988).
- 18. B. T. Bowman, Environ. Toxic. Chem., 9, 453-461 (1990).
- B. A. Sorenson, W. C. Koskinen, D. D. Buhler, D. L. Wyse, W. E. Lueschen and M. D. Jorgenson. Weed Sci., 42, 618-624 (1994).
- 20. G. C. Barbee and K. W. Brown. Soil Sci., 141, 149-154 (1986).
- 21. K. Beven and Germann. Water Resour. Res., 18, 1311-1325 (1982).
- 22. J. K. Hall, M. R. Murray and N. L. Hartwig. J. Environ. Qual., 18, 439-445 (1989).
- 23. A. R. Isensee, R. G. Nash and C. S. Helling. J. Environ. Qual., 19, 434-440 (1990).
- 24. J. L. Starr and D. E. Glotfelty. J. Environ. Qual., 19, 552-558 (1990).
- 25. C. D. Adams and E. M. Thurman. J. Environ. Qual., 20, 540-547 (1991).
- 26. D. C. Muir and B. E. Baker, J. Agric. Food Chem., 24, 122-125 (1976).
- 27. D. C. Muir and B. E. Baker. Weed Res., 18, 111-120 (1978).

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