Herbicides in the Pecatonica and Yahara Rivers in Southwestern Wisconsin, May 1996–July 1996

by David J. Graczyk[1] and James P. Vanden Brook[2]

Introduction

Herbicides, particularly those applied to corn, can be found in surface water and ground water in Wisconsin (Sullivan and Richards, 1996; Matzen and Saad, 1996). Wisconsin farmers applied 7.6 million pounds of corn herbicides during 1996. Because of public concern about the amount of herbicides applied to Wisconsin farm fields and the impact on surrounding watersheds, a study was conducted to measure herbicide runoff in sections of two rivers in southwestern Wisconsin. This is a cooperative project between the U.S. Geological Survey (USGS) and the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP).

Prior to this study, surface-water samples had not been collected frequently enough to calculate herbicide loads for entire watersheds in southwestern and south-central Wisconsin. This fact sheet summarizes herbicide concentrations in samples collected from the Pecatonica River at Martintown and the Yahara River near Fulton from May 15 to July 15, 1996. Herbicide loads and unit area loads are calculated for these two watersheds.

This study monitored commonly applied corn herbicides: alachlor, atrazine, metolachlor, cyanazine, and acetochlor. Acetochlor was introduced to the market in 1994 as a replacement for corn herbicides such as alachlor.

Data Collection

Water samples were collected from the Pecatonica River at Martintown and from the Yahara River near Fulton (fig. 1). These sites were selected because of the extensive agricultural activity within the watersheds and because they both are long-term USGS streamflow stations. Additionally, DATCP estimated that applications of atrazine to cornfields in the two watersheds were significantly different. Atrazine use was prohibited on 94 percent of the Yahara watershed whereas only 4 percent of the Pecatonica River watershed was under atrazine use prohibition. It was expected that the effect of atrazine use prohibitions would be reflected in the unit area loads of atrazine to surface waters. Farmers apply most of the herbicides used in the watersheds to corn and soybeans. The drainage area and land uses for each watershed are shown in table 1. The amounts of pesticide active ingredient applied in each watershed are shown in table 2.

Samples were collected at each site weekly from May 15 to July 15, 1996, without regard to streamflow[1] conditions at the sampling site. When the instantaneous discharge of the stream increased by at least 50 ft^3/s (cubic feet per second) more than the mean daily discharge of the previous day, additional daily storm runoff samples were collected until the streamflow decreased.

Samples were collected with a US D-77 water-quality sampler using the Equal-Width-Increment (EWI) method (Edwards and Glysson, 1988). The sample was transferred to a teflon-lined sample splitter and then split into two pre-cleaned, one-liter brown glass bottles. The samples were analyzed for commonly used herbicides by the DATCP water-quality laboratory. The sampler and churn splitter were cleaned by methods outlined in Shelton (1994). For quality assurance (QA), samples of deionized (MilliRO and MilliQ) water were processed through the sampler and splitting equipment and then analyzed for herbicides by the DATCP laboratory. These QA samples, collected and processed near the beginning and at the end of the sampling periods, contained no detectable concentrations of the herbicides analyzed in this study.

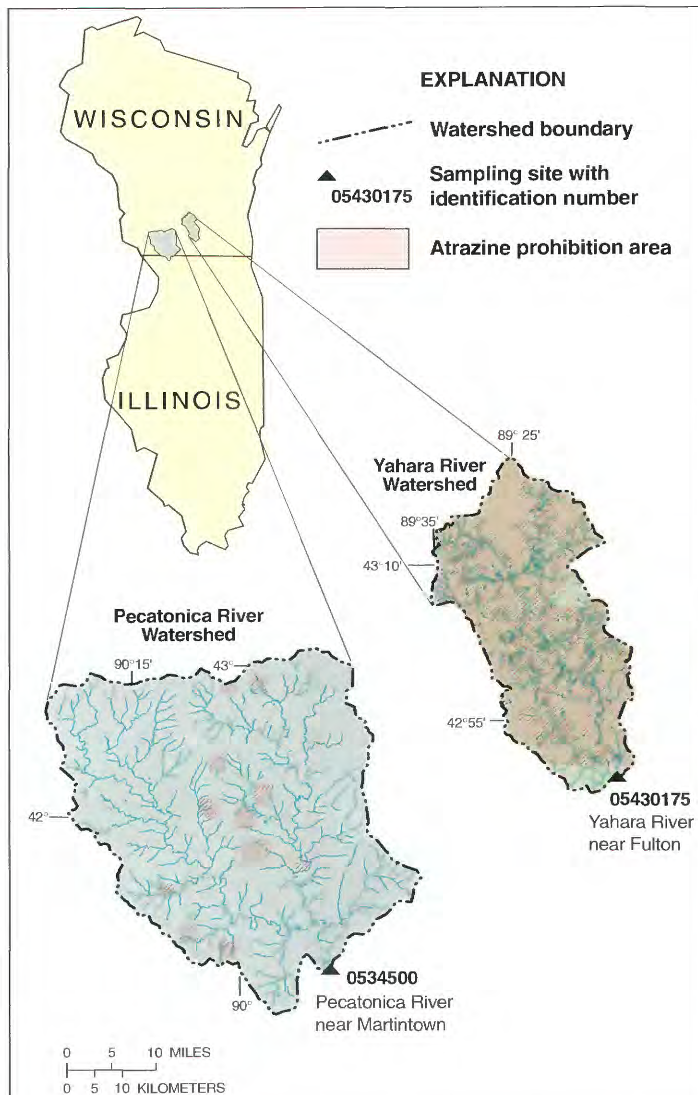

Figure 1. Location of sampling sites for herbicides.

Results

At the Pecatonica site, atrazine was the most frequently detected herbicide (88 percent) in the 17 samples collected (fig. 2). Metolachlor was the next most frequently detected herbicide (76 percent). Acetochlor and cyanazine were detected in 59 percent of the samples. Alachlor and alachlor ESA were detected in only 18 percent and 12 percent, respectively, of samples collected.

Data for the Yahara River show that atrazine and acetochlor were the most frequently detected herbicides. Fifty-seven percent of the samples had concentrations of these herbicides above the laboratory analytical detection limit (fig. 2). Cyanazine and metolachlor were the next most detected herbicides; 43 percent of the samples were above the laboratory analytical detection limit. Alachlor and alachlor ESA were detected in 29 percent and 14 percent, respectively, of 14 samples collected.

[1] U.S. Geological Survey
[2] Wisconsin Department of Agriculture, Trade, and Consumer Protection

Table 1. Land use characteristics for the two herbicide sampling watersheds (mi², square miles; land use data from DATCP)

Station Name	USGS Station Number	Drainage Area (mi²)	Percent land use or land cover		
			Agricultural land[1]	Other[2]	Atrazine Prohibition Area
Pecatonica River at Martintown	05434500	1034	96	4	4
Yahara River near Fulton	05430175	517	75	25	94

[1] Includes row crops and pasture [2] Includes forest, lakes, wetlands and urban areas

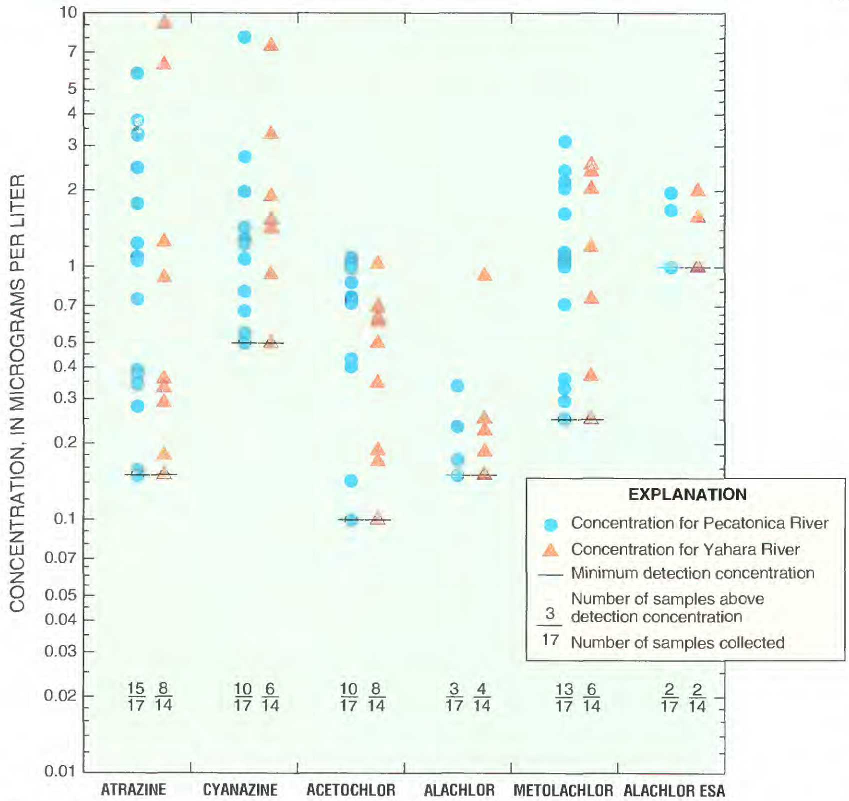

Figure 2. Herbicide concentration, minimum detection concentration, number of samples above the minimum detection concentration, and number of samples collected at the Pecatonica and Yahara Rivers.

The maximum herbicide concentration for the Pecatonica River was 8.07 µg/L (micrograms per liter) for cyanazine on June 17, 1996 (fig. 2 and fig. 3). The next highest concentration detected was for atrazine (with metabolites)—5.8 µg/L on May 29 (fig. 2 and fig. 3). The median concentrations of herbicides in the Pecatonica River samples were 0.90 µg/L atrazine, 0.86 µg/L metolachlor, 0.61 µg/L cyanazine, and 0.27 µg/L acetochlor. Median concentrations are reported here only for herbicides for which less than 50 percent of the sample concentrations were below the detection limit.

In comparison, the median concentration of atrazine for three predominantly agricultural sites in eastern Wisconsin—Duck Creek, North Branch Milwaukee River, and the Milwaukee River—ranged from approximately 0.04 µg/L to 0.30 µg/L (Sullivan and Richards, 1996). Median cyanazine and metolachlor concentrations at the Pecatonica River were also higher than at these three sites.

At the Yahara River, atrazine (with metabolites) had the highest concentration—9.93 µg/L on June 19 (fig. 2 and fig. 3). Cyanazine had the next highest concentration—7.43 µg/L on June 17. The maximum atrazine concentration detected in samples from the Yahara River was greater than that detected in eastern Wisconsin streams, but less than that for streams monitored in Indiana and Nebraska (Sullivan and Richards, 1996). The median concentrations of herbicides in the Yahara River samples were 0.18 µg/L for atrazine, and 0.17 µg/L for acetochlor. The median atrazine concentrations for the Yahara River samples were within the range of median atrazine concentrations for the three streams in eastern Wisconsin mentioned above.

Herbicide concentrations in the Pecatonica and Yahara Rivers differed from those in other streams in Wisconsin and streams in other midwestern states. The maximum cyanazine concentration for the Pecatonica and the Yahara Rivers was greater than that detected in streams in eastern Wisconsin, Indiana, and Nebraska. The median atrazine concentrations for both the Pecatonica and Yahara Rivers were less than the median concentrations for watersheds in Indiana and Nebraska that drain extensive corn and soybean agricultural areas. Watersheds in Minnesota and Missouri, where grazing and small grain farming are the major agricultural activities, had lower median atrazine concentrations than either the Yahara or Pecatonica Rivers. The median cyanazine concentration for the Pecatonica River was greater than that detected in streams in Indiana, Nebraska, Minnesota, and Missouri. The Pecatonica had lower median metolachlor concentrations however, compared to a Nebraska watershed (Sullivan and Richards, 1996).

The concentration of herbicides that are transported to a stream is a function of the physiochemical properties, such as water solubility, soil half-life, and soil sorption coefficient of the herbicides; timing and rate of the herbicide application; and overland runoff from rainfall and farming practices (Goolsby and Pereira, 1995). Peak herbicide concentration in streams is dependent upon the timing of the herbicide application and when rainfall occurs in amounts great enough to generate overland runoff. Concentrations of all herbicides were less than the laboratory analytical detection limit in late June and continued to stay below the analytical detection limit until data collection ended in July. The streamflow and the concentrations of six of the herbicides detected in samples collected at the Pecatonica and the Yahara Rivers and the approximate period of herbicide application are shown in figure 3.

At the Pecatonica River, the peak concentration of atrazine was detected in late May to early June, whereas the peak cyanazine and metolachlor concentrations occurred during a major runoff period in the middle of June (fig. 3). The monthly mean streamflow for the Pecatonica River at Martintown during May was 22 percent greater than the mean monthly flow for the period of record (1940–95) (Holmstrom and others, 1997). During June, streamflow was 122 percent greater and during July, it was 127 percent greater than mean monthly flow for the period of record.

At the Yahara River, atrazine, cyanazine, and metolachlor concentrations peaked in the middle of June (fig. 3). The monthly mean streamflow at the Yahara River during May was 20 percent greater than the mean monthly flow for the period of record (1977–95); during June it was 224 percent greater and during July it was 99 percent greater (Holmstrom and others, 1997).

The load for 5 of the 6 herbicides studied was determined for both rivers. Herbicide load is the mass transport of the herbicide by the river and is a function of water discharge and concentration of the herbicide. The integration method was used to determine the load at each site (Porterfield, 1972). For samples that contained herbicide concentrations below the laboratory analytical detection limit, the concentrations were set to one-half the analytical detection limit for the purpose of load calculation. The daily loads were summed for the period May 15 to July 15 (fig. 4). The calculated herbicide loads at the Pecatonica River ranged from 47.2 lbs (pounds) of alachlor to 484 lbs for atrazine with metabolites. For the Yahara River, loads ranged from 36.1 lbs of alachlor to 289 lbs for atrazine with metabolites (fig. 4). The unit area loads (load divided by drainage area) were greater in the Yahara River watershed than in the Pecatonica River watershed for all the herbicides except for metolachlor (fig. 4). The unit area load for the Pecatonica River ranged from 0.05 lbs/mi² (pounds per square mile) for alachlor to 0.47 lbs/mi² for

Table 2. Estimated pounds of pesticide active ingredient applied during the spring of 1996 (application data from DATCP)

Watershed	Estimated pounds of pesticide active ingredient applied in the spring of 1996				
	Acetochlor	Alachlor	Atrazine	Metolachlor	Cyanazine
Pecatonica River	42,000	32,000	85,000	106,000	88,000
Yahara River	26,000	20,000	3,200	66,000	56,000

atrazine with metabolites. For the Yahara River, unit area loads ranged from 0.07 lbs/mi^2 for alachlor to 0.55 lbs/mi for atrazine with metabolites (fig. 4).

For the most part, the unit area loads of herbicides in the Pecatonica and Yahara Rivers were consistent with the application rates of herbicides for each watershed except for atrazine (table 2, fig. 4). Alachlor and acetochlor were the least-used herbicides and had the lowest unit area loads for both watersheds (fig. 4). In the Yahara River watershed, metolachlor was applied at rates higher than cyanazine but the unit area load for metolachlor was less than that for cyanazine (fig. 4). In the Pecatonica River watershed, metolachlor was the most heavily applied herbicide and had the second highest unit area load (fig. 4). In both watersheds, atrazine had the highest unit area load as compared to the other herbicides but was the least-applied herbicide in the Yahara River watershed and the third-most herbicide applied in the Pecatonica River watershed (table 2, fig. 4).

Ninety-four percent of the Yahara River watershed is in the atrazine prohibition area (fig. 1). Because much less atrazine is applied in this watershed compared to the Pecatonica River watershed (table 2), the unit area loads would be expected to be less. It is important to note, however, that the area just upstream from the sampling site is not in the atrazine prohibition area (fig. 1). Thus the high concentrations of atrazine detected in June—9.93 µg/

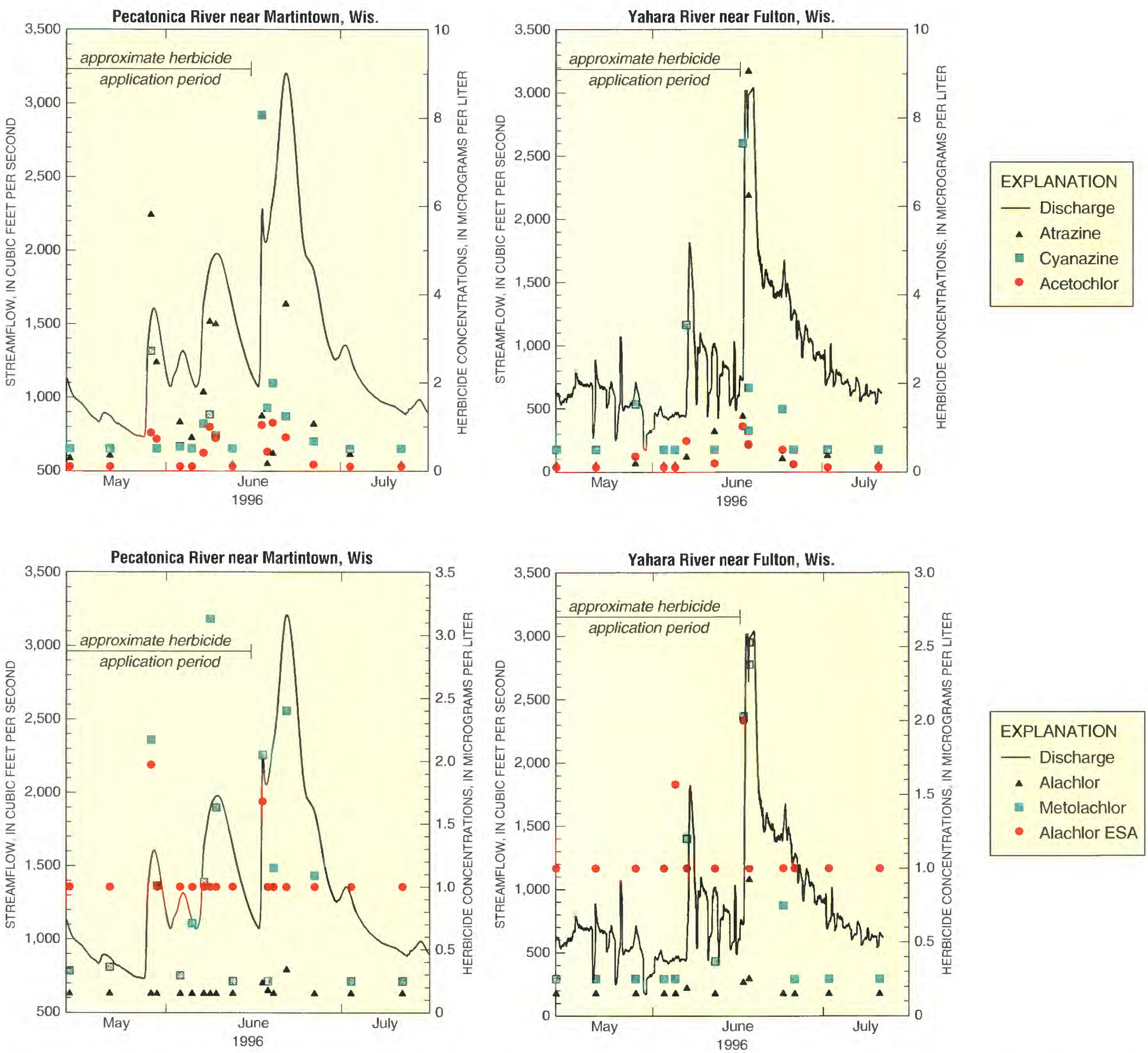

Figure 3. Discharge hydrographs, herbicide concentration, and period of herbicide application for the Pecatonica and Yahara Rivers from May 15 to July 15, 1996. (Laboratory analytical detection limit for acetochlor is 0.10 µg/L; for atrazine and alachlor is 0.15 µg/L; for metolachlor is 0.25 µg/L; for cyanazine is 0.50 µg/L and for alachlor ESA is 1.0 µg/L.)

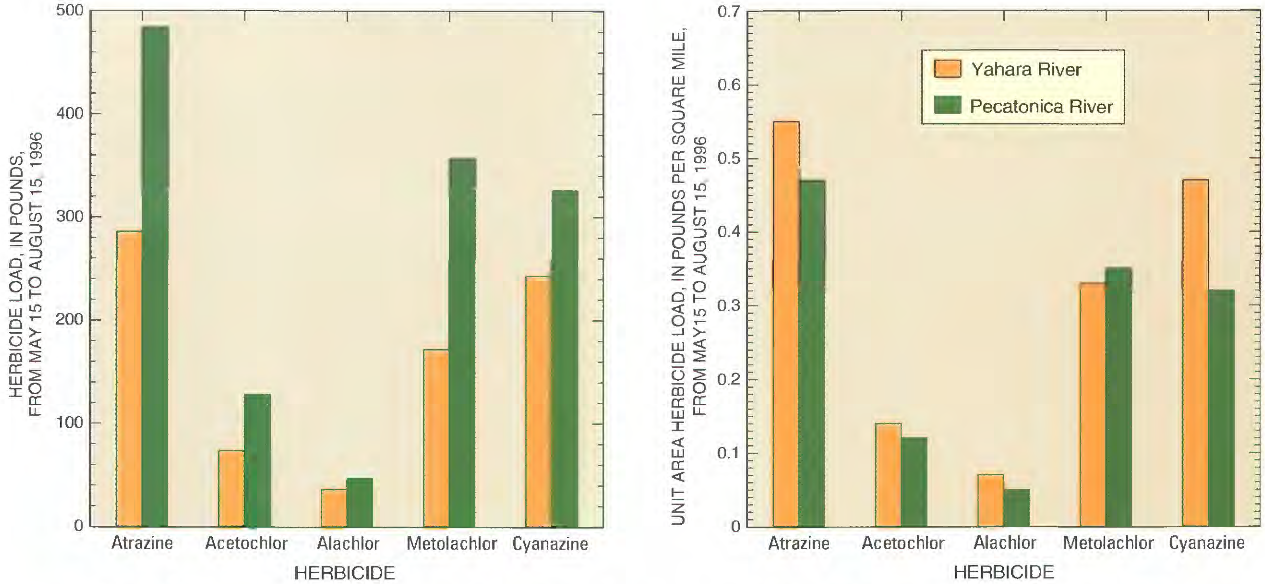

Figure 4. Herbicide loads and unit area loads for the Pecatonica and Yahara Rivers from May 15 to July 15, 1996.

L and 6.25 µg/L—may be a result of herbicides applied near the sampling site, and may not be representative of the whole watershed.

The median atrazine concentration for the Yahara River samples was less than that for the Pecatonica River samples. The higher unit area load for the Yahara River may be a result of the extreme streamflow in June (224 percent greater than the long-term mean monthly flow for June). Seventy-nine percent of the atrazine load for the study period was transported in 5 days, or 8 percent of the days monitored at the Yahara River.

Conclusions

In general, this study showed that the most heavily applied agricultural herbicides were detected more frequently and at higher concentrations in surface waters than herbicides which were less commonly used or applied at very low rates. Herbicide loadings to surface water for alachlor, acetochlor, cyanazine and metolachlor roughly correspond to the total amount of the specific herbicide applied within the watershed. Both watersheds showed a brief (two- to four- week) period of herbicide detections and elevated concentrations. This result has been seen in other studies and is probably related to the moderate to high solubility and relatively short half-life of the herbicides found, as well as the lack of ground cover in the weeks after planting, which maximizes surface-water runoff.

Unexpectedly, atrazine was found at similar concentrations and loadings in the two watersheds despite the near total prohibition of its use in the Yahara River watershed. Illegal use of atrazine in the Yahara River watershed was not considered to be the reason for the unexpected atrazine unit area loads. A study that determined farmers' compliance with atrazine restrictions in Wisconsin, including Atrazine Prohibition Areas, showed that farmers had a greater than 98 percent compliance rate with atrazine prohibition areas (Nowak and others, 1993). Unusually heavy rainfall (and subsequent runoff) in the Yahara River watershed preceding and during the study period, and the presence of an area just upstream of the sampling point in which atrazine use is allowed, may account for the higher atrazine unit area loads for the Yahara River watershed as compared to the Pecatonica River watershed. During the sampling period, the Yahara River watershed had a similar amount of surface-water discharge as the Pecatonica River watershed, despite having about 50 percent of the drainage area. Although the atrazine use area upstream from the Yahara River watershed sampling point comprises only four percent of the watershed, the abnormally heavy rains falling on fields just recently treated with atrazine could have resulted in very high rates of runoff, which in turn, accounted for the high atrazine loadings in the watershed.

Both the Yahara and Pecatonica watersheds experienced much greater than average surface-water discharge during the 1996 sampling period and this may have skewed some of the study results, especially those for atrazine. To shed further light on the issues brought up by this study, USGS and DATCP plan to continue this study in 1997. To address the unexpected atrazine results in the Yahara River watershed, an additional sampling point will be located in the upper third of the watershed, within an atrazine prohibition area.

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For more information, please contact:

District Chief
U.S. Geological Survey
8505 Research Way
Middleton, WI 53562
(608) 828-9901

Layout and illustrations: Michelle Greenwood
Text editing: Gail Moede
Banner graphic: Karen Lonsdorf