

Changes in Herbicide Concentrations in Midwestern Streams in Relation to Changes in Use, 1989–98

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ABSTRACT

Water samples were collected from Midwestern streams in 1994–95 and 1998 as part of a study to help determine if changes in herbicide use resulted in changes in herbicide concentrations since a previous reconnaissance study in 1989–90. Sites were sampled during the first significant runoff period after the application of preemergent herbicides in 1989–90, 1994–95, and 1998. Samples were analyzed for selected herbicides, two atrazine metabolites, three cyanazine metabolites, and one alachlor metabolite. In the Midwestern United States, alachlor use was much greater in 1989 than in 1995, whereas acetochlor was not used in 1989 but was commonly used in 1995. The use of atrazine, cyanazine, and metolachlor was about the same in 1989 and 1995. The median concentrations of atrazine, alachlor, cyanazine, and metolachlor were substantially higher in 1989–90 than in 1994–95 or 1998. The median acetochlor concentration was higher in 1998 than in 1994 or 1995.

INTRODUCTION

During 1989, a reconnaissance study of 147 streams in 10 Midwestern States (as shown in fig. 1A) was conducted to determine the geographic and seasonal distribution of herbicides and nutrients (Scribner et al., 1993). Sites were selected to ensure geographic distribution and regional-scale interpretation of the data. Results from the 1989 study showed that large amounts of alachlor, atrazine, cyanazine, and metolachlor were flushed into streams during the first post-application runoff (Thurman et al., 1991; Goolsby and Battaglin, 1995).

A follow-up study was conducted in 1990 because of increased concern about the findings of high post-application concentrations of herbicides in 1989. On the basis of a ranking of 1989 concentrations from highest to lowest values, 50 sampling sites were selected using a stratified random approach. The distribution of major herbicide concentrations detected in these streams was essentially the same in 1989 and 1990 for both the pre- and the post-application samples. Results further indicated that the flush of herbicides following application is an annual occurrence (Goolsby et al., 1991). At three additional sites, automatic samplers were operated in 1990 to determine the temporal distribution of herbicides in several Midwestern streams (Scribner et al., 1994). These sites were also sampled in 1989. Thus, the 53 sites selected for this study had been sampled previously during post-application runoff in both 1989 and 1990.

In 1994 and 1995, post-application runoff samples were collected at 53 of the sites sampled in 1989–90. In 1998, post-application runoff samples were collected at 52 of the 53 sites sampled in 1994–95 (Fig. 1B). These samples were collected to help determine

if changes in the application rates recommended by the manufacturers of atrazine had resulted in a reduction of atrazine concentrations in early summer (post-application) runoff (Goolsby et al., 1994; Scribner et al., 1998). The samples also were used to help determine if concentrations of other major herbicides had changed since 1989–90 and if ace-tochlor (a herbicide used only since 1994) would be detected.

METHODS

Sample Collection

In 1994, sites were sampled twice, but in 1995 and 1998, sites were sampled only once. All water samples were collected using a depth-integrating technique at three or more locations across each stream (Ward and Harr, 1990). Herbicide samples were withdrawn from the compositing container and filtered through a 0.70- μm (micrometer) glass-fiber filter using a peristaltic pump. Measurements were made onsite for specific conductance and pH. Filters were leached with about 200 mL (milliliters) of sample prior to filtration of herbicide samples. Samples were collected, where possible, after the first significant post-application rainfall when a subsequent rise in stream level was occurring.

Laboratory methods

Herbicide samples were sent to the U.S. Geological Survey (USGS) laboratory in Lawrence, Kansas. In 1989–90, samples were analyzed for 11 herbicides and two atrazine metabolites by gas chromatography/mass spectrometry (GC/MS). In 1994–95 and 1998, samples were analyzed for 13 herbicides, two atrazine metabolites, and three cyanazine metabolites by GC/MS. Solvents used for analyzing samples included pesticide-grade methanol and ethyl acetate. Deionized water was charcoal filtered and glass distilled prior to use. Internal quantitative standard solutions were prepared in methanol and phenanthrene-d10. GC/MS procedures were completed as described by Thurman et al. (1990) and Meyer et al. (1993).

In 1989–90 and 1994–95, samples were analyzed for alachlor ethanesulfonic acid (ESA) by solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) by the method described in Aga et al. (1994). The SPE procedure was automated with a Waters Millilab (Milford, MA) workstation for extraction of the analyte. The C₁₈ (18 carbon chain) Sep-Pak Plus cartridges (Waters, Milford, MA) were preconditioned sequentially with 2 mL methanol, 6 mL ethyl acetate, 2 mL methanol, and 2 mL distilled water. Each 100-mL water sample was passed through a cartridge at a flow rate of 20 mL/min (milliliters per minute). The cartridge was eluted first with 3.5 mL ethyl acetate to remove the parent compound alachlor. A second elution with 3.5 mL methanol to remove alachlor ESA was collected in a separate test tube. The methanol extracts were evaporated to dryness under nitrogen at 45 °C (degrees Celsius) using a Turbovap evaporator (Zymark, Palo Alto, CA). The samples then were reconstituted with 10 mL distilled water and analyzed using an Alachlor RaPID assay kit (Strategic Diagnostics, Inc., Newark, DE). All samples were analyzed in duplicate. The reporting limit was 0.10 $\mu\text{g/L}$. In 1998, samples were analyzed for alachlor ESA by high-performance liquid chromatography with diode-array detection (HPLC/DAD). The reporting limit was 0.20 $\mu\text{g/L}$.

Herbicide Use

Since the 1989–90 regional-scale studies were conducted, two decreases have occurred in the maximum application rate of atrazine recommended on manufacturers' labels. In 1990, the manufacturers of atrazine voluntarily reduced the maximum recommended application rate for atrazine to 3 lb (pounds) active ingredient per acre (3.4 kilograms per hectare, kg/ha) per year for corn and sorghum. Prior to this, the recommended maximum application rate was 4 lb active ingredient per acre (4.5 kg/ha) per year. The 1990 label change also restricted noncropland uses of atrazine to a maximum of 10 lb active ingredient per acre (11 kg/ha) per year. This label change occurred because of concern about ground-water contamination and was applied to all products released for shipment after September 1, 1990.

In 1992, the manufacturers of atrazine again voluntarily reduced the maximum recommended application rate of atrazine on corn and sorghum to a range of 1.6 to 2.5 lb active ingredient per acre (1.8 to 2.8 kg/ha) per year depending on soil organic residue and erosion potential. As much as 0.50 lb active ingredient per (0.56 kg/ha) acre per year can be used in subsequent applications. The total of all applications cannot exceed 2.5 lb active ingredient per acre (2.8 kg/ha) per year. A maximum of 1.6 lb active ingredient per acre (1.8 kg/ha) per year is recommended on soil with less than 30-percent plant residue remaining on the surface. Most noncropland uses of atrazine are no longer recommended on manufacturers' labels. This label change applied to all products shipped for use after August 1, 1992.

As a result of the two voluntary label changes, the maximum recommended application rate for atrazine on corn and sorghum has been reduced by approximately 50 percent since the 1989–90 studies were conducted. However, atrazine typically has not been applied at the maximum recommended rate. The actual application rate for atrazine decreased about 10 percent from an average of 1.22 lb per acre (1.37 kg/ha) in 1990 to 1.07 to 1.1 lb per acre (1.2 to 1.23 kg/ha) in 1994–95 (U.S. Department of Agriculture, 1991, 1994, 1995).

Year-to-year variability in planted acreages and subsequent herbicide use can make comparisons of change between individual years misleading. A comparison of averaged 1989–90 herbicide use with averaged 1994–95 herbicide use is made here to account to some degree for the natural year-to-year variability in herbicide application. In the Midwestern United States, alachlor use was 56 percent less in 1994–95 (7,400 metric tons (MT)) than in 1989–90 (17,000 MT), atrazine use was 2 percent less in 1994–95 (17,600 MT) than in 1989–90 (18,000 MT), cyanazine use was 26 percent greater in 1994–95 (10,200 MT) than in 1989–90 (8,100 MT), and metolachlor use was 10 percent greater in 1994–95 (16,400 MT) than in 1989–90 (14,900 MT). Acetochlor was not used until 1994, but its use has increased rapidly (9,200 MT in 1995) (Gianessi and Puffer, 1991; U.S. Department of Agriculture, 1991–97). The estimated use of acetochlor, alachlor, atrazine, cyanazine, and metolachlor from 1963 through 1995 is shown in Fig. 2.

Herbicide Concentrations

Herbicide concentrations in Midwestern streams were expected to change between 1989 and 1998 as a result of changes in herbicide use. One way to gain a measure of

that change is to consider changes in the distribution of herbicide concentrations at a set of representative sites such as those used in this study over a period of years.

The percentage of samples with herbicides detected at or above the analytical reporting limit 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 percent for every year. Ametryn was detected 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 percent), 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 distribution of concentrations for eight herbicides and four herbicide metabolites is shown in Fig. 3 using boxplots. In Fig. 3, nondetections are plotted at the GC/MS reporting limit of 0.05 $\mu\text{g/L}$ for the individual compounds.

The median concentrations of herbicides in selected Midwestern streams during post-application runoff were lower in 1995 than in 1989 for seven compounds (alachlor, atrazine, cyanazine, metribuzin, metolachlor, propazine, and simazine) and were the same (less than the detection limit) in 1989 and 1995 for four compounds (ametryn, prometon, prometryn, and terbutryn). Acetochlor was not used in 1989. The median of the sum of the concentration of 12 herbicides (total herbicides) was 22 $\mu\text{g/L}$ in 1989, 11.4 $\mu\text{g/L}$ in 1995, and 9.25 $\mu\text{g/L}$ in 1998. The median alachlor concentration was 1.90 $\mu\text{g/L}$ in 1989, 0.13 $\mu\text{g/L}$ in 1995, and less than 0.05 $\mu\text{g/L}$ in 1998. The median atrazine concentration was 10.9 $\mu\text{g/L}$ in 1989, 5.54 $\mu\text{g/L}$ in 1995, and 4.27 $\mu\text{g/L}$ in 1998. The median cyanazine concentration was 2.65 $\mu\text{g/L}$ in 1989, 1.35 $\mu\text{g/L}$ in 1995, and 0.44 $\mu\text{g/L}$ in 1998. The median metolachlor concentration was 2.50 $\mu\text{g/L}$ in 1989, 1.66 $\mu\text{g/L}$ in 1995, and 1.44 $\mu\text{g/L}$ in 1998. In contrast, the median acetochlor concentration was less than 0.05 $\mu\text{g/L}$ in 1994, 0.42 $\mu\text{g/L}$ in 1995, and 0.72 $\mu\text{g/L}$ in 1998. The median concentration of deethylatrazine and deisopropylatrazine both decreased between 1989 and 1995.

Another way to visualize the changes in herbicide concentrations over a period of years is to consider the distribution of their concentrations at a set of representative sites. The distribution of alachlor and atrazine concentrations in post-application runoff samples from Midwestern streams in 1989–90, 1994–95, and 1998 is shown in Figs. 4 and 5, respectively (nondetections are plotted at the reporting limit). Fig. 4 shows the substantial decrease in alachlor concentration between 1989 and 1998. It also shows that the frequency of alachlor nondetections was much less in 1989–90 than in 1994–95 and 1998, and that the number of samples with concentrations of alachlor greater than 1.0 $\mu\text{g/L}$ has decreased from 30 or more in 1989–90 to less than 10 in 1995 and 1998. Fig. 5 shows that the decrease in atrazine concentrations was not as great as for alachlor. Still, atrazine concentrations were generally less in 1994–95 and 1998 than in 1989 and 1990.

Discussion

A study was conducted to determine if changes in herbicide use between 1989 and 1998 would result in changes in herbicide concentrations during post-application runoff in Midwestern streams. In the Midwestern United States, alachlor use was much greater in 1989 than in 1995, whereas acetochlor was not used in 1989 but was commonly used in

1995. The use of atrazine, cyanazine, and metolachlor was about the same in 1989 and 1995. The median concentrations of atrazine, alachlor, cyanazine, and metolachlor were substantially higher in 1989–90 than in 1994–95 or 1998. The median acetochlor concentration was higher in 1998 than in 1995 or 1994. The results for alachlor and acetochlor suggest that changes in herbicide use do affect herbicide concentrations in streams.

However, the observed decreases in concentration for several other herbicides cannot be attributed solely to changes in the overall amount of their use. Other possible explanations for the decreases in herbicide concentrations during post-application runoff include increased use of split herbicide applications, decreased per-acre application rates, increased post-emergent application of traditionally pre-emergent compounds, and improved utilization of herbicide management practices. Application of the results of this study is limited by several factors. Most importantly, herbicide concentrations in Midwestern streams during post-application runoff are quite variable. Some changes in herbicide concentrations presented in this paper could be the result of unknown bias in the timing or method of sample collection and, hence, may be misleading.

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The use of brand, trade, or firm names in this paper is for identification purposes and does not constitute endorsement by the U.S. Government.

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