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Herbicides and Their Metabolites in Rainfall: Origin, Transport, and Deposition Patterns across the Midwestern and Northeastern United States, 1990–1991

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Herbicides were detected in rainfall throughout the midwestern and northeastern United States during late spring and summer of 1990 and 1991. Herbicide concentrations exhibited distinct geographic and seasonal patterns. The highest concentrations occurred in midwestern cornbelt states following herbicide application to cropland. Volume-weighted concentrations of 0.2–0.4 μg/L for atrazine and alachlor were typical in this area during mid-April through mid-July, and weighted concentrations as large as 0.6–0.9 μg/L occurred at several sites. Concentrations of 1–3 μg/L were measured in a few individual samples. Atrazine was detected most often followed by alachlor, deethylatrazine, metolachlor, cyanazine, and deisopropylatrazine. The high ratio (~0.5) of deethylatrazine to atrazine in rainfall suggests atmospheric degradation of atrazine. Mass deposition of herbicides was greatest in areas where herbicide use was high and decreased with distance from the cornbelt. Estimated deposition rates for both atrazine and alachlor ranged from more than 240 μg m^{-2} yr^{-1} for some areas in the midwestern states to less than 10 μg m^{-2} yr^{-1} for the New England states. The estimated annual deposition of atrazine on the Great Lakes ranged from about 12 to 63 μg m^{-2} yr^{-1}. The total amounts of atrazine and alachlor deposited annually in rainfall in the study area represent about 0.6% of the atrazine and 0.4% of the alachlor applied annually to crops in the study area.

Introduction

Current agricultural practices in the United States require extensive use of herbicides for economical production of corn, soybeans, sorghum, and other row crops. Data compiled in 1991 (*1*) show that about two-thirds of the estimated 218 million kg of herbicides used annually for agriculture in the United States (*2*) are applied to cropland in the Midwest, principally in the Mississippi River drainage basin. This region, referred to as the cornbelt, extends from central Nebraska eastward across Iowa, southern Minnesota, Illinois, Indiana, and Ohio. As a consequence of the high use of herbicides, this region is a major source area for transport of herbicides into streams, groundwater, and the atmosphere. Most herbicides are relatively soluble in water, and a small percentage of the amounts applied annually is transported into streams during storm runoff (*3–7*) and to groundwater (*8–10*). Herbicides and other organic compounds also can be transported into the atmosphere by various processes. Once in the atmosphere, these compounds can be dispersed by air currents and re-deposited on water and land surfaces, often at considerable distances from their origin. For example, the transport of chlorinated insecticides and polychlorinated biphenyls (PCBs) into the Great Lakes is largely from atmospheric sources (*11*). More than two dozen agricultural pesticides have been reported in fog and rainfall in the United States (*12–20*), Canada (*21*), and Europe (*22, 23*). Examples of these pesticides include carbamate insecticides (carbaryl and carbofuran), organochlorine insecticides (chlordane, DDT, lindane, mirex, and toxaphene), and organophosphorus insecticides (chloropyrifos, diazinon, fonofos, malathion, methidathion, and parathion). However, triazine and acetanilide herbicides such as atrazine, alachlor, and metolachlor are the most frequently reported pesticides in rainfall and occur in the highest concentrations. This is especially true in the midwestern United States where herbicide concentrations as high as 40 μg/L have been reported in bulk rainfall (*14*). In spite of these studies, relatively little is known on a regional or multistate scale about the occurrence and deposition patterns of herbicides in rainfall over large geographic areas or how the amounts of herbicides deposited annually in rainfall compare to annual quantities applied to cropland or to annual losses in surface runoff.

To learn more about herbicides in rainfall on a regional scale, the U.S. Geological Survey conducted a study during 1990 and 1991 to investigate the occurrence and deposition of selected herbicides in rainfall (rain and snow) for a large part of the United States. The study area (Figure 1) covered about a quarter of the conterminous United States and much of the Mississippi River basin where herbicide use is most intense. The purposes of the study were to (1) determine the occurrence and temporal distribution of major cornbelt triazine and acetanilide herbicides in rainfall over a large part of the United States; (2) estimate the annual mass deposition in rainfall for atrazine and alachlor, the two most heavily used herbicides in 1990 and 1991; and (3) relate the annual deposition of atrazine and alachlor in rainfall to the amounts applied annually to crops. Results from the 19-month study are presented in this paper.

Experimental Section

Study Area and Sampling Protocol. The study area for this investigation encompassed 26 states (Figure 1). It included states in the upper Midwest that contain the majority of the harvested cropland in the United States and where the use of atrazine and alachlor is most intense (Figure 2A,B). Rainfall samples were obtained through the cooperation and assistance of the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN), Fort Collins, CO, and the Illinois State Water Survey, Champaign, IL. The NADP/ NTN operates a network of about 200 sites nationwide to monitor the status and trends in acid deposition (*24*). Weekly accumulations of rainfall (rain and snow) were obtained at 81 NADP/NTN sampling sites located in 23 states within the 26-state study area (Figure 1). In addition, four NADP/NTN sites in high-elevation areas along the Rocky Mountains

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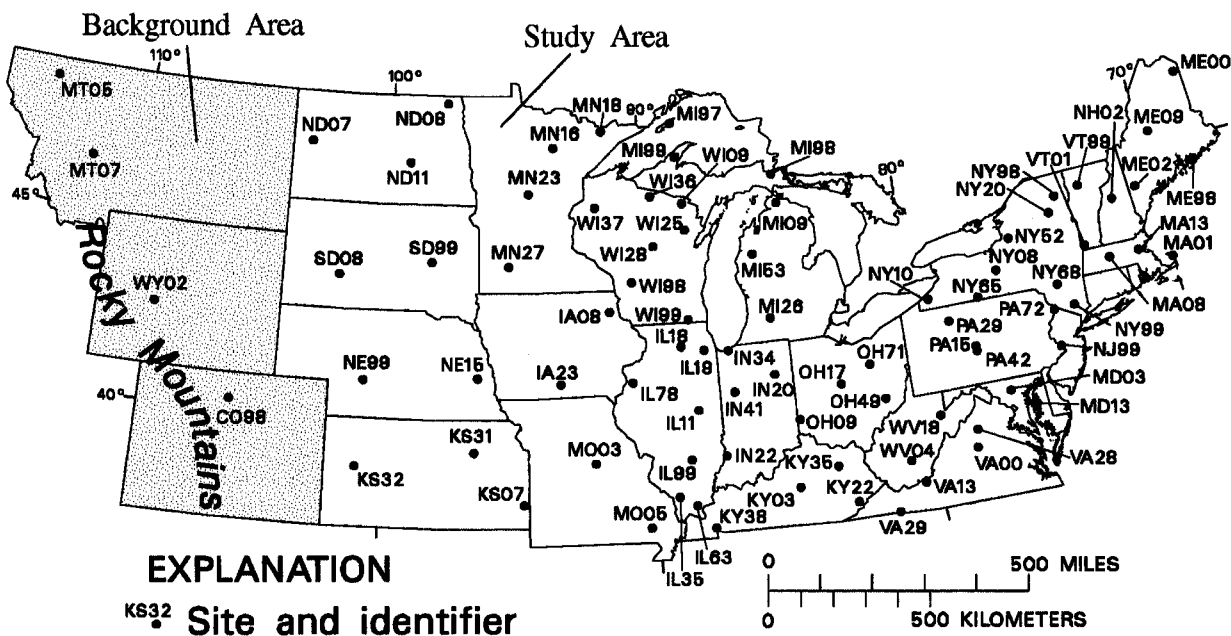§ U.S. Gelogical Survey, Raleigh, NC.

FIGURE 1. Location of study area, background area, and National Atmospheric Deposition Program/National Trends Network sampling sites. (Alaska site AK03 not shown.)

Annual herbicide
use in kilograms
per square kilometer

- No data or 0
- 0 - 2
- 3 - 5
- 6 - 10
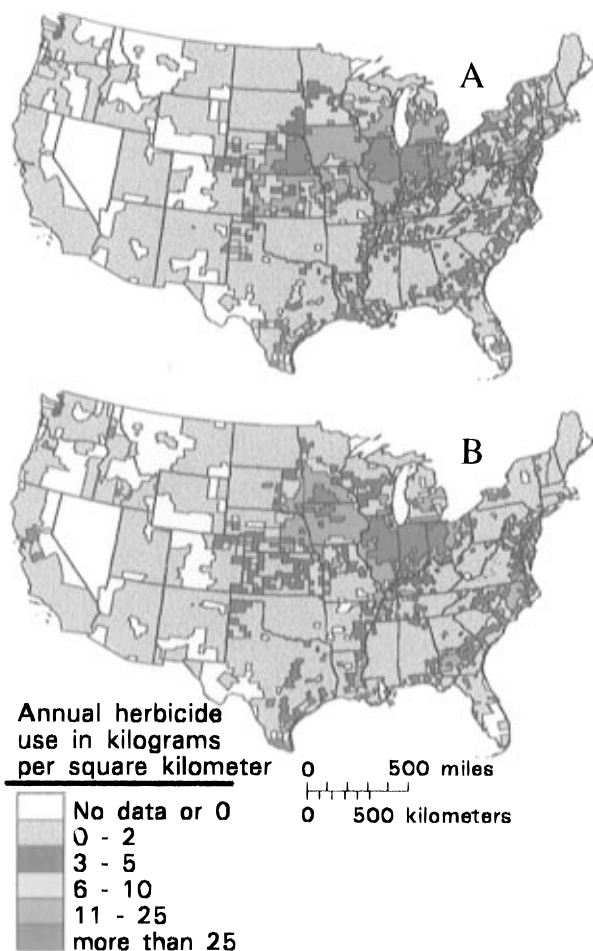- 11 - 25
- more than 25

FIGURE 2. Estimated annual use of (A) atrazine and (B) alachlor, by county, in the United States.

(Figure 1) and one site in Alaska (AK03) were sampled to provide background data on herbicides in rainfall at sites far from the study area.

Each NADP/NTN monitoring site was equipped with an Aerochem Metrics wet/dry sampler equipped with two 13-L polyethylene buckets that alternately collected wet or dry deposition (24). Rainfall was accumulated for a period of 1 week, and each Tuesday, regardless of whether rainfall occurred the previous week, a site operator removed the "wet side" bucket, sealed it with a polyethylene lid, and sent it to the Central Analytical Laboratories (CAL) of the Illinois State Water Survey in Champaign, IL for analysis. For the 86 NADP/NTN sites used in this study, a subsample consisting of 10–125 mL depending on the amount of rainfall collected was transferred to a 125-mL amber heat-cleaned glass bottle, chilled, and sent to the U.S. Geological Survey's laboratory in Lawrence, KS, for herbicide analysis. Buckets from sites where no rainfall occurred the previous week were used as system bucket blanks. No samples of dry deposition were analyzed in this study.

All samples were analyzed by enzyme-linked immuno-sorbent assay (ELISA) for both alachlor and atrazine. Samples in which herbicides were detected by ELISA and that had a sample volume of at least 60 mL were analyzed by gas chromatography/mass spectrometry (GC/MS) to determine the concentrations of selected herbicides. Samples with volumes less than 60 mL were not analyzed by GC/MS. About 10% of all negative ELISA samples also were analyzed by GC/MS. These samples were chosen randomly from all negative samples.

ELISA Analysis. Resi-Quant immunoassay kits (Immunosystems, Scarborough, ME) were used for the ELISA analyses using procedures described by Thurman and others (4). Standards were analyzed in triplicate or quadruplicate. Samples were analyzed in duplicate and the results averaged. The relative standard deviation for atrazine ranged from ±60% at 0.1 μg/L to ±15% at 1.0 μg/L, based on analysis of duplicates (25). For alachlor, the relative standard deviation ranged from ±73% at 0.15 μg/L to ±22% at 1.0 μg/L. Reporting limits were 0.1 μg/L for atrazine and 0.15 μg/L for alachlor. However, because the ELISA methods are not 100% specific for atrazine and alachlor, the ELISA results from this study are referred to as triazines and acetanilides.

GC/MS Analysis. Samples selected for GC/MS confirmation were isolated on C-18 solid-phase extraction cartridges (26) and analyzed on a Hewlett-Packard Model 5890 GC (Palo Alto, CA) and a 5970A mass selective detector (27). Eleven parent herbicides were analyzed by GC/MS analysis: alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prome-

herbicide	detections (%)	concentration (in μg/L) for indicated percentiles					
		50 (median)	75	90	95	99	100 (max)
ELISA Analysis (All Samples): $N = 5297$ Samples							
triazine	25.5	<0.10	0.10	0.24	0.42	1.3	16
acetanilides	11.8		<0.15	0.18	0.35	1.2	16
triazines and/or acetanilides	30.1	<0.10	0.12	0.29	0.48	1.3	16
GC/MS Analysis (Samples Prescreened by ELISA): $N = 2085$ Samples							
atrazine	30.2	<0.05	0.07	0.23	0.40	1.0	10.9
alachlor	19.2		<0.05	0.11	0.26	0.95	3.2
deethylatrazine	17.4		<0.05	0.09	0.15	0.39	0.75
metolachlor	13.3		<0.05	0.07	0.16	0.65	3.0
cyanazine	7.2			<0.05	0.07	0.27	2.0
deisopropylatrazine	2.6				<0.05	0.17	1.2
simazine	1.5				<0.05	0.07	1.5
metribuzin	0.7					<0.05	0.18
prometon	0.5					<0.05	0.21
propazine	0.1					<0.05	0.19

[a] Reporting limits are 0.1 μg/L for triazines and 0.15 μg/L for acetanilides by ELISA, and 0.05 μg/L for all compounds analyzed by GC/MS. Ametryn, prometryn, and terbutryn were not detected.

ton, prometryn, propazine, simazine, and terbutryn. Two metabolites of atrazine, deethylatrazine and deisopropylatrazine, were also analyzed by GC/MS.

Quality Assurance

Samples Analyzed. A total of 6230 samples were analyzed by ELISA during this study. These included 5595 samples from the study area and background area (see Figure 1), 309 blanks, and 326 other quality control samples. About 38% of the samples were also analyzed by GC/MS. About 11% of the samples analyzed were for quality control purposes. Quality assurance included experiments to determine if the NADP polyethylene collection buckets had an effect on the concentration of herbicides analyzed in this study. Both clean bucket blanks and system bucket blanks were analyzed regularly to determine if the sample buckets caused sample contamination.

Collection Container Experiments. Prior to undertaking this study, experiments were conducted to determine if the polyethylene collection buckets caused sorption, leaching, or degradation of the herbicides analyzed. Analytical results from these experiments, described elsewhere (*28*), showed no significant difference between herbicide concentrations in samples stored in the polyethylene buckets and those stored in glass containers within analytical error. These results (*28*) also confirmed that no significant sorption, degradation, or other losses of the major herbicides analyzed occurred in the buckets for periods of 3 weeks.

Blanks. Each week the Illinois State Water Survey Laboratory prepared a clean bucket blank by placing 125 mL of distilled water in contact with a clean polyethylene bucket for 24 h. Of the 62 clean bucket blanks analyzed during the study, 10% had triazine concentrations above the ELISA reporting limit of 0.1 μg/L, and the maximum concentration detected by ELISA was 0.22 μg/L. For acetanilides, 2% of the samples had concentrations above the ELISA reporting limit of 0.15 μg/L, and the maximum concentration measured was 0.32 μg/L. No herbicides were detected in 20 clean bucket blanks analyzed by GC/MS. These results indicate that little or no herbicide contamination was contributed by the sample collection buckets.

System blanks were collection buckets from NADP/NTN sites where no rainfall occurred the previous week. These buckets were leached for 24 h with 50 mL of distilled water and used to determine if contamination by herbicides had occurred anywhere during the week-long sampling process. Of the 247 system blanks analyzed during the study, 9%

contained detectable triazines and 3% contained detectable acetanilides as measured by ELISA. The percentage of system blanks with herbicide detections was essentially not different from the clean bucket blanks.

Correlation between ELISA and GC/MS Analyses. Linear regression equations, given below, were developed from the 2085 rainfall samples analyzed for atrazine and alachlor by both ELISA and GC/MS methods. The regression equations were then used to estimate the atrazine and alachlor concentration in the 3212 samples analyzed only by ELISA. Because of slight changes in methodology and differing batches of ELISA antibodies, regression results were improved slightly by developing separate equations for samples collected in 1990 and 1991.

1990:

$$\text{atrazine} = -0.01 + 0.70\ \text{ELISA};\ R^2 = 0.94; \\ \text{standard error of estimate} = 0.09\ \mu\text{g/L}. \quad (1)$$

1991:

$$\text{atrazine} = 0.00 + 0.80\ \text{ELISA};\ R^2 = 0.78; \\ \text{standard error of estimate} = 0.10\ \mu\text{g/L} \quad (2)$$

1990:

$$\text{alachlor} = 0.00 + 0.64\ \text{ELISA};\ R^2 = 0.76; \\ \text{standard error of estimate} = 0.08\ \mu\text{g/L} \quad (3)$$

1991:

$$\text{alachlor} = 0.00 + 0.84\ \text{ELISA};\ R^2 = 0.86; \\ \text{standard error of estimate} = 0.09\ \mu\text{g/L} \quad (4)$$

The slopes of the regression lines varied from 0.64 to 0.84, indicating that somewhat lower concentrations were obtained by GC/MS than by ELISA. This can be attributed, in part, to the cross reactivity of the ELISA antibodies with other triazine and acetanilide compounds. However, herbicides having significant reactivity with the ELISA methods other than atrazine and alachlor were rarely detected in this study and should have little effect on the ELISA analysis. In the following discussion, reference to atrazine and alachlor pertains to concentrations of these herbicides measured by GC/MS and concentrations estimated from ELISA results and regression eqs 1–4 for samples not analyzed by GC/MS.

Results and Discussion

Concentrations of Herbicides in Rainfall. Table 1 contains a summary of the occurrence and concentrations of herbicides
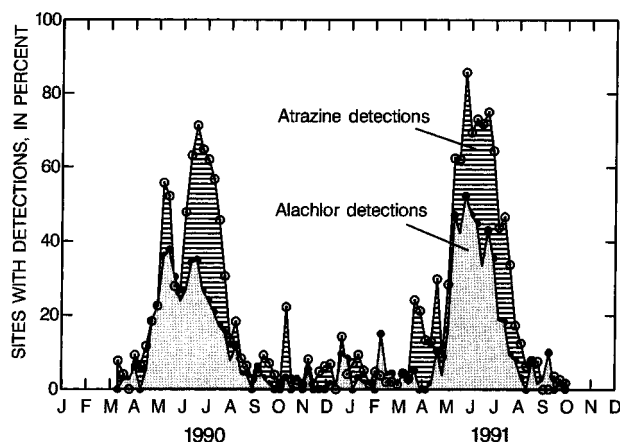
FIGURE 3. Frequency of atrazine and alachlor detections, by week, for 81 sites in the study area. (Includes detections by ELISA and GC/MS.)

detected in samples collected during the 19-month study period. Concentration data for the individual sampling sites have been published elsewhere (*28*). About one-third of the 5297 samples from the study area contained detectable concentrations of triazines and/or acetanilides. Ten of the 13 herbicides and metabolites analyzed were detected. The most frequently detected herbicides were atrazine, and alachlor which were present in 30.2% and 19.2% of the samples analyzed by GC/MS. These two herbicides also occurred in the highest concentrations. Deethylatrazine was the third most frequently detected compound in the GC/MS analyses (17.4%), followed by metolachlor (13.3%), and cyanazine (7.2%). Five other herbicides and metabolites detected in fewer than 3% of the samples. Although herbicides were detected in a significant number of samples, concentrations were relatively low. Only about 1% of the samples had herbicide concentrations exceeding 1 μg/L and only about 10% of the concentrations exceeded 0.2 μg/L. Herbicides were detected most frequently at sites in the midwestern states. However atrazine and/or alachlor were detected and confirmed by GC/MS in samples from 23 states in the study area. Atrazine was detected in low concentrations at sites remote from cropland, such as Maine and Isle Royale in northern Lake Superior. Atrazine and/or alachlor also were confirmed by GC/MS in about 4% of the 298 samples from background sites (Figure 1) in the Rocky Mountains and Alaska.

Figure 3 shows that the occurrence of atrazine and alachlor in rainfall is highly seasonal. The detection frequency of these two herbicides at the 81 sampling sites began to increase in mid-April following application of herbicides to cropland and peaked in late May or early June. During this period in both 1990 and 1991 atrazine was detected at about 70−75% of the sites sampled each week, and alachlor was detected at about 35−45% of the sites. After early July 1990, the number of sites with herbicide detections began to decrease, and by late August herbicides were detected at less than 10% of the sites. Detections remained low until the following March (1991) when the pattern was repeated.

Figure 4 shows the temporal distribution of atrazine and alachlor concentrations at four representative sites selected from all parts of the study area. The highest concentrations occurred in May and June. This temporal pattern in herbicide concentration is similar to that observed in Midwestern streams during this time of the year (*4, 5*). Concentrations were highest at sites in the Midwest cornbelt (Figure 4A,B) where herbicide use is most intense. Concentrations as high as 3 μg/L were detected in individual samples at some of these sites during mid-April through June. Maximum concentrations in the Midwest were similar to those reported by
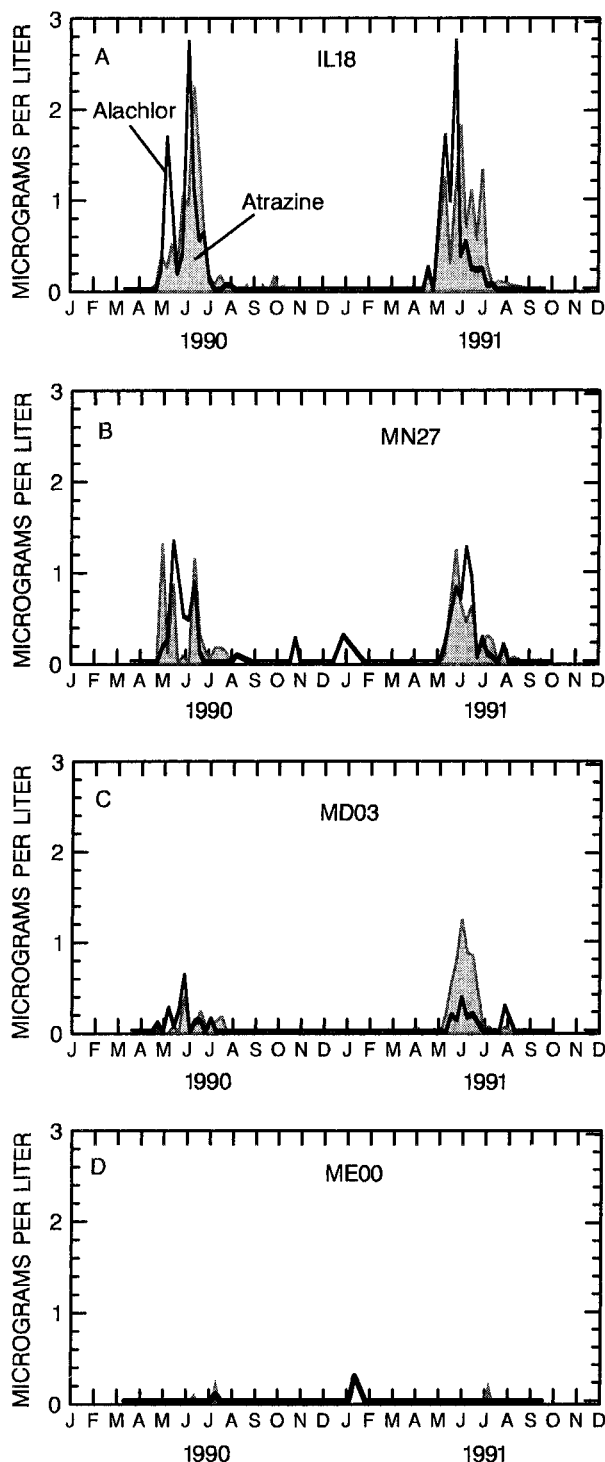

FIGURE 4. Atrazine and alachlor concentrations in precipitation, March 1990−September 1991. Some herbicide concentrations estimated from immunoassay−gas chromatography/mass spectrometry regression equations. Site locations shown in Figure 1.

Richards et al. for sites in Ohio and Indiana (*15*), but considerably less than maximum concentrations of 40 μg/L reported for bulk precipitation in Iowa (*14*). Elevated herbicide concentrations also occurred in agricultural areas along the East Coast, such as in Maryland (Figure 4C). It should be noted that several of the sampling sites are located at Agricultural Experiment Stations or near cropland. It is not known what effect, if any, the site location may have had on measured concentrations. In areas remote from the Midwest cornbelt, such as Maine (Figure 4D) and parts of Michigan, herbicide concentrations were very low and

TABLE 2. Some Physicochemical Properties at 25 °C (Except as Noted) and Soil Half-Lives of Selected Herbicides

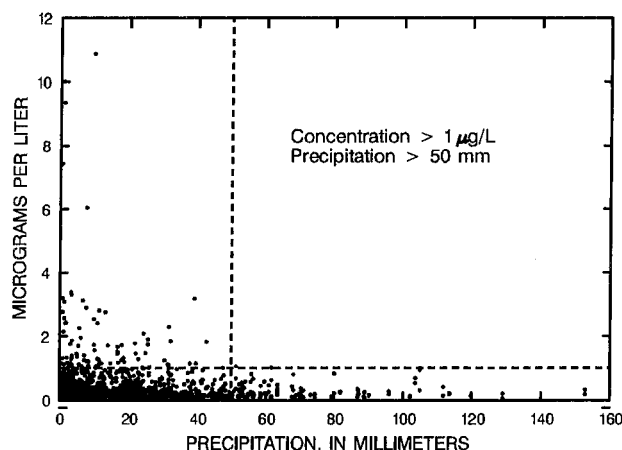| herbicide	solubility[a] (mg/L)	vapor pressure[a] (mPa)	Henry's law[a] constant $\times 10^{-3}$ (Pa·m³/mol)	soil half-life[b] (days)
alachlor	242	4.13	2.1	15
atrazine	33 (22 °C)	0.038	0.248	60
cyanazine	170	0.0002 (20 °C)	0.0003 (23 °C)	14
metolachlor	488 (22 °C)	4.17	2.44	20
simazine	3.5 (20 °C)	0.0008 (20 °C)	0.098	75

[a] From ref 30. [b] From ref 31.

FIGURE 5. Scatter plot of atrazine and alachlor concentrations versus amount of precipitation.

detections were infrequent. A few detections of alachlor and atrazine were noted during winter months at sites far from the cornbelt. These detections were at the reporting limit of the ELISA method and may be a result of low precision and sensitivity of this method, as evidenced by several detections of herbicides by ELISA methods in blanks.

In areas where the amounts of atrazine and alachlor used were similar, such as in Iowa, Illinois, and Indiana, peak concentrations of atrazine generally were lower than those of alachlor, but atrazine was usually detected for a longer period of time than alachlor. These differences in temporal patterns can, in part, be attributed to differences in the physiochemical properties and soil half-lives of these two herbicides. The vapor pressure of atrazine is about 100 times less than that of alachlor (Table 2), and the Henry's law constant, which describes the partitioning between the vapor and water phases, for atrazine is about 10 times less than for alachlor. Consequently, atrazine should volatilize from the soil into the atmosphere more slowly than alachlor. Studies by Glotfelty et al. (29) showed that the daily volatilization loss of atrazine to the atmosphere was about one-tenth that of alachlor. The slower volatilization rate of atrazine into the atmosphere should result in lower peak concentrations of atrazine in rainfall than for alachlor given similar application rates. Conversely, atrazine has a much longer soil half-life (about 60 days) than alachlor (about 15 days). As a result, atrazine should be available on the soil surface for volatilization into the atmosphere for a considerably longer period of time than alachlor. The combined effect of these two processes should be lower peak concentrations of atrazine than alachlor in rainfall near the source of application, but atrazine should be detectable in rainfall for a longer time because of its longer soil half-life. It is well-documented that atrazine is present in surface runoff to midwestern streams for a much longer time than alachlor (4–6). Other factors, such as application technique, also affect the volatilization of herbicides into the atmosphere.

Herbicide concentrations were highest during small rainfall events. As shown in Figure 5, the highest concentrations of atrazine and alachlor occurred in samples representing less

than about 20 mm of precipitation, and nearly all concentrations exceeding 1 μg/L occurred in samples representing less than 50 mm of precipitation. This pattern, which has also been reported by others (13), occurs because the first part of a precipitation event tends to scavenge most of the herbicides from the atmosphere, especially those herbicides associated with particulate material. Rainfall occurring later in the event dilutes the concentration of herbicides that were deposited during the early part of the rainfall event and contributes little to the mass of herbicides deposited.

Because of the large temporal and spatial variation in the amount of rainfall, it is difficult to make meaningful comparisons of herbicide concentrations among sites or over time on the basis of individual weekly samples. Comparisons can best be made with rainfall-weighted concentrations. Figure 6 shows the spatial distribution of rainfall-weighted concentrations of atrazine and alachlor calculated for 13-week periods from mid-April through mid-July of 1990 and 1991 when concentrations in rainfall were highest. Rainfall-weighted concentrations of 0.2–0.4 μg/L for both atrazine and alachlor were typical throughout the Midwest for this 13-week period, and weighted concentrations of 0.4–0.9 μg/L were recorded at sites in Iowa, Illinois, and Indiana. Overall, the spatial patterns of the weighted atrazine concentrations in 1990 and 1991 were similar and generally reflect the intensity of use of these herbicides (Figure 2). The same is true for alachlor. However, when the spatial pattern of weighted concentrations of atrazine are compared with those of alachlor, differences are observed (Figure 6). Atrazine was detected over a larger area and at greater distances from the Midwest cornbelt than alachlor. The higher atrazine concentration in the western part of the study area is probably the result of greater use of atrazine than alachlor in this area (see Figure 2). However, the higher atrazine concentrations north and east of the cornbelt cannot be explained by differences in herbicide use. Further, since the volatilization rate of alachlor is much greater than atrazine (29), one might expect alachlor concentrations in rain to be similar to or larger than atrazine in this area. The higher atrazine concentrations in rain suggest that atrazine is being transported over greater distances through the atmosphere than alachlor or that alachlor is less stable in the atmosphere than atrazine, or both. This is in agreement with results reported by Glotfelty et al. (18), who concluded that alachlor was far less stable than atrazine in the atmosphere in eastern Maryland.

Regional Deposition Patterns. Figure 7 shows the regional patterns of atrazine and alachlor deposited in rainfall during March through December 1990 and January through September 1991. Nearly all of the deposition of atrazine and alachlor occurred during April through July when concentrations were highest. Consequently, results shown in Figure 7 should closely represent the total annual wet deposition of atrazine and alachlor during the 2 years. As would be expected, the deposition patterns mirror the concentration patterns shown in Figure 6. Deposition rates ranged from more than 100 μg m^{-2} yr^{-1} for both atrazine and alachlor at a numerous sampling sites in the midwestern states to less than 10 μg m^{-2} yr^{-1} in the northeastern states. Deposition rates throughout most of the cornbelt ranged from 50 to more than 100 μg m^{-2} yr^{-1} for both herbicides. The maximum
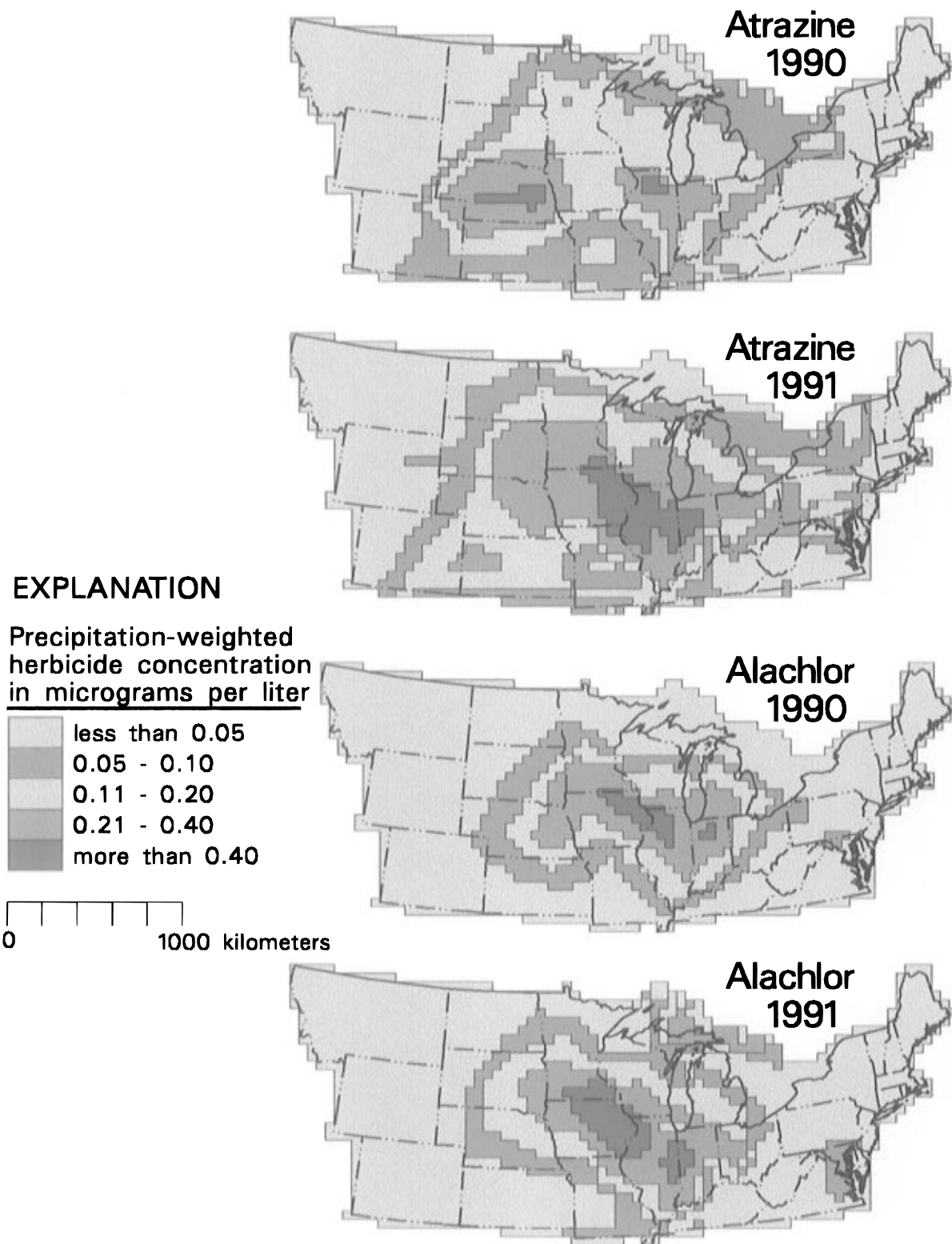
FIGURE 6. Precipitation-weighted concentrations of atrazine and alachlor during mid-April through mid-July 1990 and 1991.

deposition rates of more than 240 μg m^{-2} yr^{-1} for both atrazine and alachlor occurred at site IL18 located at the Northern Illinois Agricultural Research Center near Shabbona, IL (see Figure 1). Atrazine deposition rates of 11 to more than 60 μg m^{-2} yr^{-1} were measured in the northeastern United States and in the Great Lakes region. Very little deposition of alachlor was measured in these areas.

The total mass of herbicides deposited in rainfall over the entire study area during 1991 is estimated to be about 140 000 kg for atrazine and about 82 000 kg for alachlor (Table 3). These amounts represent about 0.6% and 0.4%, respectively,

of the annual amounts of atrazine and alachlor applied to cropland in the study area and are much smaller than volatilization losses reported in the literature. For example, Glotfelty et al. (*29*) reported volatilization losses from soil of 2.4% for atrazine and 26% for alachlor over a period of 24 days. A comparison of our results with the reported volatilization indicates that only part of the atrazine and alachlor that volatilizes into the atmosphere is actually redeposited in rainfall.

About 40% more atrazine than alachlor was measured in wet deposition even though the use of the two herbicides in
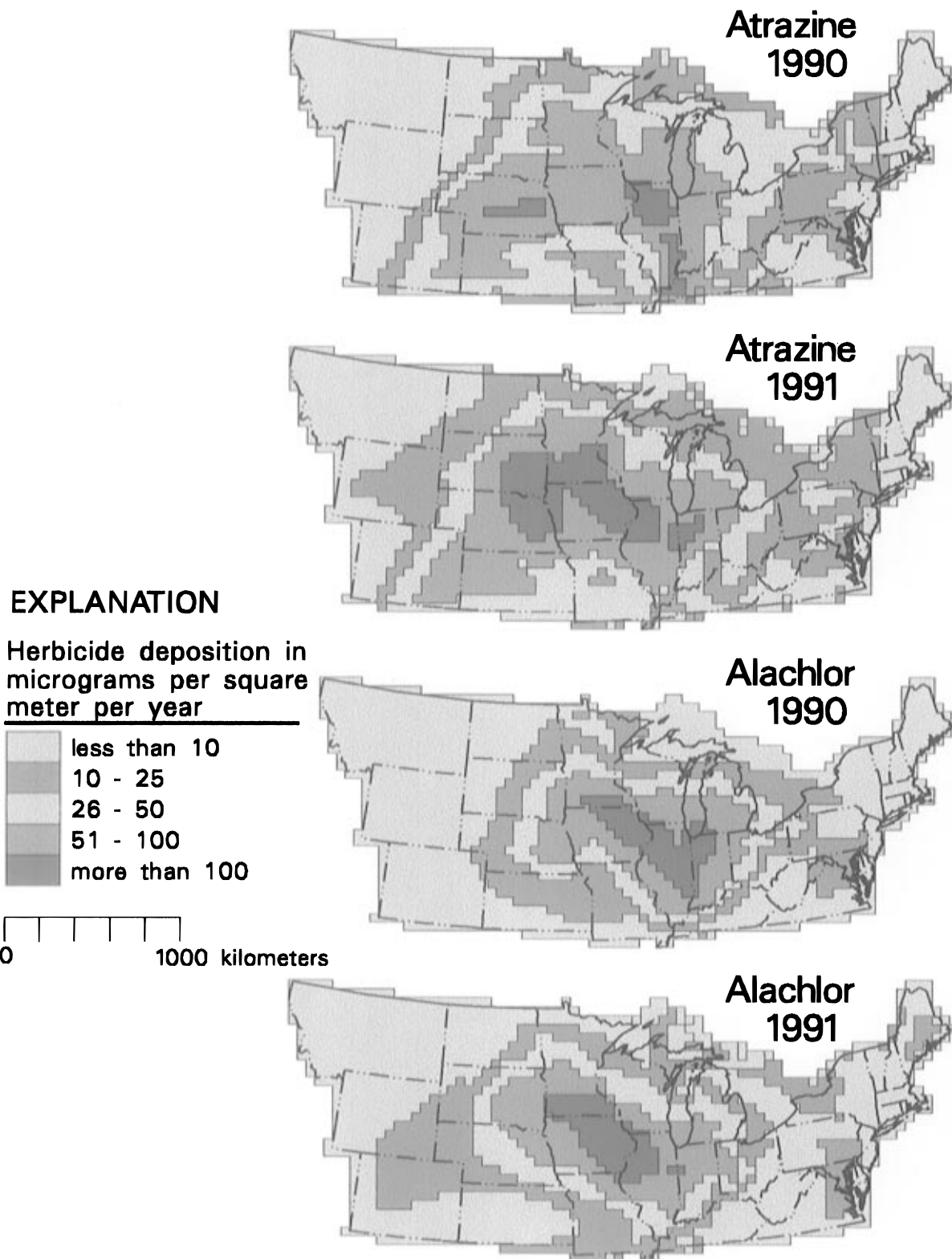
FIGURE 7. Estimated deposition of atrazine and alachlor in precipitation during March through December 1990 and January through September 1991.

the study area was similar. We hypothesize that the large difference in deposition mass measured in rainfall for these two herbicides is, in part, attributable to transport processes. Because of the differences in vapor pressure, more atrazine than alachlor would be transported on particles that are more efficiently scavenged by rainfall than are gases. Even 1 mm of rainfall can effectively cleanse the atmosphere of most particles (20). Conversely, more alachlor than atrazine would be transported in the gas phase. The smaller deposition mass of alachlor in rainfall is also consistent with the hypothesis

that alachlor is less stable in the atmosphere than atrazine. The processes for atmospheric degradation of alachlor are largely unknown. Experiments conducted by Foreman et al. (32) would seem to rule out direct photolysis. However, reaction with photochemically generated oxidants such as ozone, and hydroxyl, nitrate, or hydroperoxy radicals is plausible.

The study area (see Figure 1) included most of the Mississippi River basin above its confluence with the Ohio River and most of the Ohio River basin. The masses of atrazine

TABLE 3. Comparison of Atrazine and Alachlor Deposition in Rainfall during 1991 with Annual Usage and Annual Transport from the Upper Mississippi and Ohio River Basins in Streamflow

herbicide	annual use (kg)	wet deposition (kg)	wet deposition as % of use	transport in streamflow (kg)	transport as % of use
26-State Study Area (2 970 000 km²)					
atrazine	23 970 000	140 700	0.59		
alachlor	20 317 000	82 400	0.41		
Upper Mississippi and Ohio River Basins (2 400 000 km²)					
atrazine	18 460 000	112 000	0.61	246 000	1.3
alachlor	17 100 000	69 000	0.40	47 900	0.3

TABLE 4. Estimated Deposition of Atrazine and Alachlor on the Great Lakes Region from Rainfall in 1990 and 1991

lake	vol[a] (km³)	residence time[a] (years)	atrazine deposition				alachlor deposition			
			1990		1991		1990		1991	
			kg	μg m^{-2} yr^{-1}	kg	μg m^{-2} yr^{-1}	kg	μg m^{-2} yr^{-1}	kg	μg m^{-2} yr^{-1}
Lake Michigan	4 920	100	3 640	63	2 380	41	3 060	53	1 420	25
Lake Superior	12 230	172	2 140	26	980	12	560	7	160	2
Lake Huron	3 537	20	1 930	32	1 190	20	800	13	230	4
Lake Erie	483	2.3	990	39	920	36	1 030	40	460	18
Lake Ontario	1 636	6.5	690	35	470	24	190	10	6	<1

[a] From Table 3.1 of Eisenreich et al. (34).

and alachlor deposited in rainfall in this part of the study area during 1991 can be compared with the masses discharged by the upper Mississippi and Ohio Rivers in streamflow. Battaglin et al. (33) estimated that 246 000 kg of atrazine and 47 900 kg of alachlor were discharged from this area in streamflow during April 1991−March 1992 (Table 3). Most of this transport occurred during April−September 1991. In comparison, we estimate that about 112 000 kg of atrazine and 69 000 kg of alachlor were deposited in rainfall on this area during January−September 1991. These results show that the amount of atrazine deposited in rainfall on the basin was less than one-half the amount transported out of the basin in streamflow. Conversely, about one-third more alachlor was re-deposited in the Mississippi River basin through rainfall than was transported out of the basin in streamflow. An explanation for these results lies in the short soil half-life and higher volatility of alachlor relative to atrazine. Because alachlor has a much shorter soil half-life than atrazine, it degrades more rapidly on the soil and a much smaller fraction of the alachlor applied to cropland is available for leaching into streams. However, until degradation of alachlor occurs, it can volatilize to the atmosphere as much as 8 times faster than atrazine (29) and become available for re-deposition in rainfall. Consequently, the combination of these two effects results in a larger mass of alachlor in wet deposition than in surface runoff, the opposite of atrazine.

Deposition on the Great Lakes. One of the sampling sites (MI97) is located on Isle Royale in the northwest part of Lake Superior near the border of Canada and far from the U.S. cornbelt. Atrazine, presumably from the cornbelt, was detected and verified by GC/MS analysis in samples from several rain events at this site during June 1990. These data prompted the collection of water samples from Lake Superior and four small lakes on Isle Royale in late September 1990. The atrazine concentration in these samples, determined by isotope dilution methods, was 6.5 ng/L for Lake Superior and ranged from 2.5 to 20 ng/L for the four lakes. The main source of atrazine to Lake Superior and the only source for Isle Royale is atmospheric deposition. Using deposition rates determined from our study (see Figure 7), the annual wet deposition of atrazine and alachlor from precipitation on each of the Great Lakes was estimated. The annual wet deposition of atrazine in 1990 and 1991 ranged from more than 3600 kg in Lake Michigan to less than 500 kg in Lake Ontario (Table 4). Annual average wet deposition rates for the 2 years ranged from about 12 μg m^{-2} yr^{-1} in Lake Superior to about 63 μg m^{-2} yr^{-1} in

Lake Michigan. The wet deposition of alachlor was less than atrazine, except for Lake Erie in 1990.

Schottler and Eisenreich (35) recently reported atrazine concentrations in the Great Lakes ranging from about 3 ng/L in Lake Superior to 110 ng/L in Lake Erie. They estimated the mass of atrazine stored in the water column of Lake Superior to be about 36 000 kg, which is 17−37 times larger than the estimated mass contributed to the lake by wet deposition in 1990 and 1991 and hundreds of times larger than annual atrazine inputs to the lake from surface runoff (36). Additional input of atrazine to Lake Superior occurs via dry deposition and air−water exchange. Nevertheless, these results suggest that atrazine is slowly accumulating in Lake Superior and that degradation of atrazine in the water column of the lake is very slow. Schottler (36) has estimated the loss of atrazine from the lake by internal degradation to be about 1% per year. Accumulation of atrazine in Lake Superior will continue until the annual internal losses of atrazine equal the annual inputs.

Herbicide Metabolites in Rainfall. The triazine metabolites—deethylatrazine (DEA) and deisopropylatrazine (DIA)—were detected in 17.4% and 2.6%, respectively, of the samples analyzed by GC/MS (Table 1). DEA was present in more than half (58%) of the samples that contained atrazine and was the third most frequently detected compound. Trace concentrations of DEA were detected in 12 samples that contained no detectable atrazine. The ratio of DEA to atrazine concentrations, called the DAR, has been used to investigate surface water−groundwater interactions (4). Low DAR values, median < 0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The median DAR value calculated for the 352 rainfall samples that contained both atrazine and DEA was 0.5. All of these DAR values are from rainfall samples collected during May−July of 1990 and 1991 when the median DAR values for rivers in this area were <0.1 (4). Thus, considerably more DEA is present in rainfall relative to atrazine than in streams draining cornbelt states. There are several possible explanations for this observation. One hypothesis is that DEA evaporates from the soil into the atmosphere faster than atrazine, resulting in a higher DAR value in rainfall. This hypothesis cannot be fully explored however because we could find no data in the literature on the vapor pressure or Henry's law constant for DEA. The aqueous solubilities are 33 mg/L for atrazine and 3200 mg/L

for DEA (*37*). Unless the vapor pressure of DEA is more than 100 times larger than for atrazine, the Henry's law constant for DEA should be similar to or smaller than that for atrazine. Thus, it seems unlikely that DEA would volatilize from soil at a significantly faster rate than atrazine.

A second hypothesis for the high DAR value in rainfall is that atrazine may be transformed to deethylatrazine in the atmosphere by photochemical processes. Studies of photocatalytic degradation and ozone oxidation of atrazine have shown deethylatrazine to be a degradation product of atrazine. For example, Pelizzetti et al. (*38*) proposed that atrazine degrades through an atrazine amide to DEA and then forms a didealklyated product. Kearney et al. (*39*) showed that ozone treatment of herbicide waste yielded both the atrazine amide and deethylatrazine. Thus, it is possible that the high DAR values of 0.5 in rainfall reflect the photocatalyzed degradation of atrazine in the atmosphere. If we presume that the DAR values for evaporating water are similar to surface runoff (i.e., 0.1) and that the DAR for rainfall is 0.5, then there is about a 25−30% conversion of atrazine to deethylatrazine during its residence time in the atmosphere. More research is needed to better understand the processes and pathways for atmospheric degradation of atrazine and other pesticides.

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