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Herbicides in the Pecatonica, Trempealeau, and Yahara Rivers in Wisconsin, May 1997–July 1998

Introduction

In 1997, Wisconsin farmers applied 8.7 million pounds of herbicides on corn. The five most commonly applied herbicides (in lb (pounds) of active ingredient per acre) on corn in 1997 were atrazine, metolachlor, acetochlor, alachlor and cyanazine. A 1996 study by the U.S. Geological Survey (USGS) and the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) found that the most heavily applied agricultural herbicides were detected more frequently and at higher concentrations in the Pecatonica and Yahara Rivers in southern Wisconsin than the less heavily applied herbicides (Graczyk and Vanden Brook, 1997). The calculated herbicide loads[a] from May 15 to July 15, 1996 at the Pecatonica River ranged from 47.2 lb of alachlor to 484 lb of atrazine. For the Yahara River, loads ranged from 36.1 lb of alachlor to 289 lb of atrazine. The yields[b] (load per square mile) for atrazine were similar in the two watersheds. This result was unexpected because the use of atrazine is prohibited on 94 percent of the Yahara River Watershed, but on only 4 percent of the Pecatonica River watershed. The unexpected atrazine result led to a continuation of the study in 1997 and 1998, when samples were collected again at the two sites sampled in 1996, and at a site in the upper third of the Yahara River Watershed that is entirely under atrazine use prohibition. For comparison purposes, a site in west-central Wisconsin also was sampled to determine herbicide loads and yields in another geographic area in the state.

For this report, atrazine is defined as the sum of atrazine and its degradate, deethylatrazine. The atrazine degradates deisopropylatrazine and diaminoatrazine were excluded from the analysis because they also can be formed by the breakdown of other triazine herbicides and may obscure the effects of atrazine management.

This fact sheet summarizes herbicide concentrations in samples collected from the Pecatonica River at Martintown, the Trempealeau River at Dodge, and the Yahara River at Windsor and near Fulton, for two time periods—May 15 to July 15—in 1997 and 1998. Herbicide loads and yields are listed for these four watersheds and comparisons are made among watersheds, and between data collected in 1997 and 1998. The results of this study are also compared to data from the Pecatonica and Yahara Rivers for May 1996–July 1996 (Graczyk and Vanden Brook, 1997).

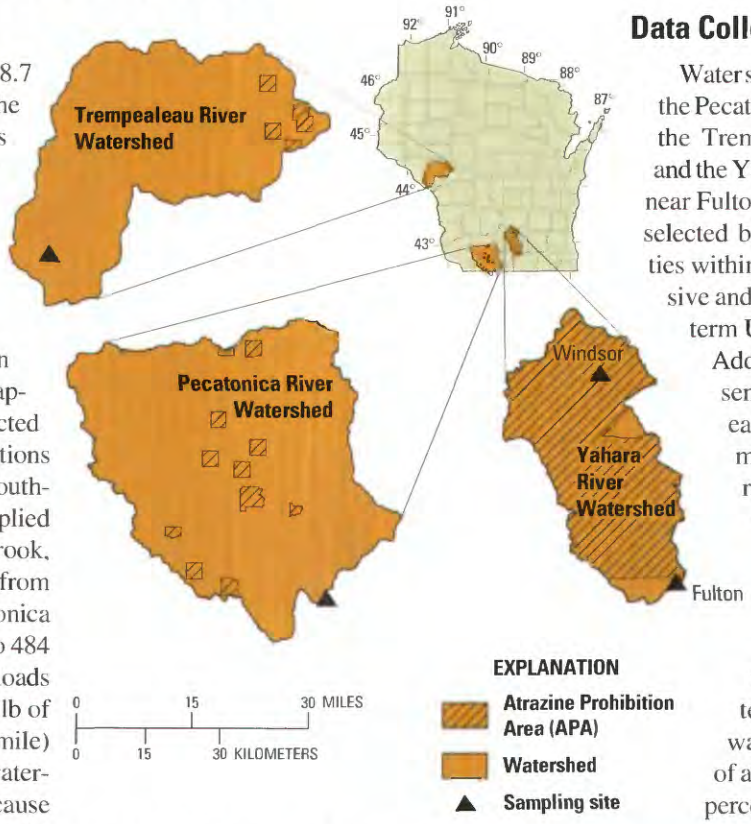


Figure 1. Location of sampling sites for herbicides.

Data Collection

Water samples were collected from the Pecatonica River at Martintown, the Trempealeau River at Dodge, and the Yahara River at Windsor and near Fulton (fig 1.). These sites were selected because agricultural activities within the watersheds are extensive and because the sites are long-term USGS streamflow stations. Additionally, the sites represent different geographic areas in the state, and the estimated atrazine application rates are different in the four watersheds. The use of atrazine is prohibited in 2.5 percent of the Trempealeau River Watershed and in 4 percent of the Pecatonica River Watershed. In the Yahara River watershed, however, the use of atrazine is prohibited in 100 percent of the watershed above

Atrazine was the most frequently detected herbicide in water samples collected from the Pecatonica and Trempealeau Rivers from mid-May through mid-July in 1997 and 1998. At two sites on the Yahara River, however, the herbicide most frequently detected was acetochlor. The loads of alachlor, acetochlor, cyanazine, and melachlor transported in the Pecatonica and the Yahara Rivers roughly correspond to the amounts of each of these herbicides applied (principally to corn) within the watersheds. Data from the Yahara River watershed indicate that the prohibition of the use of atrazine throughout that watershed has been effective in significantly reducing the amount of atrazine being transported by the river.

[a] Load is a general term that refers to the material or constituent in solution, suspension and (or) in transport.

[b] Yield is a measurement of load in discharge per unit area.

Windsor and in 94 percent of the watershed above Fulton. The drainage area, land use, and percentage of each watershed under atrazine prohibition is listed in table 1. The amounts of pesticide active ingredient applied in each watershed are listed in table 2.

Samples were collected at each site once per week from May 15 to July 15 in 1997 and 1998. These weekly samples were collected without regard to streamflow conditions at the site. Additional samples were collected daily during storm runoff (defined as an increase in instantaneous streamflow by at least 50 ft^3/s (cubic feet per second) more than the daily mean streamflow of the previous day). Daily sampling was continued until the streamflow began to decrease.

Water samples were collected by methods outlined by Edwards and Glysson (1986). The sampler and churn splitter used to collect and split the sample were cleaned by methods found in Shelton (1994). The samples were analyzed for commonly used herbicides at the DATCP water quality laboratory. Quality assurance (QA) samples collected and processed near the beginning and at the conclusion of the sampling periods had no detectable concentrations for any of the herbicides being analyzed. The QA sampling results are on file at the U.S. Geological Survey Water Resources Division office in Middleton, Wis. and the results are available on request.

Herbicide concentrations and loads

Data will be presented for 7 of the 12 analyzed herbicides and degradates at the 4 sites. The concentrations of five herbicides (acetochlor, alachlor, atrazine, cyanazine, and metolachlor) and two degradates (deethylatrazine and alachlor-ESA) were above the detection limit. The five herbicides were the most commonly applied herbicides within the watersheds. As mentioned previously, deethylatrazine detections

Table 1. Land-use characteristics for the four herbicide-sampling watersheds [mi^2, square miles; land-use data from Wisconsin Department of Agriculture, Trade, and Consumer Protection]

Station name	USGS station number	Drainage area (mi^2)	Percent land use or land cover		
			Agricultural land[1]	Other[2]	Atrazine prohibition area
Pecatonica River at Martintown	05434500	1,034	31	69	4
Trempealeau River at Dodge	05379500	643	16	84	2.5
Yahara River at Windsor	05427718	73.6	58	42	100
Yahara River near Fulton	05430175	517	34	66	94

[1] Includes row crops only. [2] Includes pastures, forest, lakes, wetlands and urban areas.

Table 2. Estimated application of pesticide active ingredient during spring 1997 and 1998 [application data from Wisconsin Department of Agriculture, Trade, and Consumer Protection]

	Amounts of pesticide active ingredient applied (pounds)									
	Acetochlor		Alachlor		Atrazine		Metolachlor		Cyanazine	
Watershed	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Pecatonica River	46,000	45,000	45,000	16,000	78,000	71,000	82,000	83,000	32,000	25,000
Trempealeau River	20,000	20,000	20,000	7,000	35,000	33,000	34,000	35,000	14,000	12,000
Yahara River at Windsor	3,600	3,600	3,500	1,200	0	0	6,300	6,500	2,500	2,000
Yahara River near Fulton	26,000	26,000	25,000	9,000	3,000	3,000	45,000	46,000	18,000	14,000

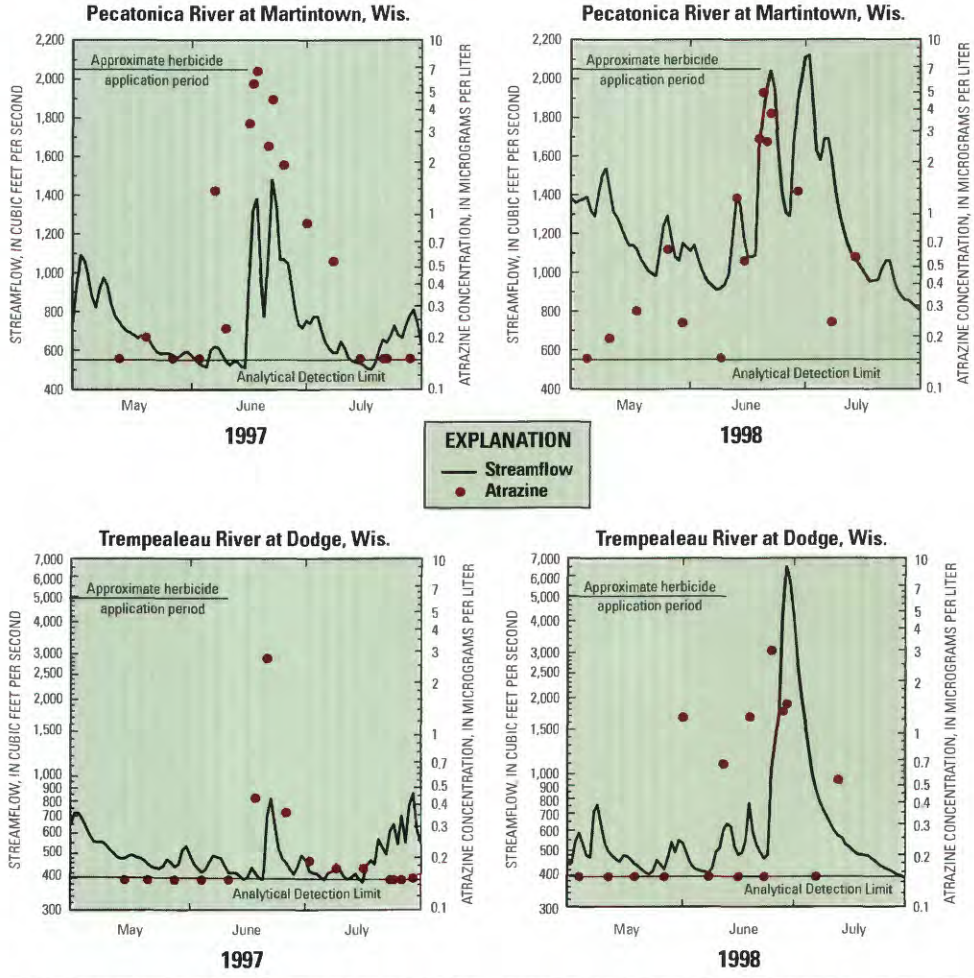


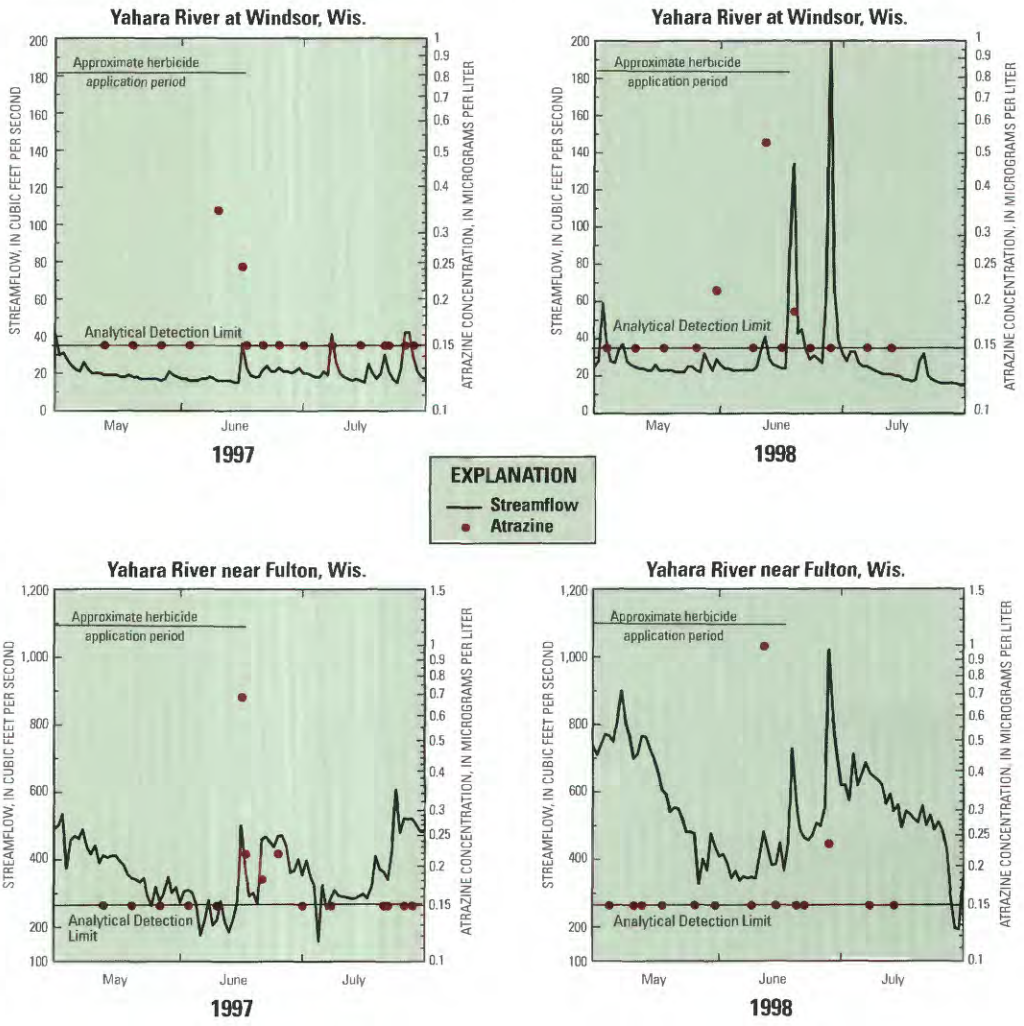
Figure 2a. Streamflow hydrographs, atrazine plus metabolite concentration, and period of herbicide application for the Pecatonica River at Martintown, Wis. and the Yahara River near Fulton, Wis., May 15–July 15, 1997 and 1998 (laboratory analytical detection limit for atrazine is 0.15 µg/L).

are included as part of reported atrazine concentrations. The maximum, minimum, mean, and median concentrations of herbicides in samples above detection limit and number of samples collected are shown in table 3. The loads and yields of these herbicides are shown in table 4.

At the Pecatonica River at Martintown, atrazine was the most frequently detected herbicide in 1997 (73 percent of samples) and in 1998 (93 percent of samples) (table 3). The peak concentrations of atrazine depend on the timing of the herbicide application and the timing of rainfall in amounts great enough to generate overland runoff. Atrazine concentration was less than the laboratory analytical detection limit in May and early June 1997 except in three samples collected during small runoff periods (fig 2a). The maximum concentration of atrazine detected in 1997 was in samples collected in mid- to late June during two major runoff periods. In July 1997, the atrazine concentrations were below the analytical detection limit despite a runoff event in late July. No atrazine was detected in the first sample collected in 1998 (fig. 2a). As soon as rain was sufficient to generate overland runoff, however, the samples contained detectable concentrations of atrazine. The maximum concentration of atrazine detected in 1998 was in a sample collected during the first major runoff period in mid-June. Metolachlor was the next most frequently detected herbicide in 1997 (67 percent) and in 1998 (57 percent) (table 3). Acetochlor was detected in 33 percent of samples in 1997 and in 50 percent of samples in 1998 (table 3).

At the Trempealeau River at Dodge, atrazine was detected at concentrations above the analytical detection limit in 54 and 50 percent of samples in 1997 and 1998, respectively (table 3; fig 2a). Storm runoff in late June 1997 resulted in the greatest atrazine concentration (fig. 2a). Smaller runoff events in early July resulted in atrazine concentrations above the analytical detection limit; but in late July, the atrazine concentration was less than the analytical detection limit even with significant overland runoff. In 1998, atrazine concentrations were scattered above and below the analytical detection limit in May and June. A major runoff event in late June and early July resulted in maximum atrazine concentrations (fig. 2a).

Figure 2b. Streamflow hydrographs, atrazine plus metabolite concentration, and period of herbicide application for the Yahara River at Windsor, Wis. and the Trempealeau River at Dodge, Wis., May 15–July 15, 1997 and 1998 (laboratory analytical detection limit for atrazine is 0.15 µg/L).



Of the 24 samples collected in 1997 and 1998 at the Yahara River at Windsor (12 samples each year), more than 50 percent had no detectable herbicide concentrations. Nevertheless, a cyanazine concentration of 12.9 *ug*/L in one sample was the highest concentration of any herbicide at any of the four sites in either year (table 3). This may be due to the increased use of cyanazine as a substitute for atrazine in a watershed with a complete atrazine use prohibition. The next greatest concentration was 11.6 *ug*/L of metolachlor at the Pecatonica River at Martintown in 1997.

At the Yahara River near Fulton, concentrations of atrazine were below the analytical detection limit for more than 50 percent of the samples (table 3). Three storms in early June 1997 resulted in detectable atrazine concentrations but in all the remaining samples collected that year, concentrations were below the analytical detection limit despite several runoff events in late June and July (fig. 2b). In 1998, atrazine concentrations were above the analytical detection limit in two samples.

The load (a function of streamflow and constituent concentration) for each of the five most heavily applied herbicides and alachlor-ESA was determined for the Pecatonica, Trempealeau and Yahara Rivers. The integration method (Porterfield, 1972) was used to determine the loading at each site. Herbicide concentrations were linearly interpolated from sample to sample. Samples in which herbicide concentrations were below the laboratory analytical detection limit were set to one-half the detection limit for the purpose of load computation. The daily loads were summed for the period May 15 to July 15 in 1997 and 1998, and are presented in table 4 and figure 3.

At the Pecatonica River at Martintown, the greatest herbicide loads were those of alachlor-ESA (an alachlor degradate) and atrazine. In 1998, 469 lb of alachlor-ESA was transported, and the atrazine load was 340 lb (table 4, fig 3).

Table 3. Summary statistics for samples collected in 1997 and 1998 [all data except numbers of samples are concentrations in micrograms per liter; ---, no data; means and medians reported only if more than 50 percent of samples had concentrations above the detection limit or all samples had concentrations less than detection limit]

Pecatonica River at Martintown

Statistic	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Maximum	6.66	4.99	0.93	0.84	0.46	<0.15	11.6	3.41	3.76	0.66
Minimum	<0.15	<0.15	<0.10	<0.10	<0.15	<.15	<0.25	<0.25	<0.50	<.50
Mean	1.90	1.40	---	0.25	---	<.15	1.79	1.02	---	---
Median	.90	0.63	---	0.11	---	<.15	.43	.51	---	---
Samples above detection limit	11	13	5	7	1	0	10	8	7	3
Samples collected	15	14	15	14	15	14	15	14	15	14

Trempealeau River at Dodge

Statistic	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Maximum	2.75	3.00	0.60	0.34	<0.15	0.56	4.05	2.54	2.14	1.04
Minimum	<0.15	<0.15	<.10	<.10	<.15	<.15	<0.25	<0.25	<0.50	<0.50
Mean	.44	.75	---	---	<.15	---	---	---	---	---
Median	.17	.34	---	---	<.15	---	---	---	---	---
Samples above detection limit	6	7	1	1	0	2	2	6	2	4
Samples collected	11	14	11	14	11	14	11	14	11	14

Yahara River at Windsor

Statistic	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Maximum	0.34	0.53	1.4	7.00	0.22	0.24	<0.25	2.22	0.74	12.9
Minimum	<.15	<.15	<0.10	<0.10	<.15	<.15	<.25	<0.25	<.50	<0.50
Mean	---	---	---	---	---	---	<.25	---	---	---
Median	---	---	---	---	---	---	<.25	---	---	---
Samples above detection limit	2	3	2	5	1	2	0	5	1	4
Samples collected	12	12	12	12	12	12	12	12	12	12

Yahara River near Fulton

Statistic	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Maximum	0.69	0.99	1.4	0.84	0.33	<0.15	2.27	2.78	2.15	1.88
Minimum	<.15	<.15	<0.10	<.10	<.15	<.15	<0.25	<0.25	<0.50	<0.50
Mean	---	---	---	---	---	<.15	---	---	---	---
Median	---	---	---	---	---	<.15	---	---	---	---
Samples above detection limit	4	2	3	6	1	0	4	3	3	2
Samples collected	12	13	12	13	12	13	12	13	12	13

At the Trempealeau River, 407 lb of alachlor-ESA was transported in 1998. This was the largest load of any herbicide transported in either 1997 or 1998 in this watershed. In 1998, 219 lb of atrazine was transported, for an increased load of about 4 times that in 1997.

At the Yahara River at Fulton, the greatest load was that for alachlor-ESA at 332 lb in 1998 (table 4, fig. 3). Only 10.1 lb to 14.8 lb of atrazine was transported in 1997 and 1998, respectively.

Alachlor-ESA was the dominant herbicide transported from the watershed above the Yahara River at Windsor site in 1997 and 1998 (table 4, fig. 3). Only 0.74 lb of atrazine was transported in 1997, and 1.13 lb of atrazine was transported in 1998 (table 4). The amount of atrazine transported from the watershed above Windsor was an order of magnitude less than that transported at Fulton, and 2 to 3 orders of magnitude less than the amount of atrazine being transported by the Pecatonica and Trempealeau Rivers.

Herbicide yields from the 4 watersheds are shown in table 4 and figure 4. At the Pecatonica River, the yield of atrazine was 1.02 lb/mi^2 (pounds per square mile of row crops) in 1997, and 1.08 lb/mi^2 in 1998. The greatest yield was 1.49 lb/mi^2 for alachlor-ESA in 1998.

As at the other three sites, the yield of alachlor-ESA (3.54 lb/mi^2) at the Trempealeau River was the greatest among all herbicides monitored (table 4, fig. 4). The second greatest yield at the Trempealeau River was for atrazine (1.90 lb/mi^2) in 1998; this was the greatest yield for atrazine in 1997 and 1998 among all the sites.

At the Yahara River at Fulton, the greatest yield was for alachlor-ESA, at 2.02 lb/mi^2 in 1998. The atrazine yield was 0.06 lb/mi^2 in 1997 and 0.09 lb/mi^2 in 1998.

At the Yahara River at Windsor, the alachlor-ESA yield was 2.46 lb/mi^2 in 1998. The atrazine yield at the Yahara River at Windsor was 0.02lb/mi^2 in 1997 and 0.03 lb/mi^2 in 1998. This is an order of magnitude

Table 4. Herbicide loads and yields for the Pecatonica, Yahara, and Trempealeau Rivers for 1997 and 1998 [loads in pounds; yields in pounds per square mile of row crops]

Herbicide loads

	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine		Alachlor-ESA	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Pecatonica River at Martintown	320	340	37.8	59.8	19.8	33.4	236	293	163	125	221	469
Trempealeau River at Dodge	48.4	219	12.7	18.0	11.5	28.4	54.7	146	61.4	152	111	407
Yahara River at Windsor	.74	1.13	.74	5.96	.66	.99	1.55	7.01	3.26	9.57	27.3	76.4
Yahara River near Fulton	10.1	14.8	8.4	14.4	8.5	13.2	22.1	36.6	36.6	49.3	168	332

Herbicide yields

	Atrazine		Acetochlor		Alachlor		Metolachlor		Cyanazine		Alachlor-ESA	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Pecatonica River at Martintown	1.02	1.08	0.12	0.19	0.06	0.11	0.75	0.93	0.52	0.40	0.70	1.49
Trempealeau River at Dodge	.42	1.90	.11	.16	.10	.25	.48	1.27	.53	1.32	.97	3.54
Yahara River at Windsor	.02	.03	.02	.19	.02	.03	.05	.23	.11	.31	.88	2.46
Yahara River near Fulton	.06	.09	.05	.09	.05	.08	.13	.22	.22	.30	1.02	2.02

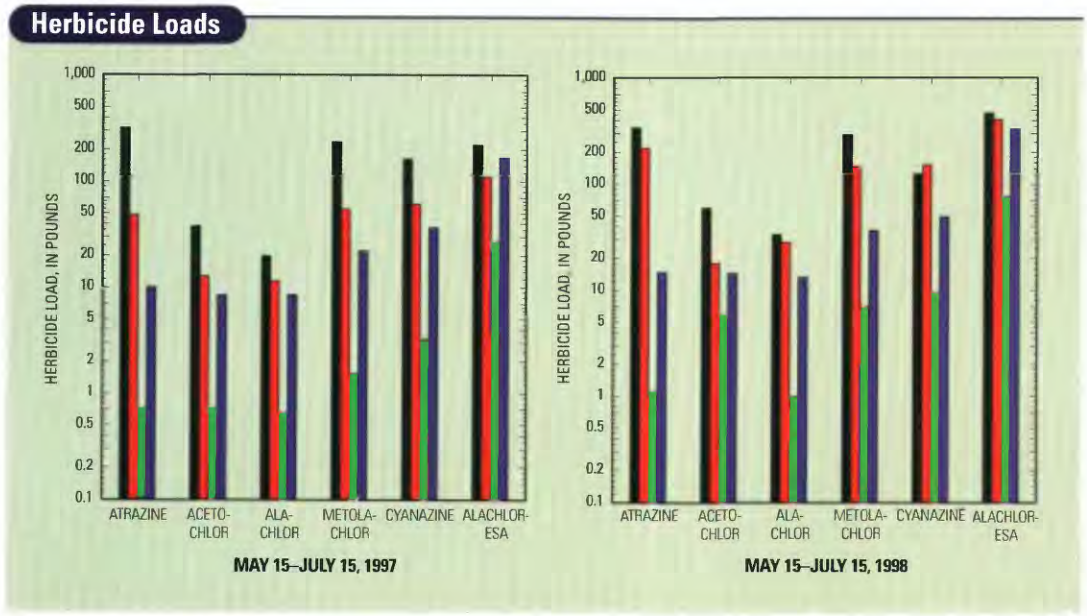


Figure 3. Herbicide loads for the Pecatonica, Yahara and Trempealeau Rivers for for the period May 15 to July 15 in 1997 and 1998.

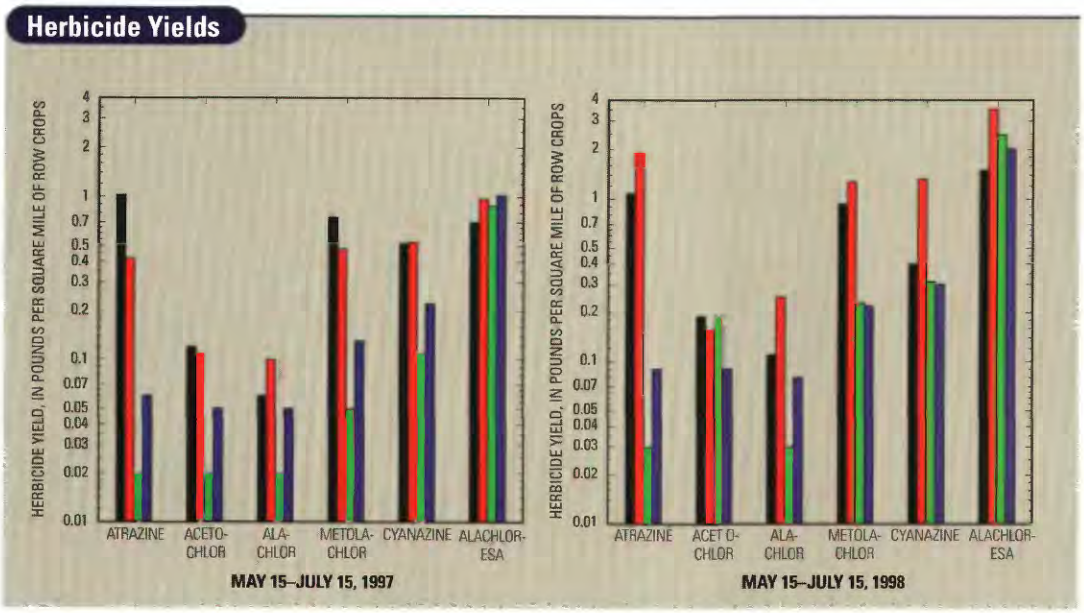


Figure 4. Herbicide yields for the Pecatonica, Yahara and Trempealeau Rivers for the period May 15 to July 15 in 1997 and 1998.

EXPLANATION

- **Pecatonica River at Martintown**
- **Trempealeau River at Dodge**
- **Yahara River at Windsor**
- **Yahara River near Fulton**

less than the yield for the Pecatonica River at Martintown. The yields for atrazine at the Yahara River at Windsor are similar to yields for the Yahara River at Fulton in 1997 and 1998.

Influences on herbicide transport

Current understanding of herbicide transport indicates that the concentration of a herbicide and the resultant load that is transported in streamwater is a function of the physiochemical properties of the herbicide, such as water solubility, soil half-life, and soil sorption coefficient; timing of the application; and rates of water/herbicide runoff that vary in response to rainfall and farming practices (Goolsby and Pereira, 1995). The results of this study confirm that the load is related to the amount of herbicide applied for certain compounds, the timing of that application, and the occurrence of runoff-producing rainstorms. The study also verifies that prohibiting the use of a herbicide in a given area is effective in reducing the load despite many years of previous use.

While the load of a given herbicide at a stream site tends to be related to the amount of that herbicide applied in the watershed above that site, some comparisons among the five active ingredients detected in this study can be made. The percentage of the triazine compounds (atrazine and cyanazine) that reaches the rivers (as computed load) in each watershed was the greatest (0.2 to 1.3 percent). The percentage of acetochlor reaching the rivers (as computed load) in each watershed was the least (0.08 to 0.13 percent), with the exception of the Pecatonica and Trempealeau watersheds in 1997, when the percentage of alachlor was the least reaching the rivers (as computed load).

The timing of herbicide transport to the rivers (as reflected by varying concentrations in streamwater) appears to be related to the timing of application of the herbicides and overland runoff generated by rainfall. As figures 2a and 2b show, atrazine is detected most frequently between late May and early July, and many of the peak concentrations occur at times of increased streamflow. These results are consistent for the other five compounds discussed.

Use prohibition appears to be effective in significantly reducing both the load and yield of atrazine reaching the Yahara River. The load of atrazine transported from the Yahara watershed above Windsor (100 percent use prohibition) is an order of magnitude less than that transported at Fulton (94 percent use prohibition) and 2 to 3 orders of magnitude less than the amount of atrazine being transported by the Pecatonica River (4 percent use prohibition) and Trempealeau River (2.5 percent use prohibition). More significantly, the yields for both the Windsor subwatershed and the Yahara Watershed as a whole are 1 to 2 orders of magnitude less than the yield for the Pecatonica and Trempealeau watersheds. Loads and yields for atrazine at the Yahara River at Windsor were lowest in 1997 and 1998 among all the study sites.

The results of this study can be compared to the results of a similar study (Graczyk and Vanden Brook, 1997) for some of the same watersheds for May 15–July 15, 1996. The low atrazine yields in the Yahara Watershed in 1997 and 1998 contrasts with an unexpected result from the 1996 study, in which the atrazine yield for the Yahara River near Fulton was greater than the yield for the Pecatonica River. For comparison, in 1997, the atrazine yield was 96 percent less than 1996, and in 1998, atrazine yield was 94 percent less than 1996 at the Yahara River near Fulton (table 4). Because 94 percent of the Yahara River watershed is under atrazine use prohibition, very little atrazine was expected to be transported by the stream. The surprisingly high yield in 1996 may have been due to two factors: the limited use of atrazine where it is allowed in the watershed, and greater than normal runoff during water year 1996. As for the first factor, a possible source of atrazine was a small area just upstream from the sampling site, where atrazine use was permitted. As for the second factor, the runoff for the period May 15 to July 15, 1996—3.44 inches—was the maximum runoff in the 20 years that streamflow data have been collected at the Yahara River near Fulton; the median runoff for May 15 to July 15 for the period of record is only 1.41 inches. Runoff for the same period in 1997 (1.44 inches) and 1998 (2.33 inches) was closer to the long-term median. Correspondingly, atrazine loads and yields were less in 1997 and 1998, when flow conditions were near normal at the Yahara River near Fulton. These reductions from the 1996 yields reflect not only less runoff during the sampling period but also a lower concentration of atrazine (table 3) in the collected samples.

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