PLAN OF STUDY TO DETERMINE THE EFFECT OF CHANGES IN HERBICIDE USE ON HERBICIDE CONCENTRATIONS IN MIDWESTERN STREAMS, 1989-94

U.S. GEOLOGICAL SURVEY

Open-File Report 94-347

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Denver, Colorado
1994

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
cubic foot per second (ft^3/s)	2.832×10^{-2}	cubic meter per second
pound	4.536×10^{-1}	kilogram
square mile (mi^2)	2.590	square kilometer
acre	4.047×10^{3}	square meter (m^2)
	4.047×10^{-1}	square hectometer (hm^2)
	4.047×10^{-3}	square kilometer (km^2)
cubic foot (ft^3)	2.447×10^{3}	cubic meter (m^3)

Temperature can be converted from degrees Celsius (°C) to Fahrenheit (°F) by using the following equation:

$$°F = 9/5(°C)+32.$$

Abbreviated Water-Quality Units

microgram per liter (µg/L)
microsiemens per centimeter at 25 degrees Celsius (µS/cm)
milligram (mg)
milligram per liter (mg/L)
milliliter (ml)

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ABSTRACT

An approach was developed to determine if recent changes in the use of herbicides has affected herbicide concentrations in Midwestern streams. This approach also provides a plan to determine if the abnormally high rainfall and flooding in 1993 has an effect on nitrate concentrations in 1994 in streams that flooded in 1993. The approach involves sampling 53 stream sites, 50 of which were sampled in 1989 and 1990 as part of a reconnaissance to determine the geographic and seasonal distribution of herbicides in 10 Midwestern States. Sites will be sampled twice, once prior to application of herbicides, in March or early April, and once during the first runoff event after application of herbicides. Samples will be analyzed for 11 herbicide and 2 atrazine metabolites by gas chromatography/mass spectrometry. Samples will also be analyzed for ESA (an alachlor metabolite), two cyanazine metabolites, and nutrients.

Changes to the manufacturers' label have decreased the maximum recommended application rate for atrazine on corn and sorghum by about 50 percent since the 1989-90 study. Conversely, the use of other herbicides, such as cyanazine, has increased by more than 25 percent since 1989. Statistical procedures such as Wilcoxon signed rank tests for paired samples will be used to determine if the distributions of herbicide and nitrate concentrations in 1994 are different from those measured in 1989 and 1990.

INTRODUCTION

In 1989 the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program conducted a reconnaissance of about 150 streams in 10 Midwestern States to determine the geographic and seasonal distribution of herbicides. These streams were sampled three times: (1) before application, (2) during the first major runoff event after application, and (3) during low flow in the fall. Results from the study showed that large amounts of atrazine, cyanazine, alachlor, and metolachlor were flushed into streams during the first post-application runoff event (Thurman and others, 1991, 1992; Goolsby and Battaglin, 1993). Both atrazine and cyanazine temporarily exceeded health-based limits in about one-half of the streams. The atrazine maximum contaminant level (MCL) is 3 μg/L (micrograms per liter); the cyanazine health advisory (HA) is 1 μg/L. In addition, alachlor temporarily exceeded the alachlor MCL of 2 μg/L in about 35 percent of the streams. Although the concentrations of some herbicides exceeded MCLs in some of the post-application samples, this does not necessarily constitute a violation of the Safe Drinking Water Act (SDWA). A violation occurs only if the average annual concentration exceeds the MCL or if the herbicide concentration in a single sample is more than four times the MCL. Thus, samples with atrazine concentrations exceeding 12 μg/L or alachlor concentrations exceeding 8 μg/L may represent violations of the SDWA if the water is used for public supply. About 25 percent of the samples collected during the post-application period had atrazine concentrations larger than four times the MCL and about 15 percent had alachlor concentrations larger than four times the MCL (fig. 1). Cyanazine has a nonenforceable HA of 1 μg/L; the cyanazine concentration in about 25 percent of the post -application samples exceeded four times the HA (fig. 1). The maximum concentration of several herbicides exceeded 50 µg/L (fig. 1). Herbicide concentrations were much lower (generally less than 1 µg/L) during the pre-application and fall low-flow sampling periods; however, more than one-half the streams had detectable concentrations in all three sampling periods.

The 1989 reconnaissance documented for the first time the seasonal and geographic distribution of herbicides in streams at a regional scale. Because of the high post-application concentrations measured, and because of an increased level of concern caused by the results, a follow-up study was conducted in 1990 to verify the 1989 results. In the verification study 50 sites were selected for resampling. Selection of the sites was accomplished by ranking all samples from the 1989 post-application sampling round from highest to lowest according to the total herbicide concentration. This concentration is defined as the sum of the concentrations of all herbicides measured in each sample. These sites were then divided into three equal groups. From the group containing the highest concentrations, 25 sites were randomly selected. Similarly, 13 sites were randomly selected from the middle group, and 12 sites were randomly selected from the low concentration group. These sites were resampled before application and during the first runoff event after application in 1990 using the same protocols developed for the 1989 study. Results from the 1990 study confirmed the 1989 results. The statistical distributions of the concentrations of the major herbicides detected in these 50 streams were essentially the same during the pre- and post-application periods of both years (Goolsby and others 1991; also see figure 2). These results and those of other studies (Baker and Richards, 1989; Frank and others 1982; Leonard, 1988; Snow and Spalding, 1988; and Wauchope, 1978) further indicated that the "flush" of herbicides following application is an annual occurrence. Additional studies by the USGS in 1990 and 1991 using automatic samplers (Thurman and others 1992; Goolsby and Battaglin, 1993) show that the herbicide "flush" lasts for several weeks to several months following application. By late summer, herbicide concentrations generally decrease to low concentrations (less than 0.5 µg/L) and remain low until the process is repeated the following year.

Changes in Herbicide Use

Since the 1989-90 regional-scale studies were conducted, two reductions have occurred in the maximum application rate of atrazine recommended by the manufacturers' label. In 1990, because of concern about ground-water contamination, the manufacturers of atrazine voluntarily reduced the maximum recommended application rate for atrazine to 3 pounds a.i. (active ingredient) per acre per year for corn and sorghum (U.S. Environmental Protection Agency (EPA), written commun., Jan. 23, 1990). Prior to this, the recommended maximum application rate was 4 pounds a.i. per acre per year. The 1990 label change also restricted noncropland uses of atrazine to 10 pounds a.i. per year. This label change applied to all products released for shipment after September 1, 1990.

In 1992, due in part to concern about surface-water contamination, the manufacturers of atrazine further voluntarily reduced the maximum recommended application rate of atrazine to a range of 1.6 to 2.5 pounds a.i. per acre per year depending on soil organic residue and erosion potential. The maximum amount recommended per application is 2 pounds a.i. per acre. Up to 0.5 pound a.i. per acre per year can be applied in subsequent applications (EPA, written commun., March 8, 1993). The total of all applications cannot exceed 2.5 pounds a.i. per acre per year.

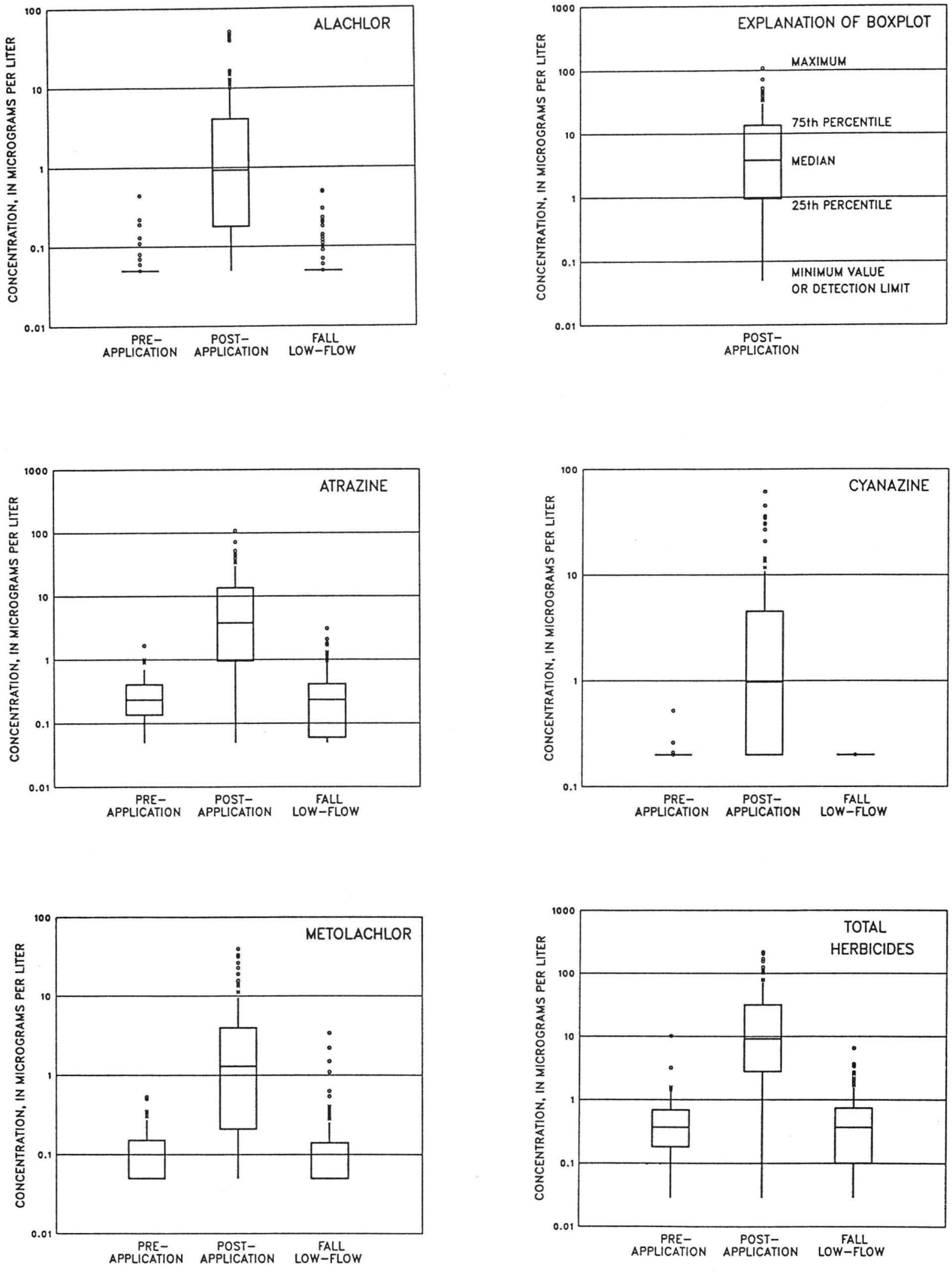

Figure 1. The seasonal distribution in concentrations of selected herbicides detected during three sampling periods in 1989.

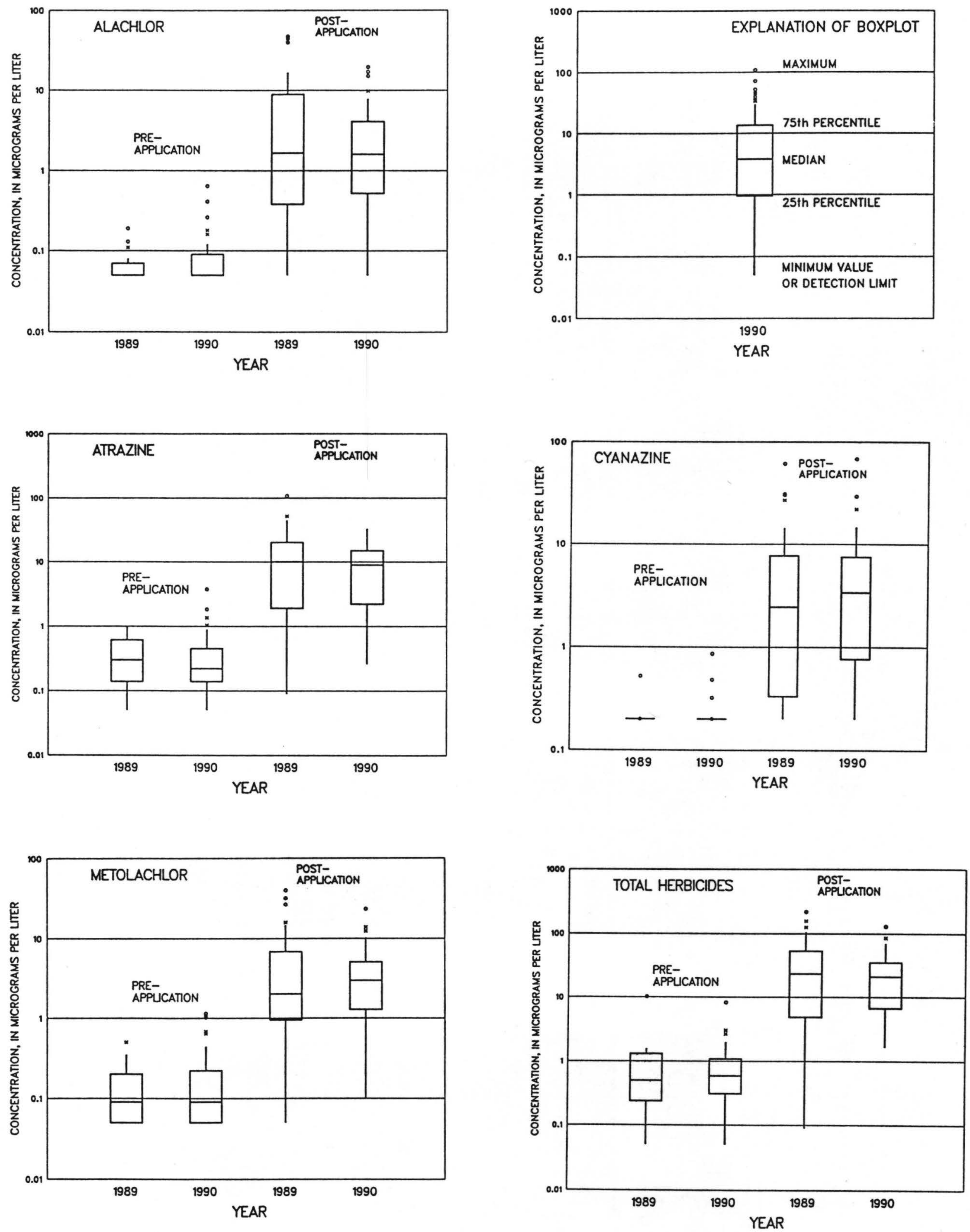

Figure 2. The distribution in concentrations of selected herbicides at approximately 50 sites sampled in both 1989 and 1990 during pre- and post-application sampling periods.

A maximum of 1.6 pounds a.i. per acre per year is recommended on soil with less than 30 percent plant residue remaining on the surface. Most non-cropland uses of atrazine are no longer recommended under the label. This label change was effective with all products shipped for use after August 1, 1992.

As a result of these two voluntary label changes, the maximum application rate for atrazine on corn and sorghum has essentially been reduced by 50 percent since the 1989-90 studies were conducted. However, no information is available to determine if atrazine was always applied at the maximum recommended rate. There is reason to believe, however, that there has been a substantial reduction in the per acre application rate of atrazine since the 1989-90 regional studies of atrazine in streams. Further, assuming there has been no substantial increase in the acres planted in corn and sorghum in the 1989-94 time period, there should have been a substantial overall reduction in the use of atrazine. This could be reflected in an overall reduction in atrazine concentrations in Midwestern streams. The 50 sites sampled in 1989 and 1990 provide a good data set from which to determine if there has been a measurable decrease in atrazine concentrations.

Conversely, the use of other herbicides, such as cyanazine has increased since 1989. According to data from the U.S. Department of Agriculture (USDA), the estimated use of cyanazine on corn and sorghum increased from 20.7 million pounds a.i. per year in 1989 to 26.7 million pounds a.i. per year in 1992 (Gianessi, 1992; USDA, 1990, 1991, 1992), an increase of more than 25 percent. Data from these sources also indicate that the use of metolachlor has increased since 1989. The 1989-90 data set would also provide a baseline from which to determine if the concentrations of these herbicides in Midwestern streams have changed.

Nitrate in Area Affected by 1993 Flood

The Mississippi - Missouri River flood of 1993 occurred throughout the western one-half of the area encompassed by the 1989-90 herbicide studies. It is unlikely that the 1993 flood will have any affect on concentrations of herbicides in the flood-affected streams in 1994, because herbicides are transported to streams primarily by overland runoff during a 1 to 2 month period following application rather than by ground-water baseflow. However, the 1993 flood may have an effect on nitrate concentrations in some Midwestern streams in 1994. In a study of the Raccoon River in Iowa, Lucey and Goolsby (1993) showed that during years of below-normal precipitation there appeared to be an accumulation of nitrate in the soil and unsaturated zone, and during subsequent years of above-normal precipitation some of this stored nitrate was leached into streams. This resulted in low nitrate concentrations in the Raccoon River during dry years and high concentrations during wet years. Similar observations have been made in other studies of nitrate in Midwestern streams and the Mississippi River (Goolsby and Battaglin, 1993; Goolsby and others, 1993). In most of the streams studied, nitrate concentrations increased as streamflow increased during winter and spring. Also, the highest nitrate concentrations in the Mississippi River during 1991-93 were measured during periods when streamflow was high. These results suggest that stream basins affected by abnormally high rainfall in 1993 could have higher concentrations of nitrate in 1994 than in 1989-90 if soil moisture content remains high and streamflow is above-normal. If streamflows in the spring and summer of 1994 are similar to or lower than in 1989-90, nitrate concentrations could be similar to those measured during the 1989-90 studies. A comparison of nitrate data collected in 1994 with data from these same streams in 1989-90 would provide a basis for determining if this is indeed true. The 1993 flood probably flushed a considerable amount of nitrate out of the soil, unsaturated zone, and ground water, but because of the high annual use of nitrogen fertilizer in the Midwest (more than 6 million metric tons per year; Battaglin and others, 1993), a large reservoir of nitrate probably remains in the hydrologic system.

PLAN OF STUDY

The following material is a plan for a study to determine if changes in herbicide usage since 1990 have resulted in changes in herbicide concentrations in Midwestern streams. The proposed study also provides a plan to determine if the abnormally high rainfall and flooding in 1993 had an effect on nitrate concentrations in 1994 in the streams that flooded in 1993. In addition, the proposed study will provide an opportunity to further examine the distribution of the alachlor soil metabolite ESA (alachlor ethane sulfonic acid) and the cyanazine metabolites deethylcyanazine and cyanazine amide. ESA is one of the most abundant herbicide compounds found in Midwestern reservoirs and shows relatively little seasonal variation (Goolsby, Battaglin, Fallon, and others, 1993). These results suggest that ESA is very persistent and is transported in a manner more similar to nitrate than to the other herbicide compounds being studied. Analyses for deethylcyanazine and cyanazine amide in sample extracts from the 1989-90 studies indicate that the abundance and distribution of these compounds is similar to cyanazine (Mike Meyer, USGS, Lawrence, Kansas, unpublished data, 1994).

Objectives and Hypotheses

The principal objective of the proposed study is to determine if changes in the application rate recommended by the manufacturers of atrazine have resulted in an overall reduction in atrazine concentrations in Midwestern streams since 1990. Secondary objectives are to: (1) determine if overall changes since 1990 in the concentrations of cyanazine, metolachlor, and nitrate can be detected in these streams, (2) determine the seasonal and geographic distribution of the alachlor soil metabolite ESA, and (3) compare the seasonal and geographic distribution of the cyanazine metabolites cyanazine amide and deethylcyanazine with 1990 results. Specific hypotheses to be tested are:

1. The overall concentrations of atrazine and desethylatrazine in Midwestern streams during runoff following application will be lower in 1994 than in 1989 and 1990.

2. The concentrations of cyanazine, cyanazine amide, and deethylcyanazine during runoff following application will be higher in 1994 than in 1990.

3. ESA will be detected at a frequency and in concentrations similar to that of atrazine.

4. ESA will show much less seasonal variation (pre-application compared to post-application) in concentrations than the other herbicides and metabolites studied.

5 Nitrate concentrations in the stream basins affected by the 1993 flood will be higher in 1994 than in 1989 and 1990.

Sampling Sites

Fifty three (53) stream sites will be sampled in this study. Of these, 50 will be the same sites sampled for the 1990 study. These sites were selected from the 1989 reconnaissance as described earlier in this workplan. Three additional sites to be sampled are those where automatic samplers were operated in 1990 to determine the temporal distribution of herbicides in several Midwestern streams. The location of the sites to be sampled and their drainage basins are shown in figure 3. Sampling sites, drainage areas, 1990 sampling dates, and 1990 streamflows are given in table 1.

Table 1.--Sites to be sampled during March-June 1994 to investigate the effects of changes in herbicide use on herbicide concentrations in streams
[mi^2, square miles; ft^3/s, cubic feet per second; --, no data]

Map no.	State	Site number	Site name	Drainage area (mi^2)	Sampling dates: Pre-planting	Sampling dates: Post-planting	1990 post-planting streamflow (ft^3/s)
1	Iowa	05411600	Turkey River at Spillville	1770	03/22/90	06/14/90	212
2	Iowa	05421000	Wapsipinicon River at Independence	1048	03/22/90	05/09/90	1270
3	Iowa	05455100	Old Mans Creek near Iowa City	201	03/15/90	05/04/90	1030
4	Iowa	05472500	N. Skunk River near Sigourney	730	03/15/90	05/21/90	776
5	Iowa	05474000	Skunk River at Augusta	4303	03/08/90	06/21/90	26800
6	Iowa	05480500	Des Moines River at Fort Dodge	4190	03/16/90	06/15/90	3880
7	Iowa	05484500	Raccoon River at Van Meter	3441	05/03/90	05/10/90	3420
8	Iowa	06606600	Little Sioux River at Correctionville	2500	03/16/90	06/14/90	788
9	Iowa	06607200	Maple River at Mapleton	669	03/16/90	06/13/90	4960
10	Iowa	06609500	Boyer River at Logan	871	03/16/90	06/13/90	15700
11	Ill.	03378000	Bonpas Creek at Browns	228	04/17/90	07/10/90	2.3
12	Ill.	03381495	Little Wabash at Carmi	3088	04/17/90	07/10/90	440
13	Ill.	05439500	South Branch Kishwaukee, Fairdale	387	04/12/90	05/14/90	1280
14	Ill.	05526000	Iroquois River near Chebanse	2091	04/04/90	05/17/90	5560
15	Ill.	05540500	Dupage River near Shorwood	324	04/04/90	06/22/90	--
16	Ill.	05569500	Spoon River at London Mills	1072	04/10/90	05/14/90	3500
17	Ill.	05576500	Sangamon River at Riverton	2618	03/26/90	05/14/90	5730
18	Ill.	05587000	Macoupin Creek near Kane	868	03/28/90	05/14/90	4020
19	Ill.	05592100	Kaskaskia near Cowden	1330	03/27/90	05/14/90	2420
20	Ill.	05594000	Shoal Creek near Breese	735	03/28/90	05/04/90	607
21	Ind.	03275000	Whitewater River near Alpine	522	03/27/90	05/15/90	1885
22	Ind.	03302800	Blue River at Fredricksburg	283	03/27/90	05/15/90	575
23	Ind.	03328500	Eel River near Logansport	789	03/26/90	05/14/90	1550
24	Ind.	03333450	Wildcat Creek near Jerome	146	03/26/90	05/14/90	560
25	Ind.	03335000	Wildcat Creek near Lafayette	794	03/26/90	05/14/90	1220
26	Ind.	03351000	White River near Nora	1219	03/26/90	05/14/90	6428
27	Ind.	03362500	Sugar Creek near Edinburgh	474	03/27/90	05/15/90	2191
28	Ind.	03371500	E. Fork White River near Bedford	3861	03/27/90	05/15/90	11590
29	Kans.	06885500	Black Vermillion River near Frankfort	410	03/22/90	05/16/90	2560
30	Kans.	06890100	Delaware River near Muscotah	431	04/04/90	05/09/90	203
31	Minn.	05317000	Cottonwood River near New Ulm	1280	05/01/90	06/05/90	316
32	Minn.	05476000	Des Moines River at Jackson	1220	05/08/90	06/19/90	424
33	Minn.	06483000	Rock River at Luverne	425	05/08/90	06/19/90	212
34	Mo.	06817700	Nodaway River near Graham	1320	04/10/90	05/22/90	612

Table 1.--Sites to be sampled during March-June 1994 to investigate the effects of changes in herbicide use on herbicide concentrations in streams
[mi^2, square miles; ft^3/s, cubic feet per second]

Map No.	State	Site number	Site Name	Drainage area (mi^2)	Sampling dates: Pre-planting	Sampling dates: Post-planting	1990 post-planting streamflow (ft^3/s)
35	Nebr.	06803000	Salt Creek at Roca	167	03/27/90	06/07/90	59
36	Nebr.	06804000	Wahoo Creek at Itica	271	03/20/90	06/08/90	126
37	Nebr.	06880800	W. Fork Big Blue River-Dorchester	1206	04/03/90	05/10/90	130
38	Nebr.	06815000	Big Nemaha at Fall City	1340	03/27/90	05/17/90	1447
39	Nebr.	06882000	Big Blue River at Barn	4447	03/21/90	05/17/90	801
40	Nebr.	06884000	Little Blue River near Fairbury	2350	03/21/90	05/17/90	258
41	Ohio	03157000	Clear Creek near Rockbridge	89	03/22/90	05/26/90	1250
42	Ohio	03219500	Scioto River near Prospect	567	03/23/90	05/15/90	2540
43	Ohio	03223000	Olentangy River at Claridon	157	03/21/90	05/14/90	1380
44	Ohio	03230500	Big Darby Creek at Darbyville	534	03/22/90	05/15/90	3090
45	Ohio	03234500	Scioto River at Higby	5131	03/26/90	05/15/90	15400
46	Ohio	03240000	L. Miami River near Oldtown	129	03/22/90	05/14/90	608
47	Ohio	03267900	Mad River at Eagle City	310	03/22/90	05/14/90	1100
48	Ohio	04185000	Tiffin River at Stryker	410	03/21/90	05/14/90	966
49	Ohio	04186500	Auglaize River near Fort Jennings	332	03/21/90	05/14/90	2100
50	Wis.	04087240	Root River at Racine	190	03/27/90	07/19/90	31
51	Wis.	05340500	St. Croix River at St. Croix Falls	6240	04/23/90	07/30/90	5600
52	Wis.	05407000	Wisconsin River at Muscoda	10400	03/20/90	06/22/90	15400
53	Wis.	05430500	Rock River at Afton	3340	04/12/90	07/06/90	2540

Figure 3. The location of drainage basins and sites to be sampled for herbicides and nitrate during March-June 1994.

Sampling Schedule

The first sample (pre-application) will be collected at each site prior to the application of herbicides in March or early April. To the extent possible, this sample will be collected when some overland runoff is occurring to help determine the extent to which herbicides are carried over from previous application periods.

A second (post-application) sample will be collected at each site after herbicides have been applied and following the first precipitation event that produces overland flow. Collection of this sample will require a special visit to the site. To the extent possible, this sample will be collected near the discharge recorded when the 1990 sample was collected. Attempts were made in 1990 to collect the sample near the peak discharge for the event. Results and hydrographs from the 1989 sampling and studies using autosamplers in 1990 show that this is when the largest concentrations occur.

Sampling Procedures

Samples will be collected with a depth integrating sampler from three or more verticals. Sufficient volume of water will be collected in glass, Teflon, or stainless-steel sampling bottles (for example, sediment bottles) to make field measurements of pH and specific conductance (unless these are measured in situ). Samples from the three or more verticals will be composited in a 1-liter or larger glass, Teflon, or stainless-steel container. All sampling equipment will be cleaned with non-phosphate detergent, rinsed thoroughly with tap water, then distilled/deionized water, followed by a final rinse with a 50-percent solution of methanol and organic-free water. Samples will be filtered through glass fiber filters for herbicide analysis, and through membrane filters for nitrogen and phosphorus analysis.

Four 125-ml glass bottles from each site will be sent to the USGS laboratory in Lawrence, Kansas, for the analysis of herbicide compounds, and a 125 ml polyethylene bottle will be sent to the USGS National Water Quality Laboratory in Denver for analysis of dissolved nitrogen and phosphorus compounds. Field measurements for specific conductance, pH, and temperature will be taken for all samples and a discharge will be obtained by direct measurement, from a rating curve, or estimated from a nearby gaging station.

Analytical Procedures

All samples will be analyzed for 11 herbicides and 2 atrazine metabolites (table 2) by gas chromatography/mass spectrometry according to procedures described by Thurman and others (1990) and Meyer and others (1993). ESA will be analyzed by the method of Aga and others (1994) and cyanazine metabolites will be analyzed by a method developed by M.T. Meyer (unpublished). Nitrogen and phosphorus compounds (table 2) will be analyzed by the method described by Fishman and Friedman (1989).

Table 2.--Physical properties and chemical compounds to be determined for samples collected during March-June 1994

[ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; N, nitrogen; P, phosphorus; SPE, solid phase extraction; GC/MS, gas chromatography/mass spectrometry; ELISA, enzyme-linked immunosorbent assay]

Property or compound	Method	Reporting limit
streamflow	meter or rating	0.01 ft^3/s
specific conductance	meter	1 µS/cm
pH	electrometric	0.1 unit
temperature	thermometer or thermister	0.1 °C
Nutrients		
nitrite as N	colorimetric	0.01 mg/L
nitrite plus nitrate as N	colorimetric	0.05 mg/L
ammonia as N	colorimetric	0.01 mg/L
orthophosphate as P	colorimetric	0.01 mg/L
Herbicides		
alachlor	SPE-GC/MS	0.05 µg/L
ametryn	SPE-GC/MS	0.05 µg/L
atrazine	SPE-GC/MS	0.05 µg/L
cyanazine	SPE-GC/MS	0.05 µg/L
metribuzin	SPE-GC/MS	0.05 µg/L
metolachlor	SPE-GC/MS	0.05 µg/L
prometon	SPE-GC/MS	0.05 µg/L
prometryn	SPE-GC/MS	0.05 µg/L
propazine	SPE-GC/MS	0.05 µg/L
simazine	SPE-GC/MS	0.05 µg/L
terbutryn	SPE-GC/MS	0.05 µg/L
Herbicide Metabolites		
cyanazine amide	SPE-GC/MS	0.05 µg/L
deethylcyanazine	SPE-GC/MS	0.05 µg/L
desethylatrazine	SPE-GC/MS	0.05 µg/L
desisopropylatrazine	SPE-GC/MS	0.05 µg/L
ESA	SPE-ELISA	0.1 µg/L

Quality Assurance

Detailed instructions will be provided for collection and processing of samples. Analytical procedures will follow published methods. Quality-assurance samples will be used to document the precision and accuracy of analytical results. Quality-assurance samples will consist of laboratory duplicates (10 percent), blind duplicates and blanks (10 percent), and distilled water spikes (5-10 percent).

DATA ANALYSIS METHODS AND REPORTS

Because of the short-term temporal variability inherent in herbicide concentrations at an individual site and the effects of precipitation and runoff patterns, results from this study cannot be used to make statements about changes in herbicide concentrations in an individual basin. Instead the 53 sites selected for this study are assumed to be a random sample of Midwestern streams. Statistical procedures will be used to analyze the results and to statistically compare the 1994 data with data collected from these same sites in 1989 and 1990. Because the herbicide data are not expected to be normally distributed, nonparametric statistical procedures such as the Wilcoxon signed rank test for paired samples and logistic regression (Helsel and Hirsch, 1992) will be used to determine if the distributions of herbicide concentrations in 1994 are different from those reported for 1989 and 1990. These procedures will be performed for all major herbicides, nitrate, streamflow, and some physical parameters. Boxplots will be used to graphically compare results.

If atrazine use has decreased and the use of other herbicides, such as cyanazine and metolachlor has increased, the ratios of the concentrations of these herbicides to atrazine may be more sensitive to changes than the herbicides themselves. Consequently, the statistical tests described above will also be made for these ratios. The above statistical comparisons between the 1994 and 1989-90 time periods will also be attempted on a subregional scale for individual and combinations of States.

Results of the statistical analysis and results of the atrazine, cyanazine, and alachlor metabolite analyses will be interpreted and presented in one or more scientific papers. The data will be published in a USGS Open-File Report.

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