

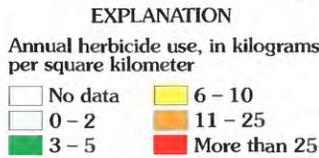
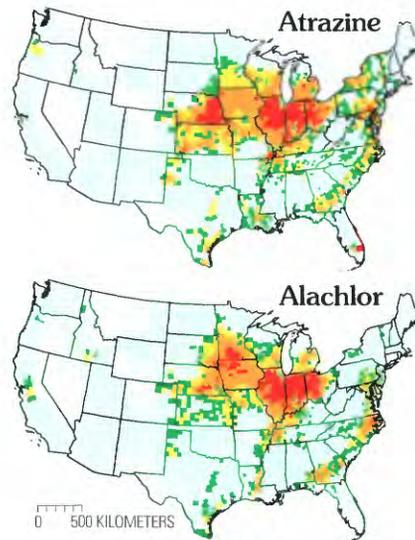
Herbicides in Rainfall Across the Midwestern and Northeastern United States, 1990–91

FS-181-97



Introduction

Current (1998) agricultural practices in the United States require extensive use of herbicides for producing the Nation's three principal row crops—corn, soybeans, and grain sorghum. Approximately, 140 of the 218 million kg (kilograms) of herbicides used annually in the United States are applied to cropland in the Midwest, principally in the upper Mississippi River drainage basin (see maps at right). Atrazine and alachlor were the two most extensively used herbicides in the Nation in 1990–91 (Aspelin and others, 1992). Maps of use rates for these two herbicides show that the largest rates, as indicated by the red and orange colors, occurred in parts of Illinois, Indiana, Iowa, Ohio, Minnesota, and Nebraska, an area often referred to as the "Corn Belt." As a consequence, this region is a major source for herbicide transport into surface and ground water and into the atmosphere. Because some herbicides are relatively water soluble, a small percentage of the amounts applied annually may be transported into surface and ground water. Herbicides can be transported into the atmosphere by volatilization and entrainment on dust particles and then dispersed by air currents for possible re-deposition on watersheds at considerable distances from their application.



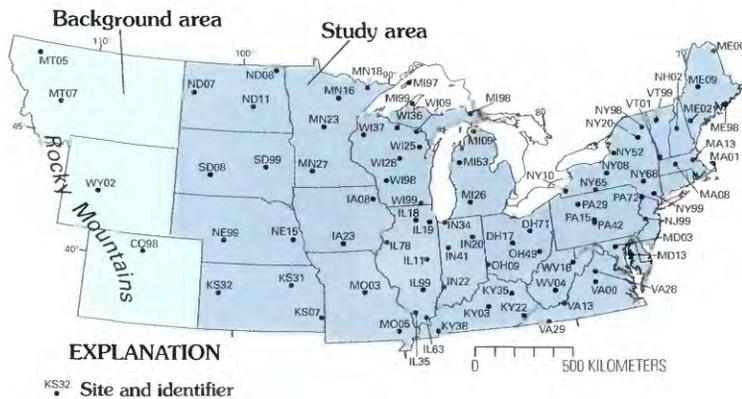
The herbicides found in rainfall most frequently and in the largest concentrations were atrazine and alachlor. Although previous studies had shown that herbicides occurred in rainfall in the Midwest, little was known about depositional patterns on a regional scale or about the amount of herbicide deposition in relation to usage. To assess the occurrence and deposition of selected herbicides and associated degradation products in rainfall for a large part of the

United States, weekly samples of rainfall were collected from a network of 81 sites in 23 States (see study area map below) from March 1990 through September 1991. Samples from four sites in high-elevation areas in the Rocky Mountains and one site in Alaska (not shown) were also collected to provide background information. The 86 sites are part of the National Atmospheric Deposition Program/National Trends Network, which comprises a network of about 200 sites nationwide.

During the 19-month data-collection period, 6,230 samples were analyzed for atrazine and alachlor using an immunoassay technique. A subset of 2,085 samples was analyzed for 11 herbicides and 2 triazine degradation products (shown in the table on the next page) using gas chromatography/mass spectrometry (GC/MS) methods. About 11 percent of the samples analyzed were for quality-control purposes. Statistical relations between the two techniques were developed to estimate concentrations of atrazine and alachlor for 3,212 samples not analyzed by GC/MS. Reporting limits were 0.1 $\mu\text{g/L}$ (microgram per liter) for atrazine and 0.15 $\mu\text{g/L}$ for alachlor using the immunoassay techniques. However, because the immunoassay techniques were not 100 percent specific for atrazine and alachlor, the immunoassay results for these compounds are referred to as triazines and acetanilides, respectively. Reporting limits were 0.05 $\mu\text{g/L}$ for the 11 herbicides and 2 triazine degradation products using GC/MS.

Results

A summary of the herbicides and associated degradation products detected in rainfall from the 81 sampling sites in the Midwestern and Northeastern regions of the United States during the 19-month



EXPLANATION

Site and identifier

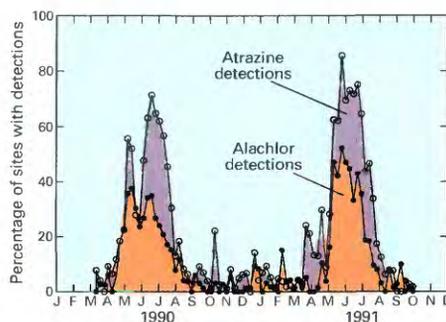
Herbicide or degradation	Percent detections	Concentration, in rainfall samples, in micrograms per liter for indicated product percentiles				
		50	75	90	95	99
Immunoassay results of 5,297 samples						
Triazines	25.5	<0.10	0.10	0.24	0.42	1.3
Acetanilides	11.8		<.15	.18	.35	1.2
Triazines and (or) acetanilides	30.1	<.10	.12	.29	.48	1.3
GC/MS results of 2,085 samples screened by immunoassay						
Atrazine	30.2	<.05	.07	.23	.40	1.0
Alachlor	19.2		<.05	.11	.26	.95
Deethylatrazine	17.4		<.05	.09	.15	.39
Metolachlor	13.3		<.05	.07	.16	.65
Cyanazine	7.2			<.05	.07	.27
Deisopropyl-atrazine	2.6				<.05	.17
Simazine	1.5				<.05	.07
Metribuzin	.7					<.05
Prometon	.5					<.05
Propazine	.1					<.05

Reporting limits were 0.1 microgram per liter for triazines and 0.15 microgram per liter for acetanilides by immunoassay, and 0.05 microgram per liter for herbicide compounds analyzed by gas chromatography/mass spectrometry. Ametryn, prometryn, and terbutryn were not detected.

study is shown in the table. About one-third of the 5,297 samples from the study area were analyzed using immunoassay techniques and contained detectable concentrations of triazine and (or) acetanilide herbicides. Ten of the 13 herbicides and associated herbicide degradation products were detected by GC/MS techniques. The most frequently detected herbicides in samples analyzed by GC/MS were atrazine (30.2 percent) and alachlor (19.2 percent). These two herbicides also occurred in the largest concentrations. The atrazine degradation product, deethylatrazine, was the third-most frequently detected herbicide compound (17.4 percent) using GC/MS followed by metolachlor (13.3 percent) and cyanazine (7.2 percent). The frequency of detection of the remaining herbicides was less than 3 percent. Ametryn, prometryn, and terbutryn were not detected in any of the samples. Although several herbicides and associated degradation products were frequently detected in rainfall, concentrations were relatively small. Only about 1 percent of the samples had herbicide or associated degradation product concentrations greater than 1.0 µg/L, and only about 10 percent of the concentrations were greater than 0.2 µg/L. Herbicides and associated degradation products were more frequently detected and occurred in the larger concentrations at sites in the

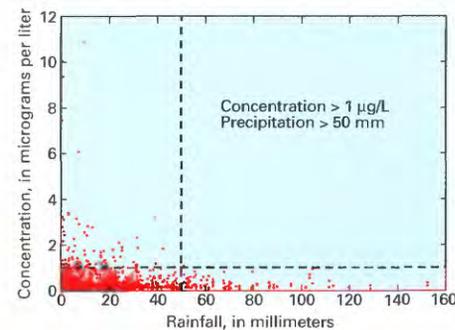
Midwestern States than in the Northeastern States. Concentrations of atrazine and (or) alachlor were detected and confirmed by GC/MS in samples from each of the 23 States in the study area. Atrazine concentrations were small at sites remote from cropland, such as in Maine. Atrazine and (or) alachlor also were confirmed by GC/MS in about 4 percent of the 298 samples from background sites (see map of study area) in the Rocky Mountains and Alaska.

The occurrence of atrazine and alachlor in rainfall varied seasonally, as shown in the graph below. For 1990, the detection frequency for these herbicides at the 81 sites began to increase in mid-April following application of the two 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 to 75 percent of the sites sampled each week, and alachlor was detected at about 35 to 45 percent of



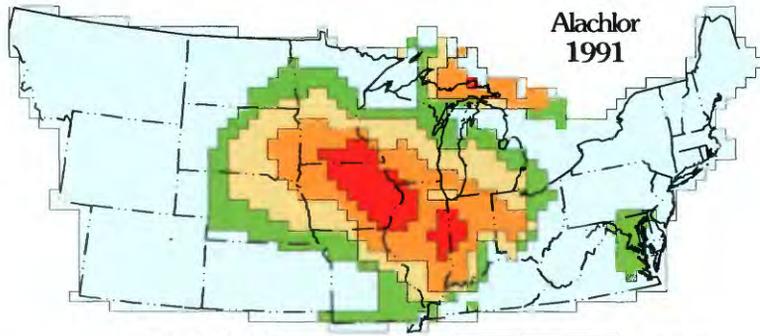
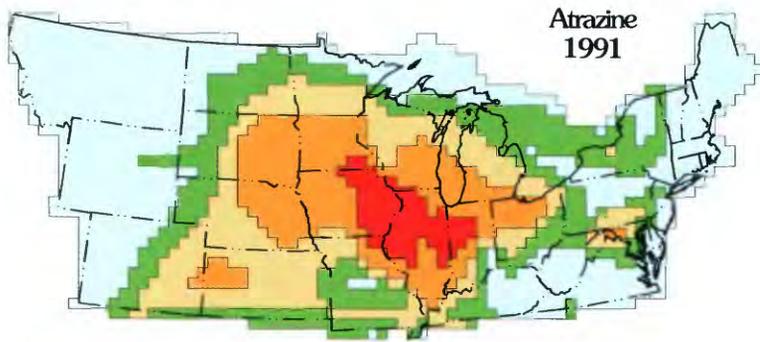
the sites. After early July 1990, the frequency of herbicide detection began to decrease; fewer than 10 percent of the sites had detectable concentrations by late August. The frequency of detections remained small until March 1991 when the cycle was repeated. The larger number of sites with atrazine detections and the longer period of atrazine detections compared to alachlor probably reflect the fact that atrazine is more extensively used than alachlor across the study area. Atrazine is also less volatile and persists longer in the soil than alachlor, thus making atrazine available for volatilizing into the air over a longer period of time.

Concentrations of atrazine and alachlor were smaller during periods of high rainfall and larger during periods of low rainfall, as shown in the graph below. Most concentrations larger than 1 µg/L occurred in samples representing less than 50 mm (millimeters) of rainfall, and the largest concentrations occurred in samples representing less than 20 mm of rainfall. This pattern occurs because



the initial rainfall tends to scavenge most of the herbicides from the atmosphere, especially those herbicides associated with particulate matter. Rainfall occurring later in the event dilutes the concentration of herbicides that were deposited early in the event and contributes little to the overall mass of herbicides deposited.

The maps on the next page show the spatial distributions of rainfall-weighted average concentrations of atrazine and alachlor for 13-week period from mid-April to mid-July 1991, when concentrations in rainfall were the largest. Average concentrations of 0.2 to 0.4 µg/L for both atrazine and alachlor were typical throughout the Midwest during this period, with concentrations of 0.4 to 0.9 µg/L



EXPLANATION

Rainfall-weighted herbicide concentration, in micrograms per liter

Light blue	Less than 0.05	Orange	0.21 – 0.40
Green	0.05 – 0.10	Red	More than 0.40
Yellow	0.11 – 0.20		

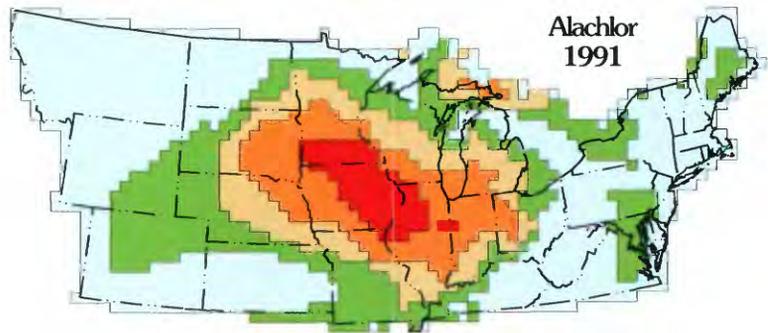
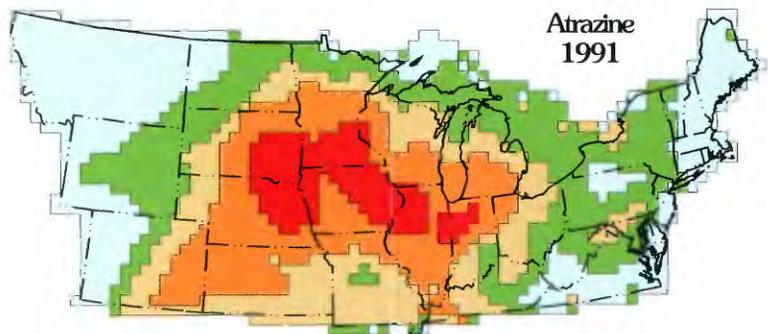
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recorded at sites in Iowa, Illinois, and Indiana. Overall, the spatial pattern of atrazine and alachlor concentrations reflect the intensity of use of these two herbicides. However, when the spatial distributions of atrazine and alachlor concentrations are compared, differences are apparent. Atrazine was detected over a larger area and at greater distances from the Midwest Corn Belt than alachlor. Differences in the western part of the study area probably can be attributed to greater atrazine use than alachlor use in this area (see usage maps on first page of this fact sheet). Differences north and east of the Corn Belt suggest that atrazine was transported over greater distances through the atmosphere than alachlor, or that alachlor is less stable in the atmosphere than atrazine, or both.

The regional patterns of atrazine and alachlor deposition in rainfall for January through September are shown in the maps at right. Because nearly all of the deposition of atrazine and alachlor occurred from April through July when concentrations were largest, the deposition during this period closely represents the total wet deposition for the year. Deposition rates ranged from more than 100 ($\mu\text{g}/\text{m}^2/\text{yr}$) (micrograms per

square meter per year) for both atrazine and alachlor at numerous sampling sites in the Midwestern States to less than 10 ($\mu\text{g}/\text{m}^2/\text{yr}$) in the Northeastern States. Deposition rates throughout most of the Corn Belt ranged from 50 to more than 100 ($\mu\text{g}/\text{m}^2/\text{yr}$) for both herbicides. The total mass of herbicides deposited by rainfall over the entire study area during 1991 is estimated to be about 140,000 kg for atrazine and 82,000 kg for alachlor. These amounts represent about 0.6 and 0.4 percent, respectively, of the annual amounts of atrazine and alachlor applied to cropland in the study area.

The atrazine degradation products, deethylatrazine (DEA) and deisopropylatrazine (DIA) were also detected in rainfall samples analyzed by GC/MS as shown in the summary table on the previous page. DEA was present in more than one-half (58 percent) of the samples that also contained atrazine. The ratio of concentrations of DEA to atrazine has been used to examine the interaction of surface and ground water. Low ratio values, median less than 0.1, occur in streams during runoff shortly following application of atrazine to cropland. Larger values of the ratio, median about 0.4, occur later in the year after



EXPLANATION

Herbicide deposition, in micrograms per square meter per year

Light blue	Less than 10	Orange	51 – 100
Green	10 – 25	Red	More than 100
Yellow	26 – 50		

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considerable degradation of atrazine has occurred in the soil. The median value of the DEA-to-atrazine ratio was 0.5 for the 352 rainfall samples that contained both detectable DEA and atrazine concentrations. A possible explanation for the large DEA-to-atrazine ratio in rainfall samples is that a significant amount of the atrazine in the atmosphere is transformed into DEA by photochemical processes.

Implications

The volatilization, atmospheric transport, and deposition of herbicides and associated degradation products have important implications both for areas where herbicide usage is high and for areas where herbicide usage is low. In the Midwest, where herbicide usage is high, the redeposition of herbicides from rainfall contributes to the problem of large concentrations and transport of herbicides in streams. For example, during 1991 an estimated 246,000 kg of atrazine were transported out of the upper Mississippi and Ohio River Basins in streamflow. A small, but undetermined, amount of this was contributed by the 112,000 kg of atrazine deposited on these basins in rainfall during 1991. Also, a small but undetermined amount of the 47,000 kg of alachlor transported from these basins in streamflow during 1991 was contributed by the 69,000 kg of alachlor deposited in rainfall.

The deposition of herbicides in areas where herbicide usage is low, such as the Great Lakes, presents a different but potentially serious, long-term problem. For example, one of the sampling sites was located on an island in the northwest part of Lake Superior, far from the Corn Belt. The dominant source of atrazine to Lake Superior and the only source on the island site is atmospheric deposition. Using data from this study, the estimated annual wet deposition rate for the period of the study on Lake Superior was about 12 ($\mu\text{g}/\text{m}^2$)/yr. Schottler and Eisenreich (1994) estimated the atrazine concentration in Lake Superior to be about 0.003 $\mu\text{g}/\text{L}$. The estimated mass of atrazine stored in the water column of Lake Superior was about 36,000 kg, which was anywhere from 17 to 37 times larger than the estimated mass contributed by rainfall during 1990–91 and hundreds of times larger than

surface-water inputs to the lake (Schottler and Eisenreich, 1997). Although there may be inputs of atrazine to Lake Superior from other sources, such as dry deposition and air-water exchange, the results strongly suggest that atrazine in rainfall is slowly accumulating in the lake and that degradation of atrazine in the water column is very slow (about 1 percent per year). Thus, atrazine is likely to continue to accumulate in Lake Superior until the annual internal losses of atrazine equal the annual inputs.

This Fact Sheet is based largely on information contained in the following publications and references cited therein:

Aspelin, A.L., Grube, A.H., and Torla, R., 1992, Pesticide industry sales and usage—1990 and 1991 market estimates: Washington, D.C.. U.S. Environmental Protection Agency, Office of Pesticide Programs, 37 p.

Goolsby, D.A., Scribner, E.A., Thurman, E.M., Pomes, M.L., and Meyer, M.T., 1995, Data on selected herbicides and two triazine metabolites in precipitation of the Midwestern and Northeastern United States, 1990–91: U.S. Geological Survey Open-File Report 95–469, 341 p.

Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M.T., and Battaglin, W.A., 1997, Herbicides and their metabolites in rainfall—Origin, transport, and deposition patterns across the Midwestern and Northeastern United States, 1990–1991: *Environmental Science & Technology*, v. 31, no. 5, p. 1325–1333.

—John K. Stamer, Donald A. Goolsby, and E. Michael Thurman

Additional References

Schottler, S.P., and Eisenreich, S.J., 1994, Herbicides in the Great Lakes: *Environmental Science & Technology*, v. 28, no. 12, p. 2228–2232.

—1997, Mass balance model to quantify atrazine sources, transformation rates, and trends in the Great Lakes: *Environmental Science & Technology*, v. 31, no. 9, p. 2616–2625.

For additional information and selected reading about the Midcontinent Herbicide Project, write to:

U.S. Geological Survey
Mail Stop 415, Box 25046
Building 53, Wing F–200
Denver Federal Center
Lakewood, CO 80225

Additional information on the Midcontinent Herbicide Project and other USGS programs can be found by accessing "<http://www.rcolka.cr.usgs.gov/midconherb/index.html>" on the World Wide Web.

Factors for converting metric units to inch/pound units of measurement:

To convert from	To	Multiply by
millimeter (mm)	inch	0.03937
kilogram (kg)	pound	2.205
microgram per liter ($\mu\text{g}/\text{L}$)	part per billion	1.0
kilogram per square kilometer (kg/km^2)	pound per square mile	5.711
microgram per square meter per year [$(\mu\text{g}/\text{m}^2)/\text{yr}$]	ounce per acre per year	1.427×10^5