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In many Midwestern rivers, elevated concentrations of herbicides occur during runoff events for 1−3 months following application. The highest or "peak" herbicide concentration often occurs during one of these runoff events. Herbicide concentrations in rivers are affected by a number of factors, including herbicide use patterns within the associated basin. Changing agricultural practices, reductions in recommended and permitted herbicide applications, shifts to new herbicides, and greater environmental awareness in the agricultural community have resulted in changes to herbicide use patterns. In the Midwestern United States, alachlor use was much larger in 1989 than in 1995, while acetochlor was not used in 1989, and commonly used in 1995. Use of atrazine, cyanazine, and metolachlor was about the same in 1989 and 1995. Herbicide concentrations were measured in samples from 53 Midwestern rivers during the first major runoff event that occurred after herbicide application (postapplication) in 1989, 1990, 1994, and 1995. The median concentrations of atrazine, alachlor, cyanazine, metribuzin, metolachlor, propazine, and simazine all were significantly higher in 1989/90 than in 1994/95. The median acetochlor concentration was higher in 1995 than in 1994. Estimated daily yields for all herbicides and degradation products measured, with the exception of acetochlor, were higher in 1989/90 than in 1994/95. The differences in concentration and yield do not always parallel changes in herbicide use, suggesting that other changes in herbicide or crop management are affecting concentrations in Midwestern rivers during runoff events.

Introduction

A review of studies of long-term trends in pesticide occurrence in surface water is given by Larson et al. (*1*). Many of these studies were targeted at identifying trends in organochlorine and organophosphorus insecticide concentrations. Larson et al. (*1*) indicated that the lack of consistent and detailed data on herbicide concentrations in surface waters of the United States has limited researchers' ability to determine if long-term changes in herbicide concentrations are occurring. A study (*2*) of Lake Erie tributaries from 1983 to 1991 showed no significant trends in monthly mean concentrations of alachlor, atrazine, or metolachlor over the 9-year period. Annual mean atrazine concentrations for the Mississippi River at Vicksburg for 1975−1989 were computed from data collected by Ciba-Geigy (*3*). Over the 14-year period, no significant trend was observed, but there was some indication that annual mean concentrations decreased recently from the highest levels, measured in the early 1980s (*4*). More recent data indicate that between 1991 and 1997, estimates of annual atrazine, cyanazine, and metolachlor flux to the Gulf of Mexico stayed about the same, whereas estimates of annual alachlor flux decreased, and estimates of acetochlor flux increased (*5*).

A few studies have investigated changes in herbicide concentration in groundwater. Kolpin et al. (*6*) studied temporal trends in herbicide concentration from selected wells in Iowa. Results indicate that between 1982 and 1995, the concentration of atrazine in Iowa groundwater showed a significant downward trend, concentration of metolachlor showed a significant upward trend, and concentrations of alachlor and cyanazine showed no discernible trend. The changes in concentration were only marginally related to changes in herbicide use. In Iowa, between 1982 and 1995, the use of alachlor decreased the most (more than 60%), atrazine use decreased by 12%, cyanazine use decreased by 26%, and metolachlor use increased by 54%. A study of Wisconsin groundwater also identified a downward trend in atrazine concentration and associated that trend with a downward trend in atrazine use (*7*).

The objective of this study was to determine if reductions that were expected in the use of atrazine and alachlor between 1989 and 1995 would result in a reduction in atrazine and alachlor concentrations or daily yields during postapplication runoff events in Midwestern rivers. Secondary objectives included determining if changes since 1989/90 in the concentrations or daily yields of other herbicides have occurred and determining something about the occurrence of acetochlor, a new herbicide, as well as alachlor ethanesulfonic acid (ESA) and cyanazine amide, herbicide degradates not previously looked for in Midwestern rivers. The data collected for use in this study consist of only one postapplication runoff event sample per site per year. This is clearly less than ideal, but the large number of sites (53) still make this data set adequate to determine if changes in herbicide concentrations or daily yields during postapplication runoff events in Midwestern rivers have occurred between 1989 and 1995. The data set is not adequate to determine if changes in annual mean concentrations or annual yields have occurred.

Experimental Section

Study Area and Sampling Strategy. The study area consists of 53 Midwestern streams (Figure 1). These streams were originally selected to represent a stratified random sample of streams in 10 Midwestern States (*8*, *9*). Water samples were collected from the streams numerous times during the period 1989−95. Samples were collected three times in 1989: in spring, before herbicide application (preapplication), in early summer, after herbicide application and during a major, ideally the first, postapplication runoff event (postapplication), and in fall during base-flow conditions (low-flow) (*8*−*11*). In 1990, samples were collected during pre- and postapplication periods. In 1994 and 1995, samples were again collected during postapplication periods (*12*). Only the postapplication samples from each year of sampling were used in this analysis. The intent of the postapplication samples was to capture the peak preemergence herbicide concentrations expected during the year (*1*, *9*, *13*, *14*). Herbicide concentration data collected using automatic samplers in 1990 and 1991 (*15*) suggest that the peak herbicide concentrations often coincide with the first significant

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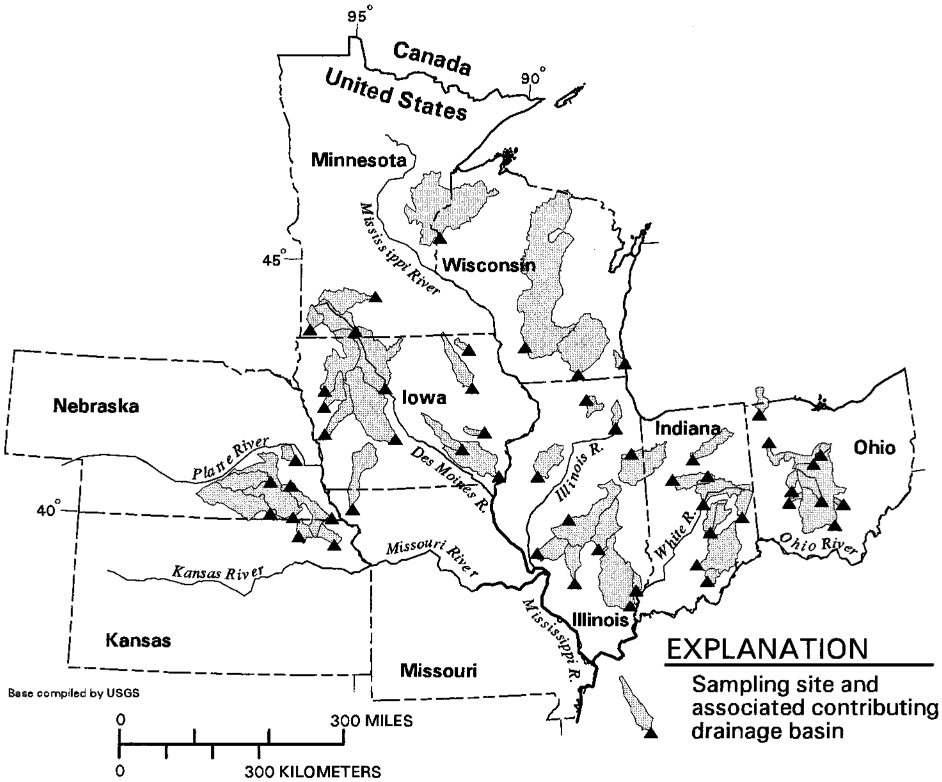


FIGURE 1. Location of sampled sites and associated drainage basins.

streamflow rise (runoff-event) after herbicide application. However, this same data set demonstrates that peak herbicide concentrations are highly variable and, on some streams, can occur later in the summer or during lower flow conditions than were sampled.

Sampling and Analytical Procedures. All samples were collected in glass or Teflon sampling bottles by U.S. Geological Survey personnel using a depth-integrating sampler from three or more verticals. The samples were filtered through glass fiber filters (0.7- or 1-μm nominal pore size) at the time of collection to remove suspended materials. Streamflow, specific conductance, pH, and temperature of the water were measured at the time of sample collection (*10*, *12*, *16*). All samples were analyzed for 11 herbicides and 2 herbicide degradation products by gas chromatography/mass spectrometry (*17*). All samples from 1994 and 95 were also analyzed for one additional herbicide (acetochlor) and two additional herbicide degradation products (alachlor ESA and cyanazine amide) (*18, 19*). A list of analytes is given in Table 1. Complete details of the study methods, analytical procedures, and the raw analytical results are presented by Scribner et al. (*12*, *16*).

Results and Discussion

Changes in Herbicide Use. Since 1989, changes in agricultural practices, reductions in recommended and permitted herbicide applications, shifts to new herbicides, and greater environmental awareness in the agricultural community have resulted in changes to herbicide use patterns. In 1990 and again in 1992, the producer of atrazine voluntarily reduced the maximum labeled application rates (*20*). Most noncropland uses of atrazine were not permitted after the 1992 label change. Ribaudo and Bouzaher report (*21*) that the average rate for atrazine on corn declined from 1.46 pounds per acre (lb/acre) in 1985 to 1.09 lb/acre in 1993, a decrease of 25%.

Estimates of the use of five herbicides and planted corn and soybean acreages in eight Midwestern states (IA, IL, IN, KS, MN, NE, OH, and WI) for 1989 through 1996, are shown in Figure 2 (*22*−*24*). Herbicide use estimates and crop acreages from Michigan and Missouri are omitted from these totals even though parts of these states fall within the Corn Belt; this is due to the paucity of sampling sites in these states. Dramatic changes in use are shown for acetochlor and alachlor, but little change is observed for the other three herbicides or for planted corn and soybean acreages. In 1995, approximated 40 different herbicides were reported to have significant use on either corn or soybeans in the major producing states (*24*). Use of the 12 herbicides studied equaled about 80% of the approximately 75 000 metric tons (MT) of active ingredient applied to corn, but only 20% of the approximately 25 000 metric tons of herbicide active ingredient applied to soybean (*24*).

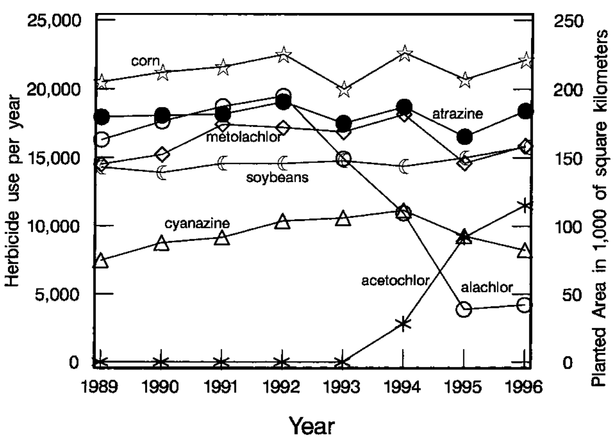
Year-to-year variability in planted acreages and subsequent herbicide use can make comparisons of change between individual years misleading. The use of atrazine and metolachlor clearly follow the pattern of corn acreage. A comparison of averaged 1989−90 herbicide use with averaged 1994−95 herbicide use is made here so that these changes can be compared with the changes in averaged herbicide concentrations and yields later in the report. The intent of this averaging is to account to some degree for the natural year-to-year variability in herbicide use, concentration, and yield. In the eight Midwestern states, alachlor use was 56% less in 1994/95 (7400 MT) than that in 1989/90 (17 000 MT), atrazine use was 2% less in 1994/95 (17 600 MT) than that in 1989/90 (18 000 MT), cyanazine use was 26% greater in 1994/95 (10 200 MT) than that in 1989/90 (8100 MT) and metolachlor use was 10% greater in 1994/95 (16 400 MT) than that in 1989/90 (14 900 MT). Acetochlor was not used until 1994, but its use has increased rapidly (9200 MT in 1995).

Changes in Herbicide Concentrations. Herbicide concentrations in Midwestern rivers were expected to change between 1989 and 1995 as a result of shifts in herbicide use

TABLE 1. Percentage of Samples with Concentrations at or above the Analytical Reporting Limit (detections) and Median Concentration from Postapplication Samples Collected in 1989, 1990, 1994, and 1995

property or compound	reporting limits (μg/L)	percentage of samples with compound detections and median concentrations (μg/L)							
		1989 (n = 50)		1990 (n = 52)		1994 (n = 52)		1995 (n = 50)	
		%	median	%	median	%	median	%	median
Herbicides									
acetochlor	0.05	*a*		*a*		34.6	<0.05	84.0	0.42
alachlor	0.05	94.0	1.90	94.2	1.62	78.8	0.77	82.0	0.13
ametryn	0.05	0.0		1.9	<0.05	0.0		2.0	<0.05
atrazine	0.05	100.0	10.9	100.0	8.98	100.0	3.98	100.0	5.54
cyanazine	0.05	76.0	2.65	82.7	2.24	94.2	1.15	90.0	1.35
metribuzin	0.05	70.0	0.28	53.8	0.10	46.2	<0.05	42.0	<0.05
metolachlor	0.05	94.0	2.50	98.1	3.07	94.2	1.74	100.0	1.66
prometon	0.05	26.0	<0.05	15.4	<0.05	7.7	<0.05	38.0	<0.05
prometryn	0.05	0.0		0.0		0.0		2.0	<0.05
propazine	0.05	54.0	0.07	61.5	0.11	30.8	<0.05	58.0	0.06
simazine	0.05	70.0	0.21	65.4	0.09	55.8	0.07	68.0	0.08
terbutryn	0.05	0.0		0.0		0.0		0.0	
Herbicide Degradation Products									
alachlor ESA	0.10	*a*		*a*		100.0	4.75	100.0	1.55
cyanazine amide	0.05	*a*		*a*		94.1	0.57	90.0	0.47
deethylcyanazine	0.05	*a*		*a*		15.7	<0.05	*a*	
deethylcyanazine amide	0.50	*a*		*a*		3.9	<0.05	*a*	
deethylatrazine	0.05	96.0	0.77	100.0	0.87	96.2	0.75	96.0	0.43
deisopropylatrazine	0.05	69.2	0.47	86.5	0.44	92.3	0.44	96.0	0.42
Field Parameters									
streamflow (m^3/s)		100.0	27.8	100.0	35.7	100.0	27.1	100.0	28.4
streamflow as a percentile		100.0	82.4	100.0	89.0	100.0	79.9	100.0	87.6

[a] Not analyzed.



Herbicide use estimates are in metric tons of active ingredient
Data Sources: Gianessi and Puffer, 1991; USDA, 1990−1997

FIGURE 2. Estimated use of five herbicides and planted corn and soybean acreage in eight Midwestern States (IA, IL, IN, KS, MN, NE, OH, and WI) for 1989−1996.

such as the decrease in alachlor use or the increase in acetochlor use. Alterations to crop management practices such as increased conservation tillage may also affect herbicide concentrations in some Midwestern rivers. One way to gain a measure of change is to look at the distribution of herbicide concentrations from a set of representative sites such as those used in this study over a period of years. The distributions of concentrations for all herbicide and herbicide degradation products measured in this study, for all years, are positively skewed, suggesting that medians may be more appropriate descriptors of central tendency of concentration distributions than means (*25*) and that nonparametric tests may be more appropriate for analysis than parametric tests, which are based on the assumption of data normality (*26*).

The percentage of samples with herbicides detected at or above the analytical reporting limit (detections) was greater in 1995 than in 1989 for five compounds (acetochlor, cyanazine, metolachlor, prometon, and propazine) and less in 1995 than in 1989 for three compounds (alachlor, metribuzin, and simazine). The detection frequency for atrazine was 100% in all 4 years (Table 1). Ametryn was detected only twice, prometryn was detected only once, and terbutryn was not detected. The frequency of detection of deethylatrazine was the same in 1989 and 1995 (96%), but the frequency of detection of deisopropylatrazine was greater in 1995 than in 1989. Alachlor ESA, cyanazine amide, deethylcyanazine, and deethylcyanazine amide were not analyzed in 1989 or 1990.

The median concentrations of herbicides in selected Midwestern rivers during postapplication runoff events was smaller in 1995 than that in 1989 for seven compounds (alachlor, atrazine, cyanazine, metribuzin, metolachlor, propazine, and simazine) and was the same (less than the detection limit) in 1989 and 1995 for four compounds (ametryn, prometon, prometryn, and terbutryn) (Table 1). Acetochlor was not used in 1989. The distributions of concentrations for eight herbicides and four herbicide degradation products are shown using boxplots in Figure 3. In Figure 3, nondetects are plotted at the reporting limit of the individual compounds (Table 1), the boxes show the 25th, 50th (median), and 75th percentiles, the whiskers extend to the 5th and 95th percentiles, and outliers less than the 5th or greater than the 95th percentiles are shown as circles. The concentration distributions for alachlor, atrazine, cyanazine, metolachlor, metribuzin, and simazine all are shifted down (lower concentrations) in 1994 and 1995 samples relative to those of 1989 and 1990 samples. The shift down for alachlor is most significant, with the 25th percentile concentration in 1989 approximately equal to the 75th percentile concentration in 1995.

The median concentration of the degradation products deethylatrazine and deisopropylatrazine both were less in 1995 than in 1989, but the distributions of their concentrations

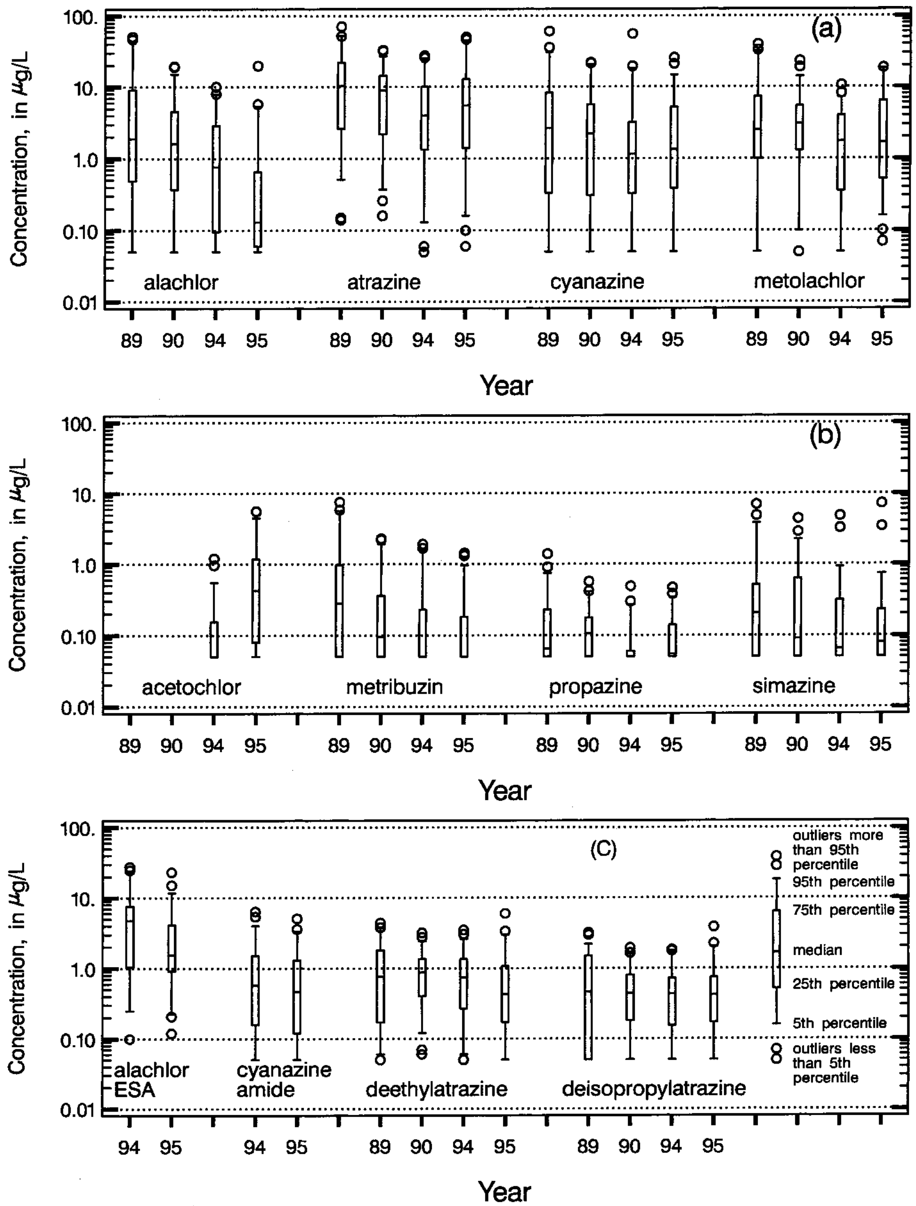


FIGURE 3. Boxplots of concentrations in selected Midwestern streams during postapplication runoff events in 1989, 1990, 1994, and 1995 for (a) alachlor, atrazine, cyanazine, and metolachlor; (b) acetochlor, metribuzin, propazine, and simazine; and (c) alachlor ESA, cyanazine amide, deethylatrazine, and deisopropylatrazine.

were very similar (Figure 3). Alachlor ESA, cyanazine amide, deethylcyanazine, and deethylcyanazine amide were not analyzed in 1989 or 1990. The median deethylatrazine concentration was 0.77 μg/L in 1989 and 0.43 μg/L in 1995, and the median deisopropylatrazine concentration was 0.47 μg/L in 1989 and 0.42 μg/L in 1995. Although median concentrations were less in 1995 than those in 1989 for seven herbicides and two herbicide degradation products, Figure 3 indicates that in some cases these declines are not large and may not be statistically or environmentally significant.

The spatial patterns of alachlor and atrazine concentrations in postapplication runoff samples from 1989, 1990, 1994, and 1995 are shown on Figure 4. At sites in the Corn Belt where alachlor concentrations were largest, concentrations generally decreased from 1989/90 to 1994/95. The exception is in Nebraska basins where concentrations of alachlor did not decrease. Concentrations of atrazine appear to have decreased at some sites in Ohio and Indiana, but the difference is not as widespread or dramatic as that observed for alachlor. There appears to have been little change in atrazine concentrations at the sites in Nebraska. The differences between 1989 and 1990 and 1994 and 1995 concentrations (Figure 4) are an indication of annual variability.

Daily Yields. Daily herbicide yields were calculated at each site by multiplying herbicide concentrations with daily mean streamflow and dividing by drainage basin area. The intent of the postapplication runoff-event sampling was to capture the peak preemergence herbicide concentrations expected during the year at each site. Other studies (*9*, *11*, *14*, *15*) have shown that the peak concentration for preemergence herbicides such as alachlor, atrazine, cyanazine, and metolachlor frequently occurs just after their application, during spring and early summer runoff events. Streamflow is also frequently near its annual maximum during these events. Hence, the daily yields of herbicides calculated from these samples could reasonably be expected to approximate the peak daily yield expected for the year. However, it is not known if the calculated yields are truly the maximum values for the year since it is not known if either the concentration or streamflow was truly at its peak.

Estimated peak daily herbicide yields were expected to change with shifts in herbicide use. The distributions of

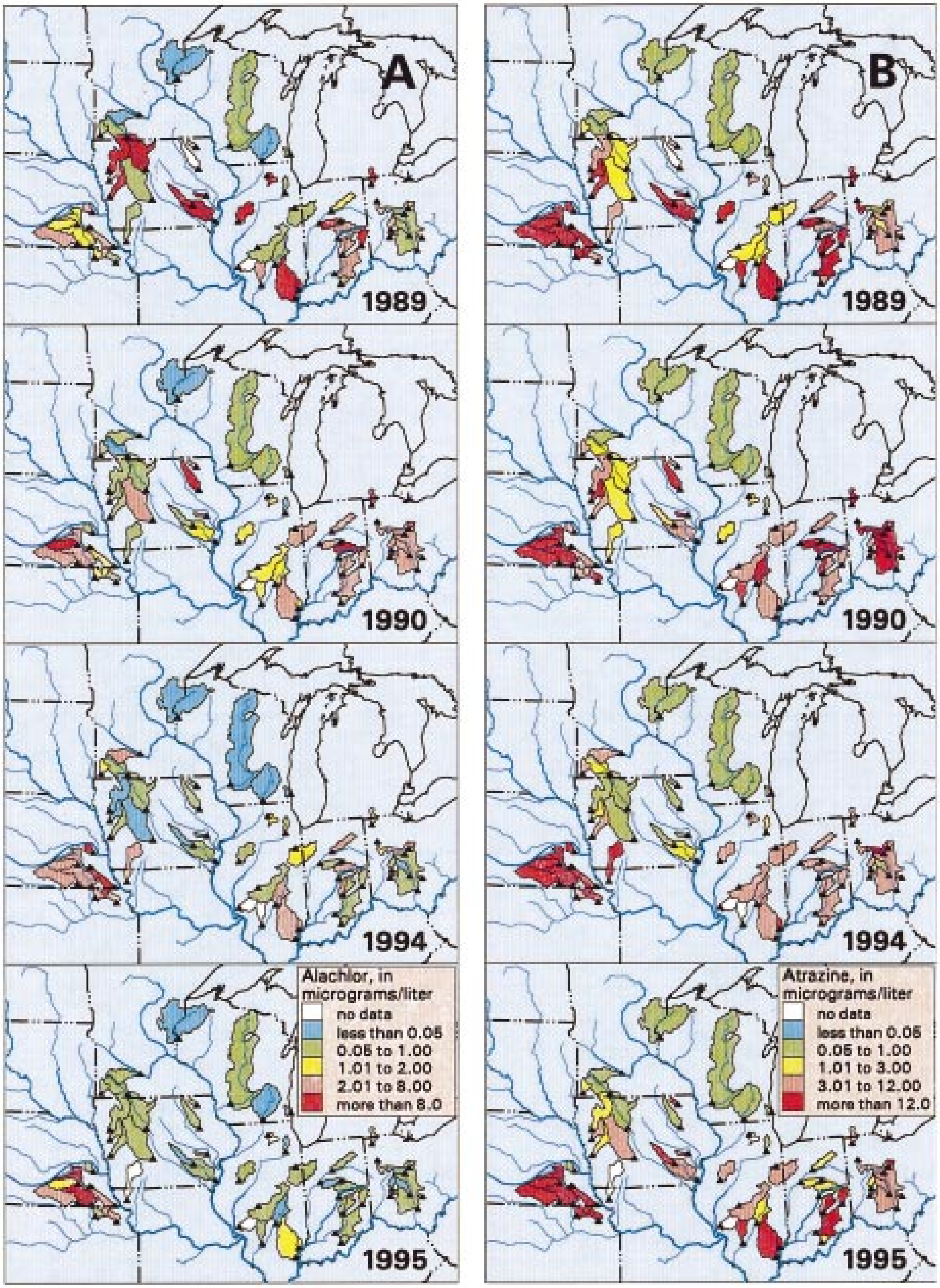


FIGURE 4. Concentrations in selected Midwestern streams during postapplication runoff events in 1989, 1990, 1994, and 1995 for (A) alachlor and (B) atrazine.

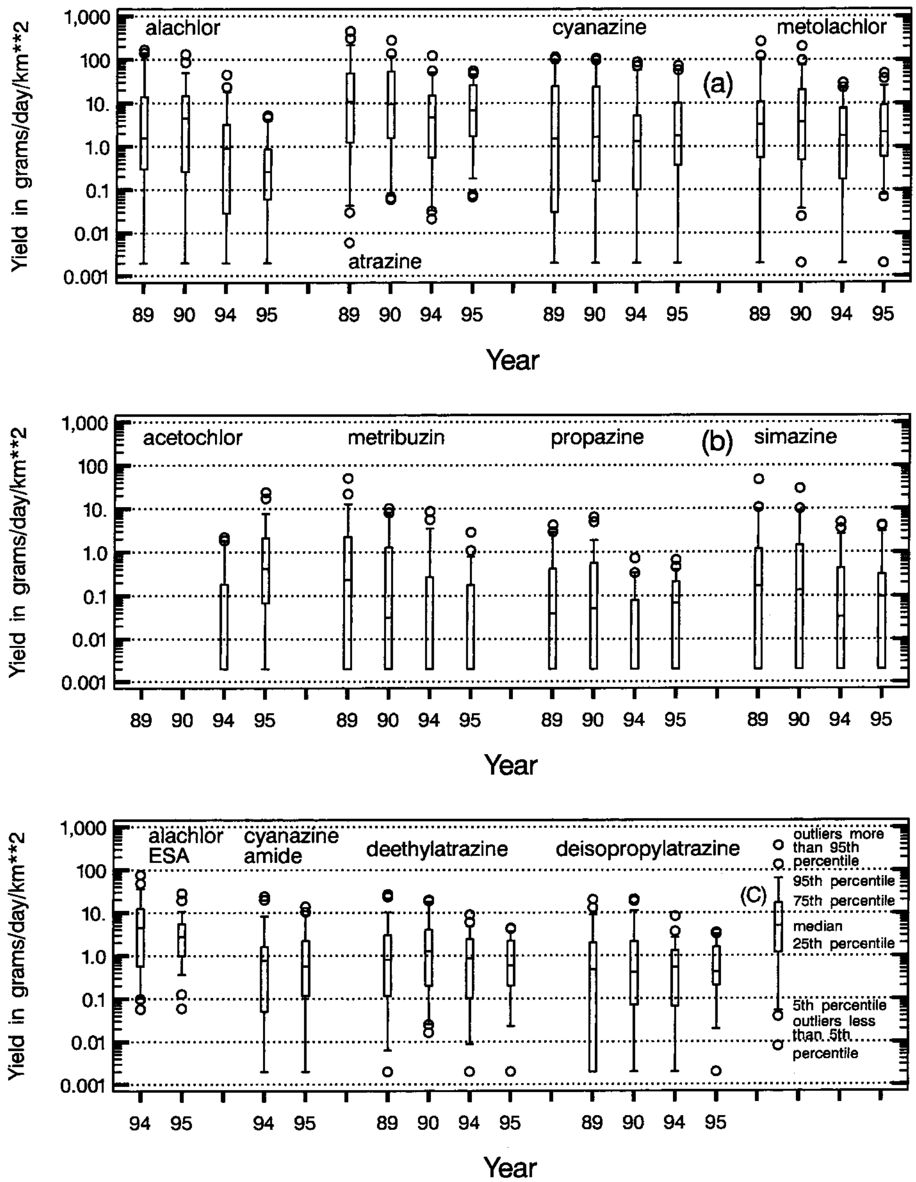


FIGURE 5. Boxplots of daily yields from selected Midwestern stream basins during postapplication runoff events in 1989, 1990, 1994, and 1995 for (a) alachlor, atrazine, cyanazine, and metolachlor; (b) acetochlor, metribuzin, propazine, and simazine; and (c) alachlor ESA, cyanazine amide, deethylatrazine, and deisopropylatrazine.

estimated daily yields for eight herbicides and four herbicide degradation products are shown in Figure 5. Distributions of estimated peak yields for all herbicides and herbicide degradation products, for all years, are positively skewed and fail tests of normality. When the herbicide or degradation product concentrations were less than the reporting limit, the daily yields were set to 0.002 g day^{-1} km^{-2}, so that the data could be plotted on a log scale.

Median estimated peak daily yields of herbicides in selected Midwestern rivers during postapplication runoff events were greater in 1995 than in 1989 for three compounds [acetochlor (not used in 1989), cyanazine, and propazine], less in 1995 than that in 1989 for seven compounds (alachlor, atrazine, metribuzin, metolachlor, simazine, deisopropylatrazine, and deethylatrazine), and the same in 1995 and 1989 (0.002 g day^{-1} km^{-2}) for four compounds (ametryn, prometon, prometryn, and terbutryn). As with herbicide concentrations, some of the changes in median peak daily yields are small and may not be statistically significant (Figure 5).

Annual Variability. Year-to-year variability may obscure or accentuate actual changes in herbicide concentrations or yields in Midwestern rivers and could limit the ability of statistics such as a Kruskal–Wallis test to identify differences in their distributions. Year-to-year variability is likely the result of differences in local and regional climatic conditions and resulting farm management practices and cannot solely be attributed to changes in herbicide use. Streamflow is one indicator of local or regional climatic condition. The amount and timing of precipitation and the resulting streamflow can have significant effects on herbicide and herbicide metabolite concentrations. The boxplots in Figure 6A show the distributions of streamflow on the day of postapplication sample collection for each of the four years. Figure 6A indicates that flows in 1989 and 1995 were similar, whereas flows in 1990 were generally higher, and flows in 1994 were generally lower. Median streamflow during sample collection was 27.8 m^3/s in 1989, 35.7 m^3/s in 1990, 27.1 m^3/s in 1994, and 28.4 m^3/s in 1995 (Table 1).

Streamflow from each sample were converted to percentile values based on the historical distributions of daily-streamflow values at each site. For example, a 90th percentile streamflow would be exceeded by only 10% of historic daily streamflow values at the site. Daily-streamflow data from

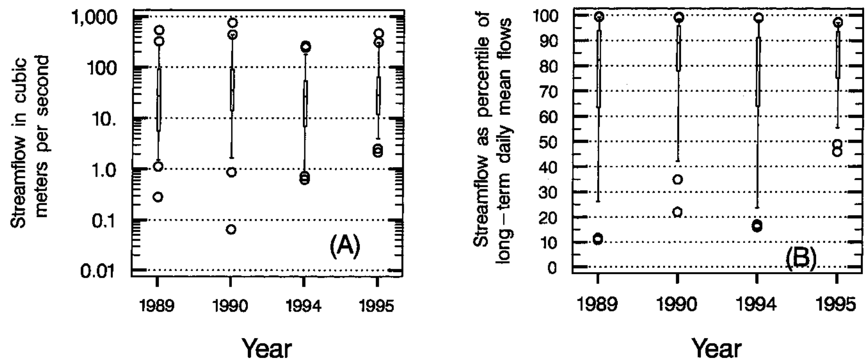


FIGURE 6. Boxplots of streamflow on the day of sample collection during postapplication runoff events in 1989, 1990, 1994, and 1995 (A) in cubic meters per second and (B) as a percentile of long-term daily streamflow.

TABLE 2. Median of Differences between Averaged 1994/95 and 1989/90 Herbicide Concentrations, Streamflow, and Streamflow Percentiles and Results from Wilcoxon Signed Rank Tests

compound or property	median of paired differences between averaged 1994/95 and 1989/90 concentrations	Wilcoxon signed rank test results		accept alternate hypothesis
		signed rank	*p* value	
alachlor	2.18	332	<0.001	yes
atrazine	3.03	269	0.005	yes
cyanazine	1.09	288	0.002	yes
metribuzin	0.12	277	<0.001	yes
metolachlor	1.32	219	0.023	yes
prometon	0.0	5	0.912	no
propazine	0.06	237	0.001	yes
simazine	0.04	228	0.005	yes
deethylatrazine	0.12	186	0.055	no
deisopropylatrazine	0.10	140	0.140	no
streamflow (m^3/s)	6.33	138	0.159	no
streamflow percentile	2.53	75	0.448	no

TABLE 3. Median of Differences between Averaged 1994/95 and 1989/90 Estimates of Herbicide Peak Daily Yields (g day^{-1} km^{-2}) and Wilcoxon Signed Rank Test Results

compound or property (yield)	median paired differences between averaged 1994/95 and 1989/90 peak daily yield	Wilcoxon signed rank test results		accept alternate hypothesis
		rank	*p* value	
alachlor	2.78	343	<0.001	yes
atrazine	5.26	281	0.003	yes
cyanazine	1.09	212	0.023	yes
metribuzin	0.217	253	0.001	yes
metolachlor	0.696	202	0.037	yes
prometon	0.0	−22.5	0.635	no
propazine	0.102	281	<0.001	yes
simazine	0.079	272	0.001	yes
deethylatrazine	0.213	258	0.007	yes
deisopropylatrazine	0.112	154	0.104	no

1972 to 1991 were used to define the distribution of flows at each site. The percentile of flow may be preferable to actual streamflow in making comparisons between years and among basins of different sizes and flow regimes. The boxplots in Figure 6B show the distributions of streamflow during sample collection as a percentile of long-term daily streamflow in each of the 4 years. Figure 6B and Table 1 suggest that the distribution of sampled streamflow in 1990 and 1995 were similar and generally higher than flows in 1989 and 1994.

To gain a measure of changes in herbicide concentrations and yields, a paired difference test was used. These tests can determine if one group of observations tends to be larger than another group. Since the distributions of concentrations (and yields) for all of the herbicides and herbicide degradation products measured in this study, for all years, are positively skewed and the distributions of streamflow as a percentile are negatively skewed, the nonparametric Wilcoxon Signed Rank test (*25*, *26*) was used. To reduce the effect of year-to-year variability, 1994 and 1995 concentrations, streamflows, flow percentiles, and estimates of daily yield at each site are averaged and subtracted from the average of 1989 and 1990 values. The following hypothesis was tested.

Null Hypothesis. Averaged 1989/90 concentrations/streamflows/yields were not significantly different from averaged 1994/95 values (median of differences = 0).

Alternate Hypothesis. Averaged 1989/90 concentrations/streamflows/yields were larger than 1994/95 values (median of differences > 0) (one-sided test).

Medians of the calculated differences and results from the Wilcoxon Signed Rank test are given in Tables 2 and 3. The median concentration differences for all analyzed herbicides and herbicide degradation products with the exception of prometon are positive, indicating that concentrations were larger in 1989/90 than those in 1994/95 (Table 2). The concentration decreases for alachlor, atrazine, cyanazine, metribuzin, metolachlor, propazine, and simazine were all statistically significantly ($\rho \leq 0.05$) according to the results of the signed rank tests. The differences between averaged 1989/90 and 1994/95 concentrations of prometon, deethylatrazine and deisopropylatrazine were not statistically significantly ($\rho > 0.05$). Averaged streamflow in cubic meters per second and streamflow percentiles were not significantly different in 1994/95 than in 1989/90 (Table 2), suggesting that when averaged 1989/90 flow conditions are comparable to 1994/95 flow conditions and that annual variability is somewhat accounted for.

Results of Wilcoxon Signed Rank tests on differences between averaged 1989/90 and 1994/95 estimates of peak daily yield are given in Table 3. The median yield differences with the exception of prometon are all positive, indicating that yields of all analyzed herbicides and herbicide degradation products were larger in 1989/90 than in 1994/95. The decreases in estimated daily yields for alachlor, atrazine, cyanazine, metribuzin, metolachlor, propazine, simazine, and deethylatrazine were statistically significantly ($\rho \leq 0.05$). The differences between averaged 1989/90 and 1994/95 estimates of daily yield for prometon and deisopropylatrazine were not statistically significantly (Table 3).

Relation to Changes in Herbicide Use. The relation between changes in herbicide concentration or estimated peak daily yield and the change in overall use of each herbicide was not always as expected. Although the significant decrease in averaged alachlor use (56%) between 1989/90 and 1994/95 paralleled significant decreases in the median alachlor concentration and daily yield, the same cannot be said for the other herbicides. Averaged atrazine use was slightly (2%) smaller in 1994/95 than in 1989/90, in the eight-state region, but large decreases in median atrazine concentration and daily yield were observed. Metolachlor use was 10% larger in 1994/95 than that in 1989/90, but large decreases in median metolachlor concentrations and daily yields were observed. Cyanazine use was 26% larger in 1994/95 than that in 1989/90, but significant decreases in median cyanazine concentrations and daily yields also were observed. The results for alachlor and acetochlor suggest that changes in herbicide use do affect herbicide concentrations. However, the observed decreases in concentration and daily yield for several other herbicides cannot solely be attributed to changes in the overall amount of their use. Other possible explanations for the decreases in herbicide concentrations and daily yields during postapplication runoff events include increased use of split herbicide applications, decreased per acre application rates, increased use of postemergence herbicides (*24*, *27*), increased postemergence application of traditionally preemergence compounds, and better utilization of herbicide best management practices.

Application of the results of this study is limited by a number of factors. First, peak herbicide concentrations are highly variable and one cannot always expect to get the true peak concentration when only one sample per year per site is collected. This is especially true now that many farms are using postemergence herbicides and some farmers apply preemergence compounds such as atrazine postemergent. Storm runoff samples need to be collected several times from several events during the spring and early summer to have a chance at observing the true peak concentrations for the most commonly used herbicides. Second, it is likely that some of the changes in herbicide use and concentration are a result of shifts to other herbicides (*24*, *27*). Some of these other herbicides such as the sulfonylureas and imidazolinones are new classes of chemicals that are applied at a fraction of the rate of older compounds. Others, such as acetochlor and dimethenamid, are new to the market but are similar in chemistry and application rate to the older compounds. Analyzing a more complete set of the herbicides that are used in Midwestern agriculture would help to better determine how herbicide concentrations as a whole are changing in Midwestern rivers. Finally, some changes in herbicide concentrations and daily yields presented in this report may be statistically significant only as a result of unknown bias in the timing or method of sample collection. Likewise, some changes in herbicide concentration may be masked by natural variability of herbicide concentrations in streams during runoff events.

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