

HERBICIDES AND TRANSFORMATION PRODUCTS IN SURFACE WATERS OF THE MIDWESTERN UNITED STATES¹

William A. Battaglin, Earl M. Thurman, Stephen J. Kalkhoff, and Stephen D. Porter²

ABSTRACT: Most herbicides applied to crops are adsorbed by plants or transformed (degraded) in the soil, but small fractions are lost from fields and either move to streams in overland runoff, near surface flow, or subsurface drains, or they infiltrate slowly to ground water. Herbicide transformation products (TPs) can be more or less mobile and more or less toxic in the environment than their source herbicides. To obtain information on the concentrations of selected herbicides and TPs in surface waters of the Midwestern United States, 151 water samples were collected from 71 streams and five reservoir outflows in 1998. These samples were analyzed for 13 herbicides and 10 herbicide TPs. Herbicide TPs were found to occur as frequently or more frequently than source herbicides and at concentrations that were often larger than their source herbicides. Most samples contained a mixture of more than 10 different herbicides or TPs. The ratios of TPs to herbicide concentrations can be used to determine the source of herbicides in streams. Results of a two-component mixing model suggest that on average 90 percent or more of the herbicide mass in Midwestern streams during early summer runoff events originates from the runoff and 10 percent or less comes from increased ground water discharge.

(KEY TERMS: water quality; hydrology; ground water; nonpoint source pollution.)

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INTRODUCTION

Prior to the 1950s, herbicides were not used extensively in agriculture in the U.S. Midwest. Farmers relied on crop rotation, tillage, and hand hoeing to limit the loss of crop yields to weeds (Mannion, 1995). By the early 1960s, many of today's most

commonly used herbicides (e.g., atrazine and 2,4-D) were available, but their use was limited and the application of insecticides (e.g., aldrin and diazinon) accounted for more than one-half of the total pesticide use in U.S. agriculture (Lin *et al.*, 1995). Between the 1960s and 1980s, herbicide use increased by more than 800 percent. Since peaking in the early 1980s, herbicide use has fluctuated with annual changes in planted corn and soybean acreage and has increased or decreased as new products have become available for use (Lin *et al.*, 1995; Aspelin and Grube, 1999; USDA, 1991 to 2001). The recent use of five herbicides analyzed in this study on corn, soybean, and potato acreage in eight Midwestern States is shown on Figure 1.

Most herbicide products applied to crops are adsorbed by plants or transformed (degraded) in the soil. However, small fractions (< 1-2 percent) are lost from fields and either move quickly to nearby streams via overland (or surface) runoff, near surface flow, or subsurface drains (Battaglin and Goolsby, 1997; Clark *et al.*, 1999; Capel *et al.*, 2001) or infiltrate slowly to ground water. Herbicides that remain in the soil or enter the slow moving ground water system have more time to be transformed than herbicides that move with runoff. Herbicide transformation products (TPs) can be more or less mobile and more or less toxic than their source herbicides. In a recent assessment of the toxicity of 89 pesticide TPs arising from 37 source pesticides, 70 percent of the TPs were equally toxic as or less toxic than their source compounds, and 30 percent were more toxic (Sinclair and Boxall, 2002).

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Monitoring and reconnaissance studies of Midwestern water resources have documented the widespread occurrence of herbicides in streams, reservoirs, ground water, and precipitation (Gilliom, 1985; Thurman *et al.*, 1992; Richards and Baker, 1993; Kolpin *et al.*, 1994; Goolsby and Battaglin, 1995; Scribner *et al.*, 1996; Larson *et al.*, 1997). Fewer studies have documented the importance of quantifying herbicide TPs in surface or ground water investigations. Initial research by the U.S. Geological Survey (USGS) focused on the formation, occurrence, and transport of only two herbicide TPs (deethylatrazine and deisopropylatrazine) in Midwestern streams and ground water (Adams and Thurman, 1991; Thurman *et al.*, 1992, 1994; Goolsby and Battaglin, 1993; Kolpin *et al.*, 1994). In later studies, alachlor ethane sulfonic acid (ESA) and cyanazine amide were added to the list of analytes being investigated (Goolsby *et al.*, 1993; Kolpin and Thurman, 1995; Thurman *et al.*, 1996; Scribner *et al.*, 1998). Several studies have documented the abundance of herbicide TPs in Iowa ground water and surface water (Kolpin *et al.*, 1995, 1998a, 2000; Kalkhoff *et al.*, 1998; Boyd, 2000; Porter *et al.*, 2001). Phillips *et al.* (1999) reported on the occurrence of metolachlor ESA and metolachlor oxanilic acid (OXA) in tile drains and streams in New York.

Objectives and Scope

The primary objective of this study is to identify the occurrence of the ESA and OXA TPs of acetochlor, alachlor, and metolachlor; deethylatrazine; deisopropylatrazine; hydroxy-atrazine; and cyanazine amide in streams that drain portions 17 Midwestern states during early summer runoff events and to describe their occurrence relative to that of their source compounds. Secondary objectives include documenting the prevalence of mixtures of herbicides and TPs in Midwestern streams and demonstrating the use of the ratio of herbicide TPs to source herbicides as a means for determining the origin (runoff or ground water) of those contaminants.

Specific hypotheses are listed below.

- (1) The ESA and OXA TPs of acetochlor, alachlor, metolachlor and hydroxy-atrazine will be detected in more than one-half of all samples.
- (2) The distribution of herbicide concentrations in Midwestern streams will correlate with the use of those herbicides in Midwestern states.
- (3) The ratios of the concentration of herbicide TPs to source herbicide will be smaller in pre-emergence samples than in post-emergence samples.
- (4) The ratios of the concentration of herbicide TPs to source herbicide can be used to estimate the proportion of herbicide coming from runoff versus that coming from ground water.
- (5) Samples will contain more than one herbicide or herbicide TP more frequently than they will contain one or fewer of these compounds.

Interpretation of this study's results is limited by spatial and temporal limitations of the data. Since only one or two samples were collected at each site, little can be concluded about the temporal variations in herbicide or TP occurrence or ratios, nor can their spatial variation outside of the Midwestern United States be quantified.

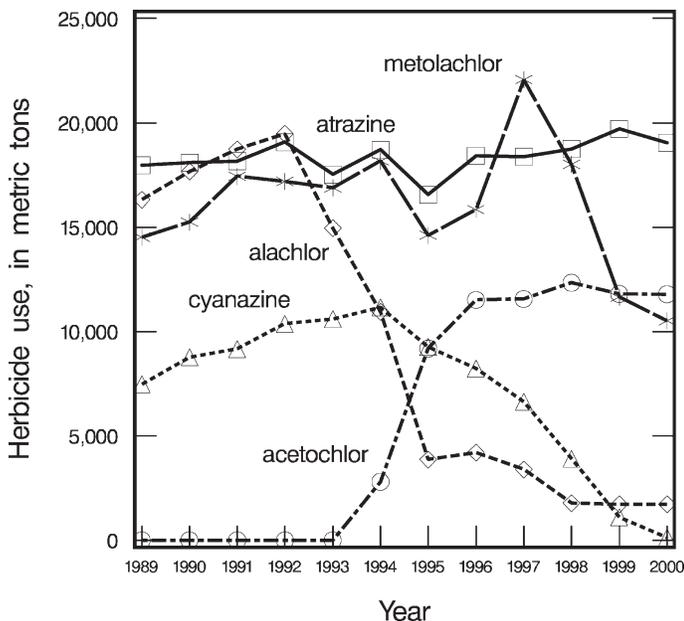


Figure 1. Use of Five Herbicides on Corn, Soybeans, and Potatoes in Eight Midwestern States (Iowa, Illinois, Indiana, Kansas, Minnesota, Nebraska, Ohio, and Wisconsin), 1989 to 2000.

METHODS

Sampling Sites, Schedule, and Procedure

This study is based on data from 151 samples collected during runoff events from nine sites on large

ivers, 62 sites on smaller free flowing streams, and five sites near reservoir outflows in early summer 1998 (Battaglin *et al.*, 2001) and on 70 samples collected during low flow conditions from 70 sites on Midwestern streams in the late summer 1997 (Sorenson *et al.*, 1999; Kalkhoff *et al.*, 2003). Many of the sites have been studied in previous investigations (Thurman *et al.*, 1992; Scribner *et al.*, 1996; 1998). Drainage areas for the nine large river sites range from 32,370 to 443,670 square kilometers. Drainage areas for the 62 small river sites range from 200 to 26,940 square kilometers, and drainage areas for the five reservoir outflow sites range from 770 to 24,940 square kilometers. The drainage areas for the 70 low flow sample sites ranged from 155 to 2,770 square kilometers. The study region consists largely of the states of Illinois, Indiana, Iowa, Kansas, Nebraska, Minnesota, Ohio, and Wisconsin.

Samples were often collected in conjunction with USGS National Stream Quality Accounting Network (NASQAN) or National Water Quality Assessment (NAWQA) activities. All sites (with one exception) were sampled twice. The first small stream samples were collected after pre-emergence herbicides were applied (May or June) and following a precipitation event that produced an increase in streamflow. Since the timing of herbicide application varies both by state and within individual watersheds, crop planting progress statistics (USDA-NASS, 1998) were used to determine when herbicide applications had occurred. Pre-emergence samples were only collected after 50 percent or more of the corn crop was planted in the watershed. The second small stream samples were collected after post-emergence herbicides were applied (June or July), again following a precipitation event that produced runoff and an increase in streamflow. Post-emergence samples were only collected after 90 percent or more of the soybean crop was emerged in the watershed. The first large river and reservoir outflow samples were collected two to three weeks after the first small stream samples were collected from nearby sites. The second large river and reservoir samples were collected two to three weeks after the second small stream samples were collected from nearby sites. By targeting two runoff events during the early summer, the intention was to measure the peak concentrations of pre- and post-emergence herbicides expected during the course of a year (Thurman *et al.*, 1991). The paired samples at each site also provide some insight into the short term temporal behavior of herbicides and their TPs in Midwestern streams. All samples were collected using protocols for the collection of samples for low levels of dissolved organic compounds, described in Shelton (1994). The equal width increment sampling method was used for all stream and reservoir outflow samples except on

some large rivers where equal discharge increment sampling was used (Edwards and Glysson, 1988).

Analytical Methods

All samples from both studies were analyzed for 13 herbicides and 10 herbicide TPs (Table 1) at the USGS Organic Geochemistry Research laboratory (OGRL) in Kansas. The 13 herbicides and three of the TPs (cyanazine-amide, deethylatrazine, and deisopropylatrazine) were analyzed by GC/MS with selected ion monitoring (Zimmerman and Thurman, 1999). The other seven TPs were analyzed by high performance liquid chromatography (HPLC) with diode array detection following solid phase extraction on C18 cartridges (Ferrer *et al.*, 1997a,b; Kalkhoff *et al.*, 1998; Hostetler and Thurman, 2000; Kish *et al.*, 2000). The analytical method reporting limit (MRL) is 0.05 µg/L for the 13 herbicides and three TPs and 0.20 µg/L for the other seven TPs (Table 1).

TABLE 1. Herbicides and Herbicide Transformation Products Analyzed and Analytical Reporting Limits.

Herbicides	Analytical Reporting Limit (µg/L)	Herbicide Transformation Products	Analytical Reporting Limit (µg/L)
Acetochlor	0.05	Acetochlor ESA	0.20
Alachlor	0.05	Acetochlor OXA	0.20
Ametryn	0.05	Alachlor ESA	0.20
Atrazine	0.05	Alachlor OXA	0.20
Cyanazine	0.05	Cyanazine-amide	0.05
Metribuzin	0.05	Deethylatrazine	0.05
Metolachlor	0.05	Deisopropylatrazine	0.05
Prometon	0.05	Hydroxy-atrazine	0.20
Prometryn	0.05	Metolachlor ESA	0.20
Propachlor	0.05	Metolachlor OXA	0.20
Propazine	0.05		
Simazine	0.05		
Terbutryn	0.05		

Statistical Methods

Not all herbicides or TPs were detected in every sample. For the instances of nondetection, it is reasonable to assume that the actual herbicide or TP concentrations are between the MRL and zero. For the statistics listed in Table 2, all nondetects were treated as zero. This "simple substitution" method for treating nondetects is likely to produce estimates of

TABLE 2. Summary of Results for Pre- and Post-Emergence Runoff Event Samples Collected at 76 Midwestern Streams or Reservoir Outflows in 1998 and Low Flow Samples Collected at 70 Midwestern Streams in 1997.

Chemical	Pre-Emergence Samples			Post-Emergence Samples			Low Flow Samples		
	Percentage at or Above the Reporting Limit in 75 Samples	Concentration in (µg/L)		Percentage at or Above the Reporting Limit in 76 Samples	Concentration in (µg/L)		Percentage at or Above the Reporting Limit in 70 Samples	Concentration in (µg/L)	
		Median	Maximum		Median	Maximum		Median	Maximum
Chloroacetanilide Herbicides									
Acetochlor	89.3	0.64	21.3	75.0	0.19	2.05	5.7	<0.05	0.21
Alachlor	50.7	0.05	18.3	35.5	<0.05	7.90	0	<0.05	<0.05
Metolachlor	97.3	1.20	124.3	90.8	0.86	12.3	60.1	0.06	0.42
Propachlor	9.3	<0.05	0.31	5.3	<0.05	0.42	0	<0.05	<0.05
Sum of 4 Herbicides	97.3	2.19	142.8	90.8	1.34	18.4	60.1	0.06	0.42
Chloroacetanilide Herbicide Transformation Products									
Acetochlor ESA	69.3	0.76	4.03	85.5	1.13	5.01	68.6	0.33	1.60
Acetochlor OXA	57.3	0.49	4.17	77.6	0.84	4.27	40.0	<0.20	1.40
Alachlor ESA	88.0	0.50	4.52	93.4	0.70	3.02	85.8	0.61	3.50
Alachlor OXA	14.7	<0.20	1.06	26.3	<0.20	4.30	22.9	<0.20	0.54
Metolachlor ESA	92.0	1.55	12.4	94.7	1.58	6.36	97.2	1.70	6.70
Metolachlor OXA	88.0	0.73	3.83	88.2	0.83	6.37	81.5	0.36	1.30
Sum of 6 TPs	93.3	4.23	22.0	96.1	5.96	18.9	98.7	3.63	12.11
Triazine Herbicides									
Ametryn	1.3	<0.05	0.06	0	<0.05	<0.05	0	<0.05	<0.05
Atrazine	100.0	4.07	172.2	98.7	2.69	34.8	95.8	0.17	1.50
Cyanazine	78.7	0.44	67.2	71.1	0.21	9.66	37.2	<0.05	0.64
Metribuzin	45.3	<0.05	0.60	34.2	<0.05	1.34	0	<0.05	<0.05
Prometon	4.0	<0.05	0.25	10.5	<0.05	0.42	17.2	<0.05	1.40
Prometryn	0	<0.05	<0.05	0	<0.05	<0.05	0	<0.05	<0.05
Propazine	49.3	<0.05	0.68	36.8	<0.05	0.29	0	<0.05	<0.05
Simazine	46.7	<0.05	14.15	35.5	<0.05	0.67	7.2	<0.05	0.20
Terbutryn	0	<0.05	<0.05	0	<0.05	<0.05	0	<0.05	<0.05
Sum of 9 Herbicides	100.0	4.38	173.1	98.7	3.13	38.4	98.7	0.20	2.12
Triazine Herbicide Transformation Products									
Deethylatrazine	92.0	0.41	2.67	94.7	0.54	3.66	82.9	0.09	0.39
Deisopropylatrazine	86.7	0.32	2.34	92.1	0.39	2.17	74.4	0.07	0.36
Hydroxy-atrazine	48.0	<0.05	12.4	54.0	0.27	4.43	61.5	0.29	8.80
Cyanazine-amide	68.0	0.20	4.97	75.0	0.22	4.99	41.5	<0.05	1.20
Sum of 4 TPs	92.0	1.47	9.44	96.1	1.58	11.5	93.0	0.47	9.38

medians (and means) that are biased low (Helsel and Hirsch, 1992). However, when the median or maximum concentration was calculated to be zero, that value was reported as less than the detection limit in Table 2 because the analytical data do not exclude the possibility that the value is less than the MRL but greater than zero.

A different method was applied for the calculation of the herbicide TP to source herbicide ratios. For the

calculation of ratio values, the substitution of zero for nondetections of herbicides can cause a problem with the division by zero. If the TP(s) is (are) present and the herbicide is not, then using zero for the ratio value is not appropriate, as the true value should be large. Zero is likely an appropriate estimate of the ratio value when the herbicide is present but the herbicide TP(s) is not. For the ratios calculated for this paper, a value of 0.001 µg/L was substituted for

nondetects of either herbicides or their TPs. This value is 1/50 to 1/200 the detection limit for the herbicides and TPs. This substitution allows ratio values to be calculated for all samples, but it may be biased high for samples in which herbicides TPs were detected and the source herbicides were not, or biased low, where the source herbicide was detected but herbicide TPs were not.

In several figures, boxplots (Helsel and Hirsch, 1992) are used to display concentrations or concentration ratios. The graphics span the range of data values with high and low outliers shown as circles. The central box extends from the 25th to the 75th percentile of the data. The line across the box is the median (50th percentile) value, and the box "whiskers" extend to the 5th and 95th percentiles of the data. The Wilcoxon signed-rank test is used to determine if observed differences between sets of paired concentration values (e.g., pre- and post-emergence atrazine concentrations) are statistically significant.

RESULTS AND DISCUSSION

Occurrence and Spatial Distribution

The detection frequencies and median and maximum concentrations for the pre- and post-emergence samples are listed in Table 2, and the distributions of concentrations are shown on Figure 2. Acetochlor, atrazine, metolachlor, alachlor ESA, deethylatrazine, deisopropylatrazine, metolachlor ESA, and metolachlor OXA were detected in 80 percent or more of the pre-emergence samples, and alachlor, cyanazine, acetochlor ESA, acetochlor OXA, and cyanazine amide were detected in 50 percent or more. The highest median concentrations in pre-emergence samples were for atrazine (4.07 µg/L), metolachlor ESA (1.55 µg/L), metolachlor (1.20 µg/L), and acetochlor ESA (0.76 µg/L). Atrazine, metolachlor, acetochlor ESA, alachlor ESA, deethylatrazine, deisopropylatrazine, and metolachlor ESA were detected in 80 percent or more of the post-emergence samples, and acetochlor, cyanazine, acetochlor OXA, cyanazine-amide, and hydroxy-atrazine were detected in 50 percent or more. The highest median concentrations in post-emergence samples were for atrazine (2.69 µg/L), metolachlor ESA (1.58 µg/L), acetochlor ESA (1.13 µg/L), and metolachlor (0.86 µg/L). Atrazine, alachlor ESA, deethylatrazine, metolachlor ESA, and metolachlor OXA were detected in 80 percent or more of the low flow samples, and metolachlor, acetochlor ESA, deisopropylatrazine, and hydroxy-atrazine were detected

in 50 percent or more. The highest median concentrations in low flow samples were for metolachlor ESA (1.70 µg/L), alachlor ESA (0.61 µg/L), and metolachlor OXA (0.36 µg/L).

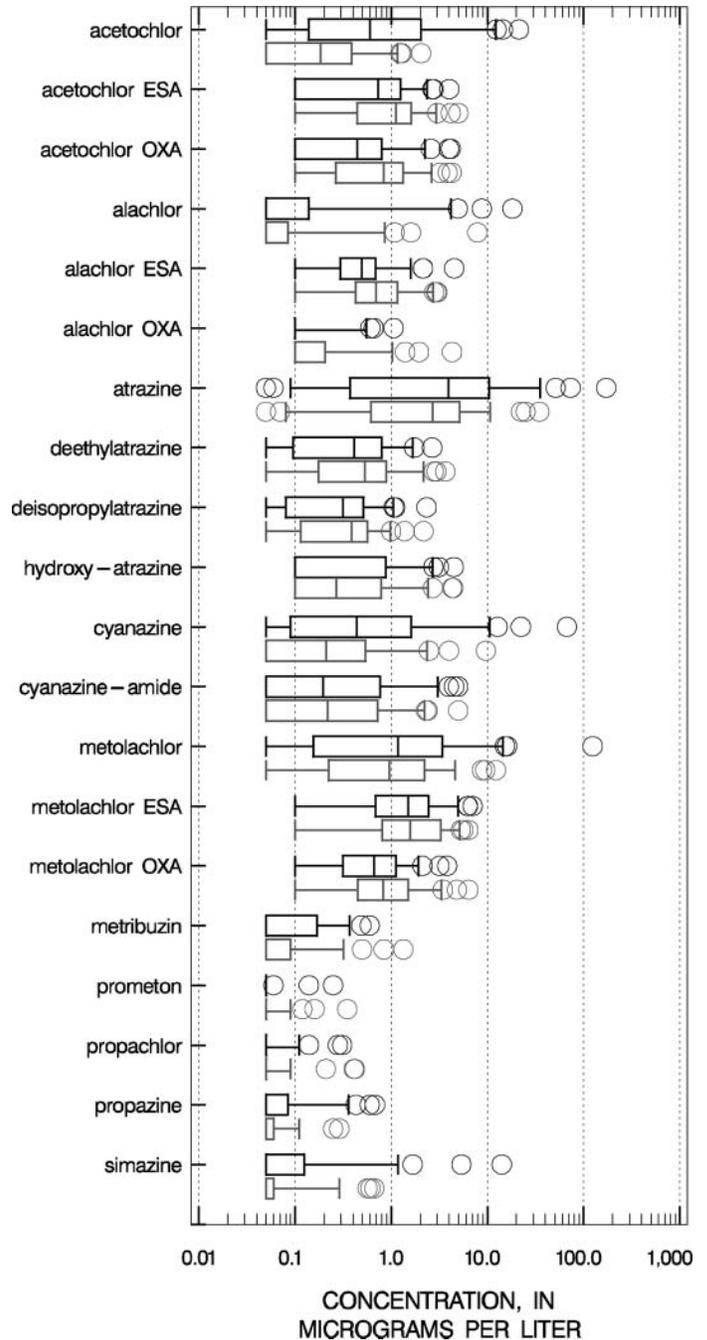


Figure 2. Herbicide and Herbicide TP Concentrations in Pre-Emergence (black) and Post-Emergence (grey) Runoff Samples From Midwestern Streams, 1998.

In general, herbicides were detected less frequently and at lower concentrations in low flow samples than in pre- or post-emergence samples. Prometon is an exception and was detected most frequently in low flow samples. For the herbicide transformation products the difference in detection frequency between higher flow and low flow samples was generally small, and metolachlor ESA and hydroxy-atrazine were detected most frequently in the low flow samples.

All of the detected herbicides, with the exceptions of prometon and simazine, are used almost exclusively for pre-emergence weed control (Meister, 2002). Hence, their detection frequencies and concentrations were expected to be larger in pre-emergence samples than in post-emergence samples. Of the 13 herbicides, prometryn and terbutryn were not detected in any sample, and ametryn was detected in only one sample. Terbutryn is not permitted for any use in the United States, and prometryn is only permitted for use on cotton, celery, and parsley (USEPA, 2002). Ametryn is permitted for use on corn and sugarcane but was applied to less than one percent of corn acreage nationally in 1998 (USDA, 1999). Detection frequencies of nine of the other 10 herbicides were larger in pre-emergence than post-emergence samples (Table 2). Only prometon was detected more frequently in the post-emergence samples. The median concentrations for all 13 herbicides were the same (at $<0.05 \mu\text{g/L}$) or larger in pre-emergence samples than in post-emergence samples (Table 2; Figure 2). The differences in concentrations between pre- and post-emergence samples were statistically significant ($p < 0.05$) and positive (pre-emergence larger than post-emergence) for acetochlor, alachlor, atrazine, cyanazine, metolachlor, metribuzin, propazine, and simazine.

In 1998, in the eight Midwestern states that comprise the study region, the order of herbicide use was atrazine $>$ metolachlor $>$ acetochlor $>$ cyanazine $>$ alachlor (Figure 1; USDA, 1991 to 2001). The order of the median herbicide concentrations in Midwestern streams during pre-emergence runoff matched the order of herbicide use (atrazine $>$ metolachlor $>$ acetochlor $>$ cyanazine $>$ alachlor) (Table 2; Figure 2), providing evidence that current use controls the concentrations of herbicides in streams.

The opposite temporal pattern was observed for herbicide TPs than for herbicides. Detection frequencies of all 10 herbicide TPs were larger for post-emergence sample than for pre-emergence samples. Likewise the median concentrations of all 10 herbicide TPs were the same (at $< 0.20 \mu\text{g/L}$) or larger in post- than in pre-emergence samples (Table 2; Figure 2). The differences in concentrations between pre- and post-emergence samples were statistically significant

and negative for acetochlor ESA, acetochlor OXA, alachlor ESA, metolachlor ESA, and metolachlor OXA.

As shown in previous studies (Thurman *et al.*, 1991; Goolsby and Battaglin, 1993, 1995; Battaglin and Goolsby, 1998; Scribner *et al.*, 2000), large ($> 10 \mu\text{g/L}$) concentrations of herbicides can occur in streams and reservoir outflows during early summer runoff events across the Midwestern United States. In 1998, atrazine concentrations in many streams across the study region exceeded $10 \mu\text{g/L}$ during pre-emergence runoff events and exceeded $3 \mu\text{g/L}$ during post-emergence runoff events (Figure 3). The concentrations of metolachlor exceeded $10 \mu\text{g/L}$ during pre-emergence runoff events and $3 \mu\text{g/L}$ during post-emergence runoff events (Figure 2) more infrequently than atrazine, perhaps due to its more rapid degradation in soils (USDA, 2002). Concentrations of atrazine TPs in Midwestern streams rarely exceeded $1 \mu\text{g/L}$ during pre- or post-emergence runoff events (Figure 2). Concentrations of metolachlor TPs in Midwestern streams frequently exceeded $1 \mu\text{g/L}$ during pre- and post-emergence runoff (Figure 2).

Herbicide Transformation Product to Source Ratios

The occurrence of herbicide TPs is an important indicator of herbicide fate. Ratios of the concentration of herbicide TPs to source herbicides have been used by several researchers to identify herbicide sources and fate in surface water and ground water (Thurman *et al.*, 1992, 1994, 1998; Kolpin and Kalkhoff, 1993; Thurman and Fallon, 1996; Boyd, 2000). Some herbicide TPs have more than one potential source herbicide. For example, atrazine, cyanazine, and simazine can all be transformed into deisopropylatrazine, and atrazine and propazine can both be transformed into deethylatrazine (Thurman *et al.*, 1994; Scribner *et al.*, 2000).

The herbicide TP to source herbicide ratios are calculated differently for this study than for other investigations. For example, here the atrazine ratio (Table 3) is the sum of the concentrations of deethylatrazine, deisopropylatrazine, and hydroxy-atrazine divided by the atrazine concentration, instead of just the deethylatrazine concentration divided by the atrazine concentration (Thurman *et al.*, 1994).

The ratios of atrazine herbicide TPs to atrazine were between 0.1 and 0.5 in pre-emergence samples from most sites (Table 3; Figures 4 and 5) but were significantly larger in post-emergence samples, with frequent occurrence of values between 0.5 and 1.0. Atrazine ratios rarely exceed 1.0 (Figures 4 and 5). The ratios of metolachlor TPs to metolachlor were generally 10 times larger than the atrazine ratios

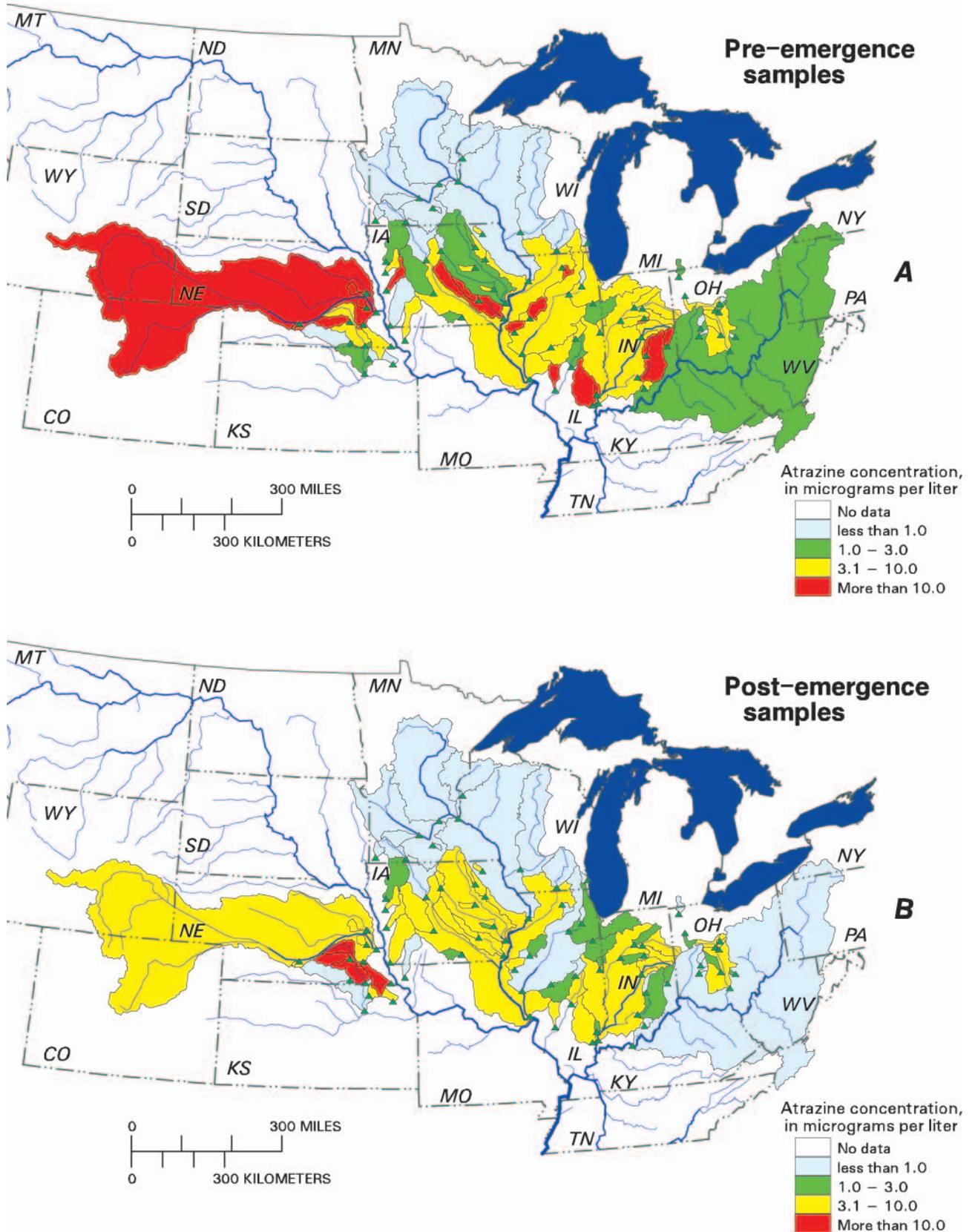


Figure 3. Spatial Distributions for Concentrations of Atrazine in (A) Pre-Emergence Samples and (B) Post-Emergence Samples.

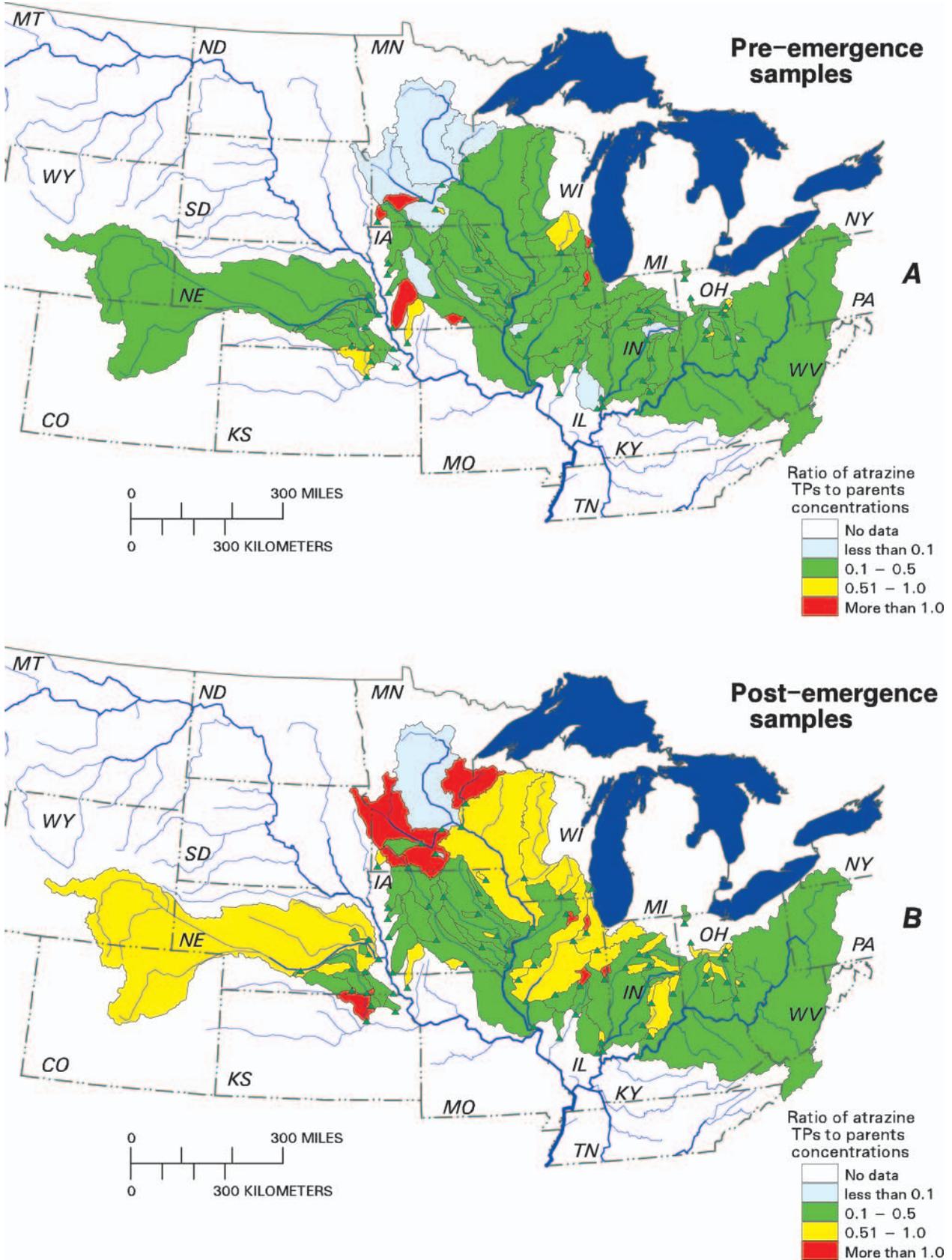


Figure 4. Spatial Distributions for the Ratios of Atrazine TP Concentrations to Atrazine Concentrations in (A) Pre-Emergence Samples and (B) Post-Emergence Samples.

TABLE 3. Summary of Herbicide TP(s) to Source Herbicide(s) Ratios for Pre- and Post-Emergence Samples Collected at 76 Surface Water Sites.

Herbicide TPs to Source Herbicides Ratios*	Pre-Emergence Samples			Post-Emergency Samples			Low Flow Samples		
	25th	Median	75th	25th	Median	75th	25th	Median	75th
	Percentile		Percentile	Percentile		Percentile	Percentile		Percentile
Acetochlor ratio	0.13	1.00	3.38	3.37	8.18	19.6	2.38	340	940
Alachlor ratio	1.47	9.00	440	8.01	335	800	260	770	1,210
Atrazine ratio	0.13	0.20	0.35	0.32	0.51	0.75	1.06	2.72	4.86
Cyanazine ratio	0.23	0.58	1.00	1.00	1.12	1.71	1	1	1.25
Metolachlor ratio	0.58	1.97	6.67	1.30	2.88	5.75	23.3	45.7	1,100

*A ratio was calculated for every sample. A value of 0.001 mg/L was used when concentrations of herbicides or herbicide TPs were reported as less than the detection limit.

(Figure 5). In pre- and post-emergence samples, metolachlor ratios from most sites were between 1.0 and 10.0. The herbicide TPs to source ratios for acetochlor, alachlor, atrazine, and cyanazine were all significantly larger in post-emergence samples than pre-emergence samples, and for metolachlor the difference was nearly significant ($p = 0.08$) (Table 3, Figure 5).

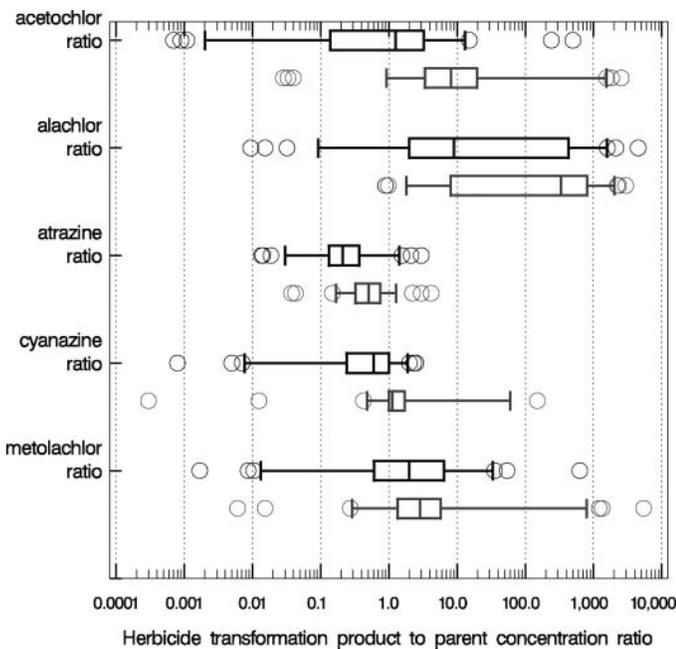


Figure 5. Ratios of Herbicide TP(s) Concentrations to Herbicide Concentrations in Pre-Emergence (black) and Post-Emergence (gray) Samples.

The ratios of herbicide TPs to source herbicides in streams are controlled by the rate of degradation of

both the sources and the TPs. Degradation rates of herbicides in soils are relatively well known, but the degradation rates of herbicides and their transformation products in other environmental systems such as streams have not been frequently measured. The available data indicate that the TPs of atrazine, metolachlor, and acetochlor are more mobile than their source compounds but have similar rates of degradation in soils (Kruger *et al.*, 1997; Aga and Thurman, 2001; Bayless, 2001).

In Midwestern streams, the ratio of herbicide TPs to source herbicides is affected largely by the mixing of two water sources. Streamflow during runoff events like those sampled in early summer 1998 is composed of both overland flow or runoff and increased input from ground water, or baseflow (Hornberger *et al.*, 1998). One can hypothesize that in runoff from a rainfall event soon after the application of herbicides, the ratio of herbicide TPs to source herbicides would be a function of the soil dissipation half-life of the source herbicide and should be very small (less than 1.0) because the recent application has had little time to degrade. In field side sampling of runoff soon after herbicide application, the deethylatrazine to atrazine and deisopropylatrazine to atrazine ratios were less than 0.05 (Thurman *et al.*, 1994). Alachlor ESA to alachlor ratios in field side runoff were significantly larger, just less than 1 in the first runoff after application and significantly greater than 1 in later events (Thurman *et al.*, 1996). The soil dissipation half-life of alachlor is about seven days, whereas the soil dissipation half-life of atrazine is about 60 days (Wauchope *et al.*, 1992; Stamper *et al.*, 1997). In contrast, herbicide TP to source herbicide ratios in ground water tend to be larger. The median deethylatrazine to atrazine ratio in approximately 600 ground water samples collected in 1991 in the Midwest was approximately 0.7 (Kolpin *et al.*, 1994). In approximately 800 ground water samples collected in 1991 to 1994 in the

Midwest, the ratios of alachlor TPs to alachlor, cyanazine TPs to cyanazine, and metolachlor TPs to metolachlor averaged about 10 (Kolpin *et al.*, 1995, 1998a).

The ratios of herbicide TPs to source herbicides in the 151 samples collected in early summer 1998 are summarized on Table 3, and the distribution of values is shown on Figure 5. The ratio values in these runoff dominated stream samples are, in general, between those expected from field side runoff and ground water sources. Atrazine ratios tended to be between 0.1 and 1.0, whereas alachlor ratios ranged from 1 to 1,000. In the early 1990s, alachlor use was similar to that of atrazine and metolachlor (Figure 1), but with its recent decline in use, the frequency of detection and measured concentrations of alachlor in Midwestern streams have declined dramatically, while alachlor ESA has persisted and detections and concentrations have not declined as rapidly (Battaglin and Goolsby, 1999; Scribner *et al.*, 2000). Cyanazine ratios should be similar to alachlor ratios because this herbicide is also experiencing a decline in use and a resulting decrease in occurrence and concentration in Midwestern streams (Battaglin and Goolsby, 1999; Scribner *et al.*, 2000). However, in this study the cyanazine ratios are more like atrazine ratios with values generally between 0.1 and 1.1 (Figure 5). The smaller than expected ratio values may be the result of not analyzing samples for three other cyanazine TPs: cyanazine acid, deethylcyanazine, and deethylcyanazine acid. In ground water samples from Iowa, these three cyanazine TPs represented more than 90 percent of the total cyanazine compound concentration (Kolpin *et al.*, 2001). Metolachlor ratios are significantly larger than atrazine ratios (Figure 5). Metolachlor concentrations tend to be smaller than atrazine concentrations, whereas the concentrations of metolachlor TPs tend to be larger than atrazine TP concentrations (Figure 2). Their use in Midwestern states in 1998 was nearly identical (Figure 1), but metolachlor degrades in soil more rapidly than atrazine (Kolpin *et al.*, 1998b; Extoxnet, 2001). Acetochlor ratios were generally smaller than expected. Though acetochlor was detected frequently, its TPs were not detected as frequently or in concentrations as large as the TPs of metolachlor (Table 2). Acetochlor degrades in soil more rapidly than metolachlor (Kolpin *et al.*, 1998b); however, it is a relatively new herbicide and widespread use did not begin until 1994 (Figure 1). It may be that the TPs of acetochlor have not yet accumulated in soils in as large of quantities as the TPs of metolachlor, which has been used for more than 20 years.

Comparison With Base Flow Conditions

Water samples collected from 70 Midwestern streams during low flow conditions in August 1997 (Sorenson *et al.*, 1999; Porter *et al.*, 2001; Kalkhoff *et al.*, 2003) were analyzed for the same 13 herbicides and 10 herbicide TPs as the pre- and post-emergence samples collected in early summer 1998. In general, herbicides and herbicide TPs were detected less frequently and at lower concentrations in these low flow samples than in the pre- and post-emergence runoff event samples. For example, the median atrazine concentration in the low flow samples was 0.17 $\mu\text{g/L}$ compared with 4.07 and 2.69 $\mu\text{g/L}$ for the pre- and post-emergence samples. Prometon was the only herbicide that was detected more frequently in low flow samples than in runoff event samples (Table 2). Metolachlor ESA and hydroxy-atrazine were detected more frequently in low flow samples than in pre- and post-emergence runoff samples, and alachlor OXA was detected more frequently in low flow samples than in pre-emergence runoff samples. The median metolachlor ESA concentration in the low flow samples was 1.70 $\mu\text{g/L}$ compared with 1.55 and 1.58 $\mu\text{g/L}$ for the pre- and post-emergence samples.

The ratios of herbicide TPs to source herbicides were generally much larger in low flow samples than in pre- or post-emergence runoff samples because of the greater contribution of ground water to streamflow during low flow conditions. For example, the median metolachlor ratio in low flow samples was 45.7, compared with 1.97 and 2.88 for pre- and post-emergence samples, and the median atrazine ratio in low flow samples was 2.72, compared with 0.20 and 0.51 for pre- and post-emergence samples (Table 3).

Two-Component Mixing Model

The herbicide TP to source herbicide ratios and a simple two-component mixing model can be used to determine if runoff or ground water is the dominant source of herbicides in Midwestern streams during early summer. Ideally, this would be done with low-flow samples collected at the same 75 sites as the runoff samples. Because this was not possible, the results from low flow samples collected in 1997 will be used in aggregate. The herbicide TP, to source herbicide ratio in the stream samples is determined by the mixing of runoff and ground water. Equation (1) describes this model where R_s is the herbicide TP to source herbicide ratio in the stream samples, R_r is the ratio in runoff, R_g is the ratio in ground water, X is the average proportion of herbicide from runoff, and Y

is the average proportion of herbicide from ground water.

$$R_s = X * (R_r) + Y * (R_g) \quad (1)$$

Because X plus Y equals 1, Equation (1) can be solved for X if the ratio values are known. The median ratio values from the low flow samples can be used for R_g , and the median ratio values from pre- or post-emergence samples are used for R_s (Table 3). The values for R_r likely vary as a function of soil dissipation half-life. From Thurman *et al.* (1994), we estimate a 1:20 ratio for each atrazine TP to atrazine; a 1:15 ratio for each TP of acetochlor, cyanazine, and metolachlor to their source herbicides; and a 1:10 ratio for each alachlor TP to alachlor. Equation (1) was solved, and the results are shown in Table 4. Results for cyanazine are suspect due to the infrequency of the detection of cyanazine and its TPs. In the pre-emergent samples, on average less than 5 percent of the mass of acetochlor, alachlor, atrazine, or metolachlor comes from ground water. Slightly more herbicide mass comes from ground water in the post-emergence samples (Table 4). The exception is alachlor, which has a much larger ground water source in post-emergence samples (Table 4), perhaps an indication of its larger historical use. See Battaglin (2002) for a more complete discussion of the use of herbicide TP to source herbicide ratios to determine the source of herbicides in streams.

TABLE 4. Estimates of the Percent Contribution of Herbicide in Runoff Verses Ground Water for Pre- and Post-Emergence Samples Collected at 76 Surface Water Sites.

Herbicide	R_r	R_g	R_s	Pre-Emergence Samples	Post-Emergence Samples
				Percent Contribution From Runoff	Percent Contribution From Runoff
Acetochlor	0.13	340	1.00	100	8.18
Alachlor	0.20	770	9.00	99	335
Atrazine	0.15	2.72	0.20	98	0.51
Cyanazine	0.08	1.00	0.58	46	1.00
Metolachlor	0.13	45.7	1.97	96	2.88

Herbicide Mixtures

The number of herbicide compounds detected in a water sample is a function of both the number of herbicides analyzed and the detection limits for the

analytes (Kolpin *et al.*, 1995). At least five herbicides or herbicide TPs were detected in 90 percent of the 151 water samples collected in early summer 1998 (Figure 6). Six or more herbicides and eight or more TPs were detected in more than 50 percent of the pre-emergence samples. Five or more herbicides and nine or more TPs were detected in more than 50 percent of the post-emergence samples (Figure 6). Wilcoxon signed rank test results indicate that significantly more herbicides were detected in pre- than post-emergence samples, significantly more TPs were detected in post- than pre-emergence samples, and there was no difference in the total number of compounds detected in pre- and post-emergence samples.

Little research has been directed at determining the impact of environmental mixtures of herbicides and herbicide TPs to nontarget aquatic organisms. Most studies have concluded that either effect summation or concentration addition models can be appropriate for estimating the toxicity of mixtures of chemicals with the same mode of action (Marking, 1985; Faust *et al.*, 2000; Silva *et al.*, 2002) and that independent action models are more appropriate for mixtures of chemicals with differing modes of action. Few data are available on the toxicity of herbicide TPs to nontarget aquatic organisms, hence including them in any toxicological models requires making assumptions about their relative toxicity. Some of the same water quality data used in this study have been used to calculate the potential toxicity of water in Midwestern streams to aquatic organisms (Battaglin and Fairchild, 2002). Battaglin and Fairchild (2002) determined that some streams contained sufficient levels of pesticides to be potentially toxic to duckweed or green algae, but almost none were potentially toxic to bluegill sunfish or chorus frogs.

CONCLUSIONS

In this study, 151 samples were collected from Midwestern streams during early summer runoff events in 1998 in which high concentrations of pre- and post-emergence herbicides were expected. Herbicide TPs were found to occur as frequently as or more frequently than source herbicides and at concentrations that were often larger than those of their source herbicides. Only four of 13 herbicide analytes were detected in 50 percent or more of the samples, whereas nine of 10 herbicide TP analytes (all except alachlor OXA) were detected in 50 percent or more of the samples. For the triazine herbicides, source herbicide concentrations tended to be larger than TP concentrations, but the opposite was true for most chloroacetanilide

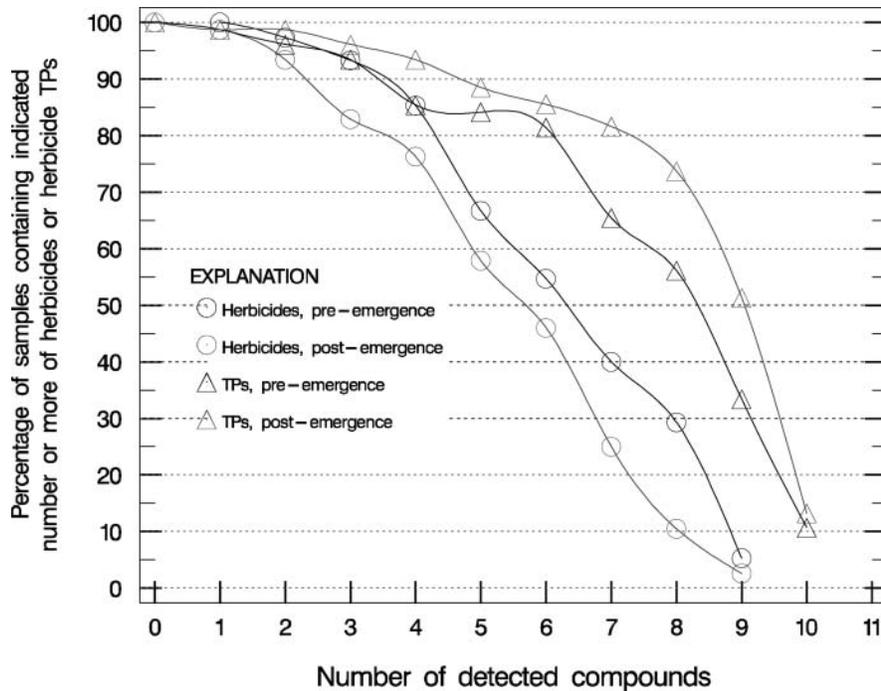


Figure 6. Number of Herbicides and Herbicide TPs Detected in Pre-Emergence (black) and Post-Emergence (grey) Samples.

herbicides, indicating their more rapid degradation in soils. Atrazine concentrations exceeded 3 $\mu\text{g/L}$ in streams across the Midwest in both pre- and post-emergence samples. Metolachlor concentrations were less than atrazine concentrations, but still exceeded 3 $\mu\text{g/L}$ in many Midwestern streams during early summer runoff. In the eight Midwestern states that comprise the study region, the order of herbicide use (atrazine > metolachlor > acetochlor > cyanazine > alachlor) matched the order of median herbicide concentrations in Midwestern streams during pre-emergence runoff, providing evidence that current herbicide use controls herbicide occurrence in Midwestern streams. The herbicide TPs to source ratios for acetochlor, alachlor, atrazine, cyanazine, and metolachlor were all smaller in pre-emergence than post-emergence samples. A simple two-component mixing model was used to determine the relative contribution of herbicides from runoff versus ground water in streams during runoff events. Results indicate that on average, 90 percent or more of the herbicide content of Midwestern streams during early summer runoff events originates from the runoff and 10 percent or less enters the streams with ground water. A mixture of 14 or more herbicides or herbicide TPs was detected in more than 50 percent of samples.

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