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## Abstract

The fate of [14C]deethylatrazine [2-chloro-4-amino-6-(isopropylamino)-s-triazine] was studied under controlled conditions by using undisturbed soil columns in the laboratory. In a 13-week leaching study, the percentage of [14C]deethylatrazine recovered was greatest in the first leaching event (1.3% of the applied 14C), suggesting that preferential flow occurred. The total concentration of deethylatrazine leached from soil columns over the 13-week period was 4.9 µg/L (3.6% of the applied 14C). Unidentified polar degradates made up 3.8% of the applied radioactivity recovered in the leachate, and didealkylatrazine [2-chloro-4,6-(diamino)-s-triazine] and deethylhydroxyatrazine [2-hydroxy-4-amino-6-(isopropylamino)-s-triazine] occurred in trace quantities. Sixty-seven percent of the applied 14C remained in the top 10 cm of soil columns, with 48% as bound residues, 12% as unidentified polar degradates, 5.5% as deethylatrazine, 0.2% as didealkylatrazine, and less than 0.1% as deethylhydroxyatrazine.

## Keywords

Atrazine, deethylatrazine, didealkylatrazine, deethylhydroxyatrazine, mobility, leaching

## Disciplines

Entomology | Soil Science

## Comments

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## Use of Undisturbed Soil Columns under Controlled Conditions To Study the Fate of [<sup>14</sup>C]Deethylatrazine<sup>†</sup>

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The fate of [<sup>14</sup>C]deethylatrazine [2-chloro-4-amino-6-(isopropylamino)-*s*-triazine] was studied under controlled conditions by using undisturbed soil columns in the laboratory. In a 13-week leaching study, the percentage of [<sup>14</sup>C]deethylatrazine recovered was greatest in the first leaching event (1.3% of the applied <sup>14</sup>C), suggesting that preferential flow occurred. The total concentration of deethylatrazine leached from soil columns over the 13-week period was 4.9 μg/L (3.6% of the applied <sup>14</sup>C). Unidentified polar degradates made up 3.8% of the applied radioactivity recovered in the leachate, and didealkylatrazine [2-chloro-4,6-(diamino)-*s*-triazine] and deethylhydroxyatrazine [2-hydroxy-4-amino-6-(isopropylamino)-*s*-triazine] occurred in trace quantities. Sixty-seven percent of the applied <sup>14</sup>C remained in the top 10 cm of soil columns, with 48% as bound residues, 12% as unidentified polar degradates, 5.5% as deethylatrazine, 0.2% as didealkylatrazine, and less than 0.1% as deethylhydroxyatrazine.

**Keywords:** *Atrazine; deethylatrazine; didealkylatrazine; deethylhydroxyatrazine; mobility; leaching*

### INTRODUCTION

Studies using undisturbed soil columns offer the advantage of field reality and laboratory control. This approach is very useful in chemical mobility studies, especially with the use of radiotracers, with which not only movement but transformation can be investigated. Soil columns that are taken from the field in such a way that no cracking or compaction occurs and that include macropores arising from roots, cracks, or earthworm channels have advantages over packed columns in that a more realistic measurement of mobility can be achieved. The ability to transfer columns of soil to a controlled environment provides an opportunity to study fate and transport mechanisms without inherent variations in climatic and hydrologic conditions that occur in the field.

Mobility of pesticides in the environment is of particular interest from a health standpoint in that contamination of drinking water sources results from groundwater contamination. The U.S. Environmental Protection Agency (U.S. EPA) has set maximum contamination levels (MCLs) for a number of pesticides in drinking water (U.S. EPA, 1994). Numerous water monitoring programs have been carried out, and reports of pesticide contamination are well documented (Thurman et al., 1992; Goolsby et al., 1990; Hallberg, 1989; Rostad et al., 1989; Spalding et al., 1989). Degradation of pesticides in the soil environment results in an additional problem due to formation of compounds that may be even more persistent and/or more mobile than parent compounds.

Although previously concerned with only parent compounds, researchers have been making an increasing effort to study the fate of degradation products in laboratory studies and to include degradates in field monitoring efforts. Along with method development and increased analytical sensitivity has come an awareness that groundwater and surface water contain trace

levels of pesticide degradates. Controlled laboratory studies incorporating radiotracer techniques can give important information about degradates that may also be potential contaminants but for which analytical methods may not yet have been established.

Deethylatrazine [DEA, 2-chloro-4-amino-6-(isopropylamino)-*s*-triazine] is an important degradate of the widely used herbicide atrazine [ATR, 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine]. This degradate is more water soluble (Erickson and Lee, 1989), less adsorptive to soil (Brouwer et al., 1990), more desorptive from soil (Roy and Krapac, 1994), in some studies more persistent (Sironi et al., 1973; Muir and Baker, 1978; Dao et al., 1979; Jones et al., 1982), in other studies less persistent (E. Kruger et al., unpublished results; Kruger et al., 1993b; Baluch et al., 1993), and more mobile (Sorenson et al., 1993; Kruger et al., 1995, 1996) than the parent compound. Its presence in groundwater and surface water is well documented (Adams and Thurman, 1991; Kolpin and Kalkhoff, 1993; Jayachandran et al., 1994; Masse et al., 1994; Schottler et al., 1994; Thurman et al., 1994).

Some pesticide degradates are just as important as parent compounds from a general environmental or public health standpoint (Hallberg, 1989). For example, in toxicological tests, both DEA and ATR have been shown to inhibit pituitary gland activity in male rats (Babic-Gojmerac et al., 1989) and to modify the pituitary activity of offspring from injected pregnant female rats (Kniewald et al., 1987). Whereas the MCL for ATR is set at 3 μg/L, there are currently no MCLs (U.S. EPA, 1994) set by the U.S. EPA for *s*-triazine degradates. In Europe, the health advisory for each triazine herbicide and metabolite is 0.1 μg/L (Thurman et al., 1994).

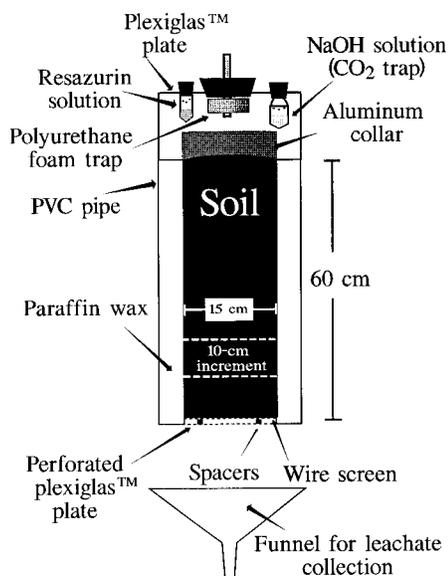
The goal of this study was to investigate the movement and degradation of DEA in undisturbed soil columns under controlled conditions. Results from this study should be useful in process control analysis for understanding the fate of atrazine degradates.

### MATERIALS AND METHODS

**Chemicals.** The following radiolabeled chemicals and analytical standards were obtained from Ciba Corp., Greensboro, NC: [U-ring-<sup>14</sup>C]DEA (94.8% radiopurity); [U-ring-<sup>14</sup>C]-

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**Figure 1.** Preparation of undisturbed soil columns for laboratory studies.

didealkyltriazine (2-chloro-4,6-diamino-*s*-triazine; DDA) (98.8% radiopurity); DEA (99% purity), DDA (97% purity), and deethylhydroxyatrazine [2-hydroxy-4-amino-6-(isopropylamino)-*s*-triazine; DEHYA].

**Soil Columns.** Large undisturbed soil columns (15-cm diameter  $\times$  60-cm length) were obtained from a field with no previous pesticide history at the Till Hydrology Site, Iowa State University Agronomy and Agricultural Engineering Farm, near Ames, Story County, IA. Methods for soil column removal have previously been described (Singh and Kanwar, 1991; Kruger et al., 1993a). Soil samples were taken as a function of depth during collection of each soil column, and soil characteristics were determined for these samples (A&L Midwest Laboratory, Omaha, NE).

**Laboratory Preparation.** Two soil columns were prepared for laboratory experiments by using a modification of the method described by Kruger et al. (1993a) (Figure 1). The vertical surfaces of the soil columns were sealed with Plasti-Dip spray (P.D.I., Inc., Circle Pines, MN). A poly(vinyl chloride) (PVC) pipe (20-cm diameter  $\times$  60-cm length) was centered around the soil column. The space between the soil column and PVC pipe was filled with molten paraffin wax to prevent boundary flow (Weber et al., 1986). An aluminum collar was fixed around the top of the soil column to prevent leachate from spreading over the wax during the leaching study. After the wax was completely hardened, each column was placed on its side, and the bottom 1 cm of soil was removed. A wire screen was placed in contact with the bottom of the soil column. Metal washers were glued to a perforated Plexiglas plate (20-cm diameter), and the plate was mounted on the bottom of the PVC pipe. The washers served as spacers between the screen and the Plexiglas to prevent air locks and to assure continuous flow of leachate during the leaching study.

Soil columns were saturated with 0.005 M CaSO<sub>4</sub> (Singh and Kanwar, 1991). This solution was chosen for soil saturation as its characteristics more closely resemble those of soil pore water than would ultrapure water. Saturation of soil columns was carried out by placing each soil column in a large metal garbage can and slowly raising the level of the CaSO<sub>4</sub> solution over a 48-h period until the columns were completely submerged. In this way, no air would be trapped within the soil column, and complete saturation would be achieved. Soil columns were then mounted in stands in a temperature-controlled room held at 25 °C and allowed to drain to field capacity (approximately -33 kPa of soil moisture tension). Thus, the soil moistures for both soil columns were similar at the beginning of the study. The soil columns were then leached with ultrapure water to obtain a background leachate sample. A chloride tracer was applied to the top of the soil

columns, and they were then leached with ultrapure water to verify their performance (Weber et al., 1986). A qualitative comparison of the precipitate, arising from the dropwise addition of 1 M AgNO<sub>3</sub> to the leachate, was made with background samples to ensure that the amount of chloride in the leachate was above the background level found normally in soil.

The top of the column was sealed with an additional section of PVC pipe (20-cm diameter  $\times$  20-cm length), and the top of this section was capped with a Plexiglas plate that had a central port and two smaller ports on each side (Figure 1). Seams were sealed with silicone rubber adhesive sealant (General Electric Co., Waterford, NY). The central port was used to access the top of the soil column during the leaching experiment and was sealed with a neoprene stopper. A glass rod through the center of this stopper provided an attachment site for a polyurethane foam trap used to trap <sup>14</sup>C organic volatiles. A sodium hydroxide (NaOH) trap containing 10 mL of 0.1 N NaOH was suspended from a neoprene stopper, inserted into a side port, to trap <sup>14</sup>CO<sub>2</sub> arising from complete mineralization of [<sup>14</sup>C]DEA. Phenolphthalein was added to the NaOH to monitor for its saturation with CO<sub>2</sub>. The NaOH was replaced weekly at the time of each leaching event. A perforated plastic centrifuge tube containing 5 mL of ultrapure water and two drops of a 4% resazurin solution was capped with a neoprene stopper and inserted in the second side port of the Plexiglas plate cap. The resazurin served as a monitor for the aerobicity of the headspace over the soil column. It was our intent to maintain aerobic conditions above the columns. All neoprene stoppers were wrapped with Teflon tape.

**Soil Treatment and Leaching.** A treating solution was prepared with a mixture of analytical grade DEA and [<sup>14</sup>C]-DEA dissolved in ultrapure water. Each column received an application of DEA equivalent to 0.5 lb of ai/acre and approximately 20  $\mu$ Ci of [<sup>14</sup>C]DEA. To minimize volatilization of DEA, a spatula was used to incorporate the treating solution into the top 2 cm of each soil column, with minimal disturbance. Soil columns were leached once weekly, beginning 3 days after treatment. An equivalent of 3.8 cm of rainfall (675 mL of ultrapure water) was applied slowly to the top of each column in such a way that ponding did not occur. This rainfall amount was chosen to represent a typical weekly amount received in Iowa during the spring. Rainfall applications usually took between 40 and 60 min. Leachate from each rain event was collected at the bottom of columns in 100-mL aliquots. Each aliquot was analyzed for radioactivity by liquid scintillation techniques using a RackBeta Model 1217 liquid scintillation spectrometer (Pharmacia LKB Biotechnology, Inc., Gaithersburg, MD).

**Solid-Phase Extraction (SPE) of Leachate.** A modified SPE method was used to isolate DEA and degradates from the leachate (Steinheimer, 1993). The aliquots from each leaching event per soil column were combined and filtered through glass microfiber filters. The pH of leachates was adjusted within the range of 7.0–7.5 by dropwise addition of aqueous ammonia or phosphoric acid. Bond Elut (Varian, Harbor City, CA) cyclohexyl SPE cartridges (1 g) were positioned on a 12-port Visiprep solid-phase extraction vacuum manifold (Supelco, Inc., Bellefonte, PA) and conditioned sequentially with at least 12 mL each of methanol and ultrapure water. Leachate was passed through the SPE cartridges immediately after conditioning at a rate of approximately 5 mL/min. After air-drying of the cartridges, acetonitrile (10 mL) was used to elute the DEA and degradates. Effluent volumes were taken, and subsamples of the effluent and eluate were counted by using liquid scintillation spectroscopy. To characterize the relative composition of radioactivity in the eluate, concentrated samples were analyzed by ascending chromatography on normal phase silica gel plates in a solvent system of chloroform/methanol/formic acid/water (100:20:4:2) (Ciba Crop Protection). Autoradiography was used to visualize the radioactive spots associated with <sup>14</sup>C-labeled standards. TLC plates were scraped and counted using liquid scintillation techniques (Kruger et al., 1993b).

**Table 1. Pertinent Characteristics of Soils at Depths in Undisturbed Soil Columns**

depth (cm)	texture	sand (%)	silt (%)	clay (%)	OM <sup>a</sup> (%)	pH <sup>b</sup>
0	sandy clay loam	52	26	22	2.7	5.7
15	sandy clay loam	54	24	22	3.0	5.5
45	loam	42	34	24	2.5	5.9
60	loam	44	30	26	1.8	6.3

<sup>a</sup> Organic matter content. <sup>b</sup> Soil pH was measured in distilled water.

**Soil Extractions and Analyses.** At the conclusion of the leaching experiment, soil columns were cut into 10-cm increments. The wax and Plasti-Dip were removed from the soil. Soils from each 10-cm increment were weighed and mixed thoroughly before subsamples were taken for soil moisture determination. Soils were extracted and analyzed as described in Kruger et al. (1993a). Two 50-g subsamples from each depth were extracted three times with 150 mL of methanol/water (9:1). The extraction efficiency was 99%. The extract was partitioned with dichloromethane, and the organic fraction was concentrated to 10 mL. Liquid scintillation techniques were used to quantify radioactivity in both the aqueous and organic fractions of the soil extracts. TLC and autoradiography were used to characterize the components in the organic fraction, as described earlier. Soil-bound residues were determined by combusting subsamples of extracted soils in a Packard sample oxidizer (Packard Instrument Co.). This method does not allow for determination of particular chemical components of this radioactivity but provides only a quantity for total unextractable <sup>14</sup>C residues. <sup>14</sup>CO<sub>2</sub> from combusted soils was trapped in Carbosorb E (Packard Instrument Co.) and Permafluor V (Packard Instrument Co.) and then quantified by liquid scintillation techniques. The total dry weight per 10-cm section was used in determination of the final mass balance of <sup>14</sup>C applied to soil columns.

**Statistical Analysis.** An analysis of variance (ANOVA) was performed on the repeated measures design for components of the leachate. Orthogonal contrasts were also determined for specific comparisons of leaching events. To determine the effect of soil depth, an ANOVA that used soil columns as a blocking variable was conducted on the components determined in soil extractions and analyses.

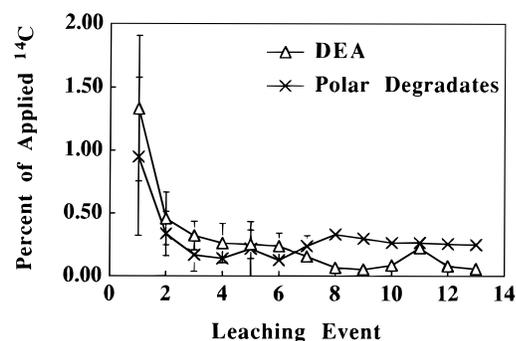
## RESULTS

**Soil Characteristics.** The soils in the columns were a sandy clay loam or loam texture and were classified as Nicollet Webster. Soil characteristics are given in Table 1. The pH of soils increased with soil depth and ranged from 5.3 to 6.3. Organic matter content decreased with depth and ranged from 3.0% to 1.8%.

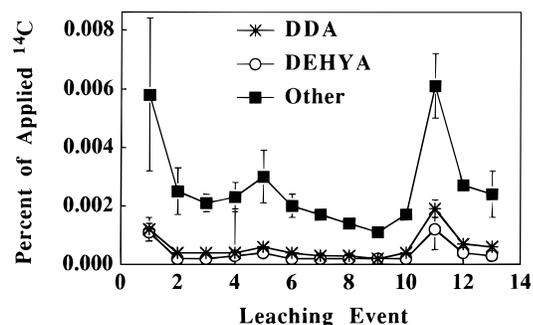
**Mass Balance.** Eighty-nine percent of the applied <sup>14</sup>C was distributed throughout soil columns at the end of the leaching study. In the leachate, 7.5% of the applied <sup>14</sup>C was recovered. Minimal mineralization of DEA in this study resulted in approximately 0.2% of the applied <sup>14</sup>C recovered as <sup>14</sup>CO<sub>2</sub>. No <sup>14</sup>C organic volatiles were detected from DEA degradation. Overall mean recovery of radioactivity in this experiment was 97%.

**Leaching Study.** A comparison of the chloride ion breakthrough, prior to treatment of the soil columns with [<sup>14</sup>C]DEA, revealed that chloride ion moved through both columns similarly, thus verifying similar flow performance of the two soil columns. Elevated concentrations of chloride ion, above background soil chloride ion content, were seen in the first 100-mL aliquot of leachate, indicating that preferential flow occurred in both soil columns.

A significantly greater percentage of <sup>14</sup>C was leached with the first rain event (2.3% of the applied <sup>14</sup>C)



**Figure 2.** DEA and polar degradates recovered in leachate of [<sup>14</sup>C]DEA-treated undisturbed soil columns (mean of two soil columns).



**Figure 3.** DDA, DEHYA, and other unidentified degradates recovered in the leachate of [<sup>14</sup>C]DEA-treated undisturbed soil columns (mean of two soil columns).

compared with all other rain events ( $p = 0.0002$ ). With the first rain event, 1.3% of the applied <sup>14</sup>C was recovered as DEA (Figure 2), suggesting the occurrence of preferential flow of DEA, possibly through macropores (Singh and Kanwar, 1991; Sophocleous et al., 1990; Thomas and Phillips, 1979). Subsequent rain events contained significantly less DEA ( $p = 0.004$ ), with no significant difference in percentages recovered among the remaining 12 rain events.

One percent of the applied radioactivity recovered in the leachate for the first rain event was classified as unidentified polar degradates (Figure 2), as determined by the amount of radioactivity in effluent (from solid-phase extraction). This quantity was significantly greater than for the remaining 12 rain events ( $p = 0.003$ ). After the sixth leaching event, the concentration of polar degradates exceeded that of DEA in the leachate.

Only trace quantities of DDA and DEHYA occurred in leachate throughout the study (<0.01% of the applied <sup>14</sup>C) (Figure 3). The percentage of applied <sup>14</sup>C as DDA and DEHYA in the leachate was significantly greater with the first rain event as compared with all of the other rain events ( $p = 0.002$  and  $0.004$ , respectively). With rain event 11, a significant increase was seen in DDA and DEHYA concentrations compared with those of the preceding rain event ( $p = 0.0004$  and  $0.04$ , respectively).

Cumulatively, 7.5% of the radioactivity applied to the top of soil columns was recovered in the leachate over the course of the 13-week leaching experiment, corresponding to a total DEA/degrade concentration of 10  $\mu$ g/L (in DEA equivalents). Of the [<sup>14</sup>C]DEA applied, 3.6% was collected in the leachate as the parent compound. Considering the amount of unlabeled analytical grade DEA associated with this amount of <sup>14</sup>C

**Table 2. Distribution of [<sup>14</sup>C]DEA and Degradates in Large, Undisturbed Soil Columns**

	soil depth					
	0–10 cm	10–20 cm	20–30 cm	30–40 cm	40–50 cm	50–60 cm
DEA	5.5 <sup>a</sup> (1.1) <sup>b</sup>	1.2 (0.3)	0.9 (0.2)	0.05 (0.3)	0.4 (0.2)	0.3 (0.1)
DDA	0.2 (0.004)	0.06 (0.02)	0.08 (0.01)	0.5 (0.4)	0.4 (0.4)	0.01 (0.003)
DEHYA	0.06 (0.003)	0.02 (0.003)	0.03 (0.007)	0.02 (0.01)	0.02 (0.005)	0.01 (0.003)
polar degradates <sup>c</sup>	12 (2.0)	2.6 (0.3)	2.3 (0.7)	0.8 (0.2)	1.2 (0.6)	1.3 (0.6)
soil bound residues	48 (2.3)	4.8 (0.5)	2.1 (0.2)	0.6 (0.1)	0.5 (0.04)	0.5 (0.04)
others <sup>d</sup>	0.8 (0.2)	0.1 (0.02)	0.2 (0.05)	0.1 (0.04)	0.1 (0.04)	0.04 (0.02)
total <sup>e</sup>	67 (1.9)	8.8 (0.7)	5.6 (0.3)	2.5 (0.4)	2.6 (0.4)	2.2 (0.5)

<sup>a</sup> Means of two soil columns reported as percentage of applied <sup>14</sup>C. <sup>b</sup> Standard errors determined by ANOVA. <sup>c</sup> Quantified by the amount of <sup>14</sup>C in eluant after solid-phase extraction of leachate. <sup>d</sup> Includes unidentifiable minor degradation products observed in the TLC system. <sup>e</sup> Total percentage of applied <sup>14</sup>C per depth; mean percentage of applied <sup>14</sup>C in all depths of soil columns was 89%.

in the treating solution and taking into account the total volume of the leachate, 4.9 μg/L DEA was present in the leachate during the study. Less than 0.02% of the applied <sup>14</sup>C in the leachate, cumulatively, was characterized as either DDA or DEHYA, whereas 3.8% of the applied radioactivity was leached as unidentified polar degradates.

**Distribution of DEA and Degradates in the Soil Profile.** The majority of the applied <sup>14</sup>C remained in the top 10 cm of the soil columns (67%) (Table 2). The percentage of DEA remaining at this depth was 5.5%, which was significantly more than the percentage of DEA in deeper soils (≤1.2%) ( $p = 0.0001$ ). DEA was distributed equally among soil increments below 10 cm.

DDA made up 0.2% of the applied <sup>14</sup>C in the top 10 cm of the soil columns, with no significant difference in percentages of DDA among all depths of the soil columns. The percentage of DEHYA ranged from 0.01% to 0.06% of the applied <sup>14</sup>C in the soil columns.

Unidentified polar degradates, as determined by the amount of <sup>14</sup>C in the aqueous phase after partitioning of the soil extract, made up a substantial portion of the applied <sup>14</sup>C in soil. Significantly larger quantities were formed in the top 10 cm (12%) compared with deeper soils (≤2.6%) ( $p = 0.001$ ). Other degradation products, not identified with available standards (by using TLC methods), were also detected in the leachate at low concentrations (<0.1% of the applied radioactivity).

Soil-bound residues made up the greatest portion of radioactivity in soil columns (57%), with a significantly greater percentage in the top 10 cm (48%) compared with deeper soils (≤4.8%) ( $p = 0.0001$ ). In the 10–20-cm depth, 4.8% of the applied <sup>14</sup>C was characterized as soil-bound residues, and this amount was significantly greater than amounts formed below 20 cm (≤2.1%) ( $p \leq 0.01$ ). No significant differences in quantities of bound residues were seen among depths below 20 cm.

## DISCUSSION

With the use of undisturbed soil columns, two processes of movement of DEA and degradates were indicated in this study: displacement with soil water and preferential flow. Detection of DEA in the first rain event of the leaching study indicates preferential flow through channelization of percolating water. Preferential flow of ATR has also been reported (Kruger et al., 1993a; Sophocleous et al., 1990).

The greatest amount of radioactivity was recovered with the first rain event compared with subsequent rain events. It has been stated that the greatest potential movement of surface-applied pesticides occurs with the first water input after application. Once preferential transport has occurred, pesticides are less subject to

preferential flow because of diffusion of the pesticide into the soil matrix (Gish et al., 1991).

In comparison with a similar study conducted in this laboratory (Kruger et al., 1993a), DEA was more mobile than ATR. Whereas 7.5% of the applied [<sup>14</sup>C]DEA was recovered in the leachate after 13 weeks in the current study, 1.2% of the applied [<sup>14</sup>C]ATR was recovered in the leachate over a 12-week period (Kruger et al., 1993b). This is consistent with other results in the literature (Kruger et al., 1995, 1996; Sorenson et al., 1993; Bowman, 1991; Schiavon, 1988).

The peak of DDA, DEHYA, and (although not significant) DEA in leachate of the 11th week may represent a breakthrough of chemicals moving through the soil matrix. Only a partial displacement of soil water occurs with each addition of rainfall (Thomas and Phillips, 1979). In a study comparing relative mobilities of ATR and degradates using soil TLC (Kruger et al., 1996), DDA and ATR exhibited similar mobilities, and both were significantly less mobile than DEA in this soil type. Therefore, DDA formed in surface or subsurface soils would move through the soil matrix at a slower rate than DEA.

Although the relative mobility of DEHYA was not determined in the soil TLC study mentioned (Kruger et al., 1996), it would likely be less mobile than DEA inasmuch as two other hydroxy *s*-triazine analogues (hydroxyatrazine and ammeline) were less mobile than DEA in that study. Russell et al. (1968) indicated that the protonated hydroxy species of *s*-triazines is bound to clay, which may restrict vertical movement and entrance into groundwater.

The presence of DDA and DEHYA in subsurface soil of the soil columns may be due to degradation of DEA at that depth (Baluch et al., 1993) or movement from higher regions. The small amounts of DDA detected in soil in this study may be a result of its rapid degradation once formed or its tendency to form bound residues quickly (Winkelmann and Klaine, 1991; Schiavon, 1988). Information on the fate of DEHYA is lacking in the literature.

Recent work has focused on methods for isolation of polar degradates (Lerch and Donald, 1994). The current study used a SPE method that, while efficient for DEA isolation (100%), may not have been as efficient for polar degradates including DDA and DEHYA. Thus, polar degradates quantified in the effluent after SPE may actually include these degradates.

Soil-bound residues made up a significant portion of the mass balance of applied DEA (57%) in this study. Others have reported a considerable portion of [<sup>14</sup>C]-*s*-triazines converted to bound residues (Kruger et al., 1993a,b; Winkelmann and Klaine, 1991; Schiavon, 1988; Capriel et al., 1985). Without the use of radiotracers,

it is not possible to determine the presence of such residues. The methods used in this study did not allow for determination of the chemical composition of bound  $^{14}\text{C}$  residues. The contribution of bound residues to pesticide soil burden in the field is often underestimated (Capriel et al., 1985).

With the greater mobility of DEA (as compared with ATR) and quantities of unidentified polar degradates in concentrations similar to or exceeding concentrations of DEA in leachate during this experiment, the need for monitoring pesticide degradates in groundwater is evident. Method development for detection of polar degradates will likely reveal additional input of pesticide residues to groundwater.

#### ABBREVIATIONS USED

DEA, deethylatrazine; DDA, didealkylatrazine; DEHYA, deethylhydroxyatrazine; ATR, atrazine.

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