Herbicides and their Metabolites in Cayuga Lake and its Tributaries, New York

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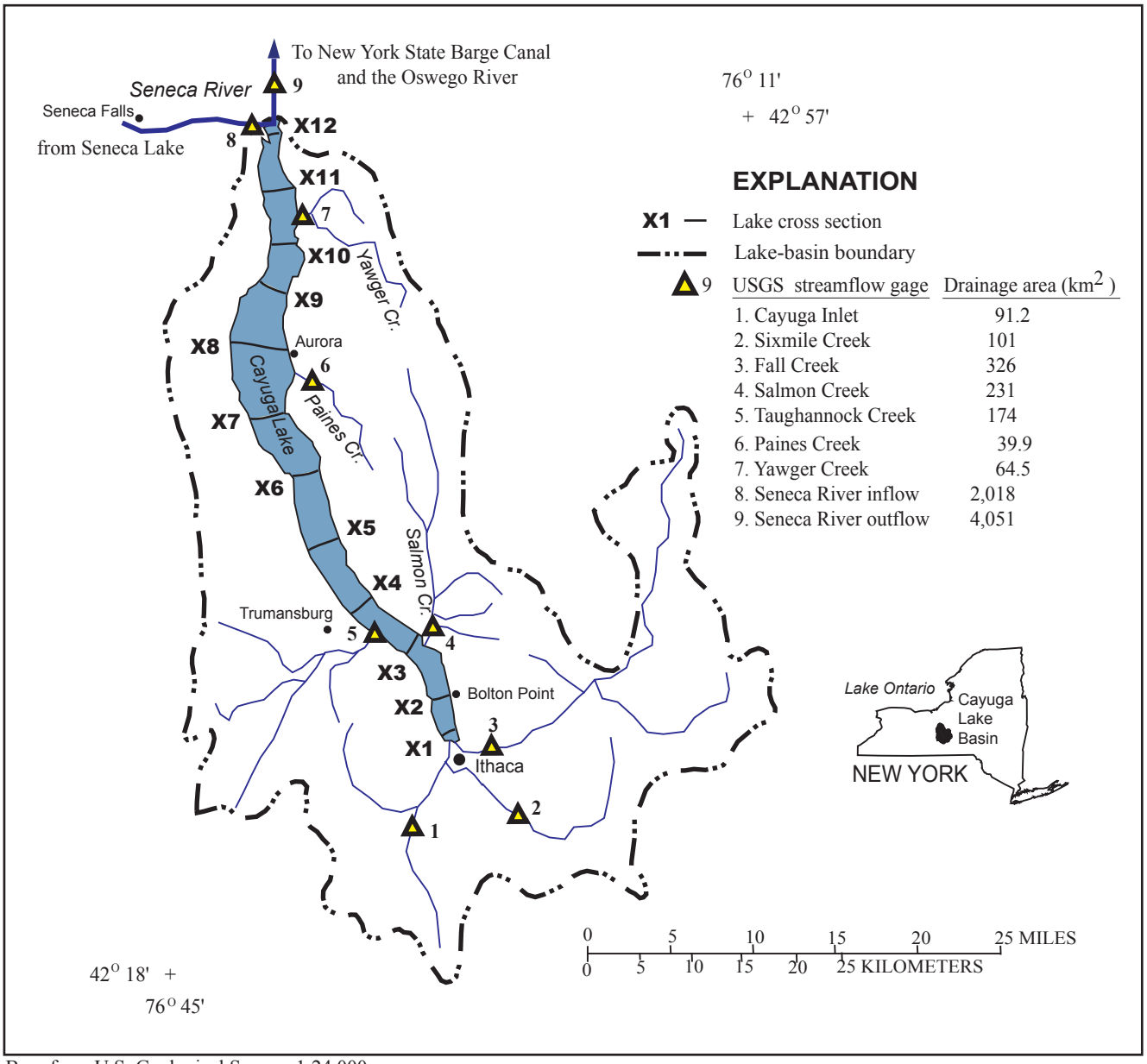
ABSTRACT

Analyses of stormflow samples collected from tributaries to Cayuga Lake in western New York shortly after application of atrazine and metolachlor to agricultural fields in June 1998 indicate that the highest concentrations, and the bulk of the loads of the two herbicides in the three tributaries was transported during peak flows. Concentrations of metolachlor metabolites remained high after the flow peaked as the soils drained. In contrast, deethylatrazine concentrations, which were generally low, increased only slightly during stormflow, apparently because the parent compound (atrazine) degrades at a much slower rate than metolachlor. Far more metolachlor-ESA (a degradation compound) was transported than any other pesticide or degradate; this indicates that it is relatively stable and mobile in the hydrologic environment. The ratios of a metabolite concentration to that of other metabolites and the parent compound in stream-water samples showed that base flow in the tributaries before the storm was enriched with metolachlor-ESA, but not with metolachlor or metolachlor-OA. After the storm, the ratio of metolachlor-OA to metolachlor increased markedly in the base flow; apparently metolachlor-OA that is formed in soils after pesticide application is readily leached but does not persist in ground water as much as metolachlor-ESA does. Water samples taken from Cayuga Lake in July, after the early-summer flush of pesticide residues in June, indicated fairly uniform concentrations of herbicides throughout the lake — from 0.2 to 0.6 µg/L for atrazine and from 0.05 to 0.3 µg/L for metolachlor. The ratios of the three metabolites to their parent compounds were significantly higher in lake water than in the three tributaries, possibly as a result of (1) the inflow of ground water that enters the lake directly from adjacent agricultural land, and (2) the transformation of the parent compounds during their residence in the lake.

INTRODUCTION

The Finger Lakes of western New York lie within 11 north-south trending basins that were deepened by Pleistocene glaciation. Cayuga Lake (fig. 1) occupies a deep glacial trough and is the longest of these lakes (61 km); it also has the largest drainage area (2,033 km^2). Its average width is 2.8 km, its maximum depth is 140 m (Birge and Juday, 1914), and its estimated water-retention time is 12 years (Oglesby, 1978). The predominant land use in the southern (upper) end of the basin is forest with some agriculture and urbanization; the extent of agricultural land increases northward, and the northern tributaries drain pastures and fields planted mostly in corn, soybean, and forage crops. Agricultural pesticides that are widely used in these areas are commonly detected in Cayuga Lake and its tributaries.

Cayuga Lake is used for public-water supply by several communities, and citizens are concerned about their exposure to pesticides in the drinking water. Water that is discharged from Cayuga Lake ultimately enters Lake Ontario through the Seneca and Oswego Rivers. Preliminary water-quality surveys of the Finger Lakes have shown that, of all the Finger Lakes, Cayuga Lake has been most severely affected by agricultural runoff that carries pesticide residues, and that its basin is a main source of pesticide loads from New York to Lake Ontario. For these reasons, Cayuga Lake was selected for detailed study.



Base from U.S. Geological Survey, 1:24,000

Figure 1. Locations of streamflow and lake-water sampling sites in Cayuga Lake basin, N.Y.

In 1998, the U.S. Geological Survey, in cooperation with New York State Department of Environmental Conservation, conducted an appraisal of pesticide occurrence in Cayuga Lake and its major tributaries as part of a statewide program for monitoring pesticides in surface water. The work included collection of stormflow samples from six major tributaries that together account for nearly half of the total area draining to the lake. The intent of the tributary sampling was to assess pesticide concentrations in storm runoff that directly followed the May and early June applications of herbicides to agricultural land. After this early-summer flush of pesticide residues to the tributaries, water samples were collected along 12 cross sections in Cayuga Lake for 2 consecutive

weeks in late July to assess the spatial distribution and range of herbicide concentrations.

This paper presents results of (1) the sampling of June 17, 1998 storm runoff in three of the six tributaries to Cayuga Lake whose drainage basins are predominantly agricultural, and (2) the July 1998 sampling within the lake. Results are presented for two herbicides — atrazine and metolachlor — and their principal metabolites.

METHODS

Three tributaries — Yawger Creek, Paines Creek, and Salmon Creek (fig. 1, table 1) — were sampled after a storm on June17-18, 1998 that delivered about 50 mm of rain within 2 hours to the northeastern part of the Cayuga Lake basin. These tributaries drain land that is between 50 to 75 percent agricultural. Samples were collected and filtered by the methods of Shelton (1994). Pesticides were extracted from the sampled water by solid-phase methods (Meyer and others, 1993) and analyzed by gas chromatography with mass spectrometry (GCMS) (Thurman and others, 1990) and high-performance liquid chromatography (HPLC) (Ferrer and others, 1997). Target analytes were triazine and acetanilide herbicides, which are commonly used in the study area, and the main metabolites, or degradation products, of these herbicides.

Lake-water samples were taken 1 month after the storm runoff during 2 consecutive weeks in July at 12 cross sections in Cayuga Lake (fig. 1). Samples were taken at 3 to 5 equally-spaced locations along each section, and at each location water was sampled at the 2-m depth in the warm surface layer (epilimnion) and at the 30-m depth in the colder water (hypolimnion) below the thermocline. The lake-water samples were analyzed by two methods: (1) enzyme-linked immunosorbent assay (ELISA), which provided a field method for specific measurements of atrazine and metolachlor concentrations, and (2) solid-phase extraction and GCMS/HPLC, which provided concentrations of the suite of pesticides and their metabolites for which the stormflow samples had been analyzed.

HERBICIDE CONCENTRATIONS IN TRIBUTARIES TO CAYUGA LAKE

Water from Salmon Creek, which drains coarse-grained glacial deposits that contain aquifers that provide water for farm and rural homes, contains more ground water than Paines Creek, which drains an area of thin till overlying shale bedrock. Paines Creek basin produces sharp peak flows but little base flow to its stream, whereas the glacial deposits in Salmon Creek basin absorb more rainfall and thus reduce peak flows and prolong stormflow recessions. Yawger Creek drains an area of karstic limestone and also has prolonged runoff recessions and baseflows that are sustained by ground-water discharge after storms. Despite the differing hydrologic response of the three tributaries, pesticide concentrations in the stormflow samples showed similar patterns among the three basins.

Metolachlor

Concentrations of metolachlor and its metabolites in the tributaries increased as water discharge increased in response to rainfall. Concentrations are plotted in relation to discharges in figure 2, and loads are given in table 1. The maximum concentration of metolachlor in Paines Creek, whose basin is 78 percent agricultural, was 29 µg/L near the peak of the runoff. Concentrations in Salmon Creek (70 percent agricultural) were substantially lower than in Paines and Yawger Creeks; this was due in part to a storm (37 mm) earlier in June that produced rainfall in the lower part of Salmon Creek basin (but not in the other two basins) and caused the first flush in Salmon Creek to occur earlier than in Paines or Yawger Creeks. The lower concentrations in Salmon Creek also are consistent with the smaller amount of agricultural land in this basin than in the Paines or Yawger Creek basins. The highest metolachlor concentrations at all three sites occurred during peak flow, which indicates that the bulk of metolachlor is transported in storm runoff.

The metolachlor metabolites (metolachlor-ESA and metolachlor-OA) are formed by transformation of metolachlor as it moves through soil (Phillips and others, 1999). Concentrations of

Table 1. Pesticide loads in stormflow of three tributaries to Cayuga Lake, N.Y., June 1998

[km^2, square kilometers; mm, millimeters. Locations are shown in fig. 1.]

Site Name	Basin area (km^2)	Agricultural land use (percent)	Runoff duration (hours)	Runoff volume (mm)	Load (grams per square kilometer)				
					Atrazine	Deethyl-atrazine	Metolachlor	Metolachlor ESA	Metolachlor OA
Paines Creek	39.9	78	36	6.4	67	27	60	84	63
Yawger Creek	64.5	82	36	4.5	35	8	53	69	61
Salmon Creek	231	70	60	9.4	27	8	47	66	31

metolachlor-ESA in base-flow samples that were collected before the storm were several times higher than those of the parent metolachlor (fig. 2), which indicates that ground water discharging to the streams is enriched with the ESA metabolite. Concentrations of the metolachlor-OA metabolite in the initial baseflow were quite low, which suggests that this compound is less stable in ground water than the ESA metabolite and less preferentially formed or less mobile. Concentrations of the OA metabolite increased quickly during the rising flows, however, and its transport pattern became similar to that of the ESA metabolite, although at slightly lower concentrations. In general, the transformation of metolachlor into either metabolite appears fairly efficient in the glacially-derived soils of this region.

Concentrations of the metabolites during rising flows and peak flows were typically less than those of the parent (metolachlor), when the metolachlor that was transported from the fields to the stream in overland flow had only minimal soil-contact time (fig. 2). Metabolite concentrations increased as the discharge increased, however, which suggests that the metabolite mass that was formed and stored in the soil was quickly flushed into streams, probably through shallow subsurface flow paths on the adjacent hillslopes (interflow). Some of the metabolite mass in the runoff may have been residues that had remained in soils from the previous year. As the stormflow receded, the metabolite concentrations continued to increase and exceeded the parent concentrations; the metabolite concentrations remained high after the rain had ceased as soils drained (interflow) and ground-water discharge continued to contribute metabolite mass while the direct surface runoff gradually ceased.

Atrazine

Atrazine concentrations in stormflow exceeded 10 µg/L in Yawger and Paines Creeks but were half of that value in Salmon Creek. Peak atrazine concentration in samples coincided exactly in time with peak metolachlor concentration. In contrast to the metolachlor metabolites, the atrazine metabolite (deethylatrazine) increased only slightly in stormflow and never exceeded values that were half those of its parent. Deethylatrazine concentrations remained relatively low compared to those of its parent and the metolachlor metabolites, probably because atrazine degrades at a much slower rate than metolachlor (Wauchope and others, 1992). The deethylatrazine that appeared in stormflow may have been resident in the soils and was flushed into streams, probably in interflow from the hill slopes.

Herbicide Loads

Mass loads of metolachlor, atrazine, and their metabolites and the total runoff volume per unit basin area are summarized in table 1. A comparison of loads among basins is complicated by (1) spatial differences in rainfall amount and intensity and pesticide use, and (2) the arbitrary selection of hydrograph duration (fig. 2), but certain conclusions can be made: (1) Far more metolachlor-ESA was transported than any other constituent; this indicates that it is relatively stable and mobile in the hydrologic environment. (2) Significantly less deethylatrazine was transported than any other constituent. (3) The smallest basin (Paines Creek) yielded the largest loads per unit area as a conse-quence of its high runoff volume and its high proportion of agricultural land use. (4)

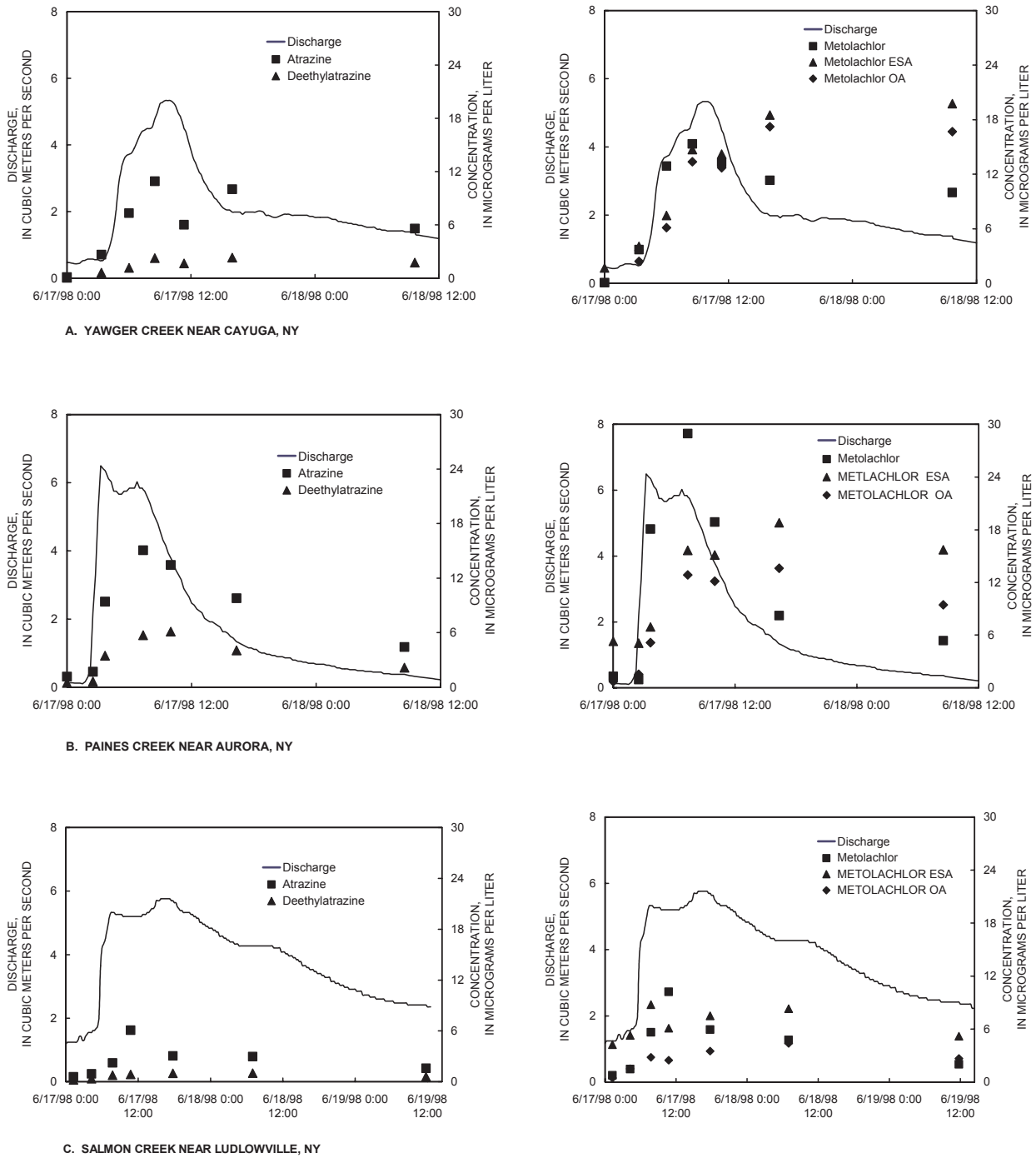


Figure 2. Concentrations of selected herbicides and their metabolites in three tributaries to Cayuga Lake, N.Y., during storm of June 17-18, 1998. (Locations are shown in fig. 1.)

The smallest herbicide loads per unit area were in Salmon Creek, which had the least amount of agricultural land, the most permeable soils, and the largest antecedent rainfall.

Metabolite Ratios

The concentration ratios of one metabolite to another metabolite, and to its parent compound, in a sample provide information on the relative abundance of the metabolite and assist in the interpretation of its fate and transport (Adams and Thurman, 1991; Phillips and others, 1999). The ratios in table 2 indicate that base flow in the three tributaries before the June storm contained more metolachlor-ESA than metolachlor or metolachlor-OA. The ratios of metolachlor-ESA to its parent decreased to less than 1 during peak flow, when the parent compound concentrations were highest from their rapid flush in surface runoff. After the peak flow, the ratios increased again through the stormflow recession; the most notable increase was in the ratios of metolachlor-OA to metolachlor, which nearly tripled the prestorm values in base flow. Apparently, metolachlor-OA can be formed and remains in soil after pesticide application, but it does not appear to persist as a ground-water contaminant as does metolachlor-ESA.

Table 2. Median ratios of metabolite concentrations to concentrations of parent compounds and other metabolites in surface waters of Cayuga Lake basin, N.Y., June-July 1998

Water sample	Deethyl-atrazine/ Atrazine	Metolachlor ESA / Metolachlor	Metolachlor OA / Metolachlor	Metolachlor ESA / Metochlor OA
Tributaries, June 1998				
Baseflow	0.40	4.1	0.57	6.8
Peakflow	.21	.60	.42	1.2
Recession	.38	2.6	1.7	1.7
Cayuga Lake, July 1998				
Shallow	.79	8.0	3.2	2.4
Deep	.87	18	7.0	2.6

HERBICIDE CONCENTRATIONS IN CAYUGA LAKE

The early-summer tributary runoff was relatively warm (20 °C) and soon dispersed into the lake's upper, warm layer (epilimnion). In general, herbicide concentrations were fairly uniform throughout the lake — from 0.2 to 0.6 µg/L for atrazine and from 0.05 to 0.3 µg/L for metolachlor (fig. 3). The two northern tributaries (Yawger and Paines Creeks), however, produced a seasonal loading in June 1998 that caused slightly higher herbicide concentrations above the thermocline (in the epilimnion) in the northern part of the lake than in the southern part, as shown by the statistically significant trend lines (atrazine $p = 0.009$; metolachlor $p = 0.09$) in fig. 3. This result is consistent with the hypothesis that parts of Cayuga Lake basin that have a high percentage of agricultural land can produce seasonal loadings of herbicides that cause elevated concentrations in those parts of the lake that receive the loadings.

Water below the thermocline (hypolimnion) was well mixed from the previous winter's turnover, and herbicide concentrations were less variable than in the epilimnion and showed no north-to-south trend. The range in concentrations below the thermocline remained fairly constant throughout the year, as indicated by analyses of water samples collected quarterly since 1996 at Ithaca's public-water supply intake at Bolton Point near the southern end of the lake (fig. 1). Herbicide concentrations below the thermocline were also slightly lower than above it, as shown by t-test comparisons of group means (atrazine $p = 0.001$; metolachlor $p = 0.03$).

Degradation rates for metolachlor and atrazine apparently become nearly negligible after entering streams and lakes (Buser, 1990; Mueller and others, 1997). The range and distribution of metabolite concentrations in Cayuga Lake could not be defined because the data were insufficient. The ratios given in table 2, however, indicate that (1) metolachlor-ESA concentrations were from 8 to 18 times greater than those of metolachlor, (2) metolachlor-OA concentrations were from 3.2 to 7 times greater than those of metolachlor, and (3) deethylatrazine concentrations were about 17 percent lower than those of atrazine. The ratios for all three metabolites were significantly higher in lake water than in the tributaries; this indicates that

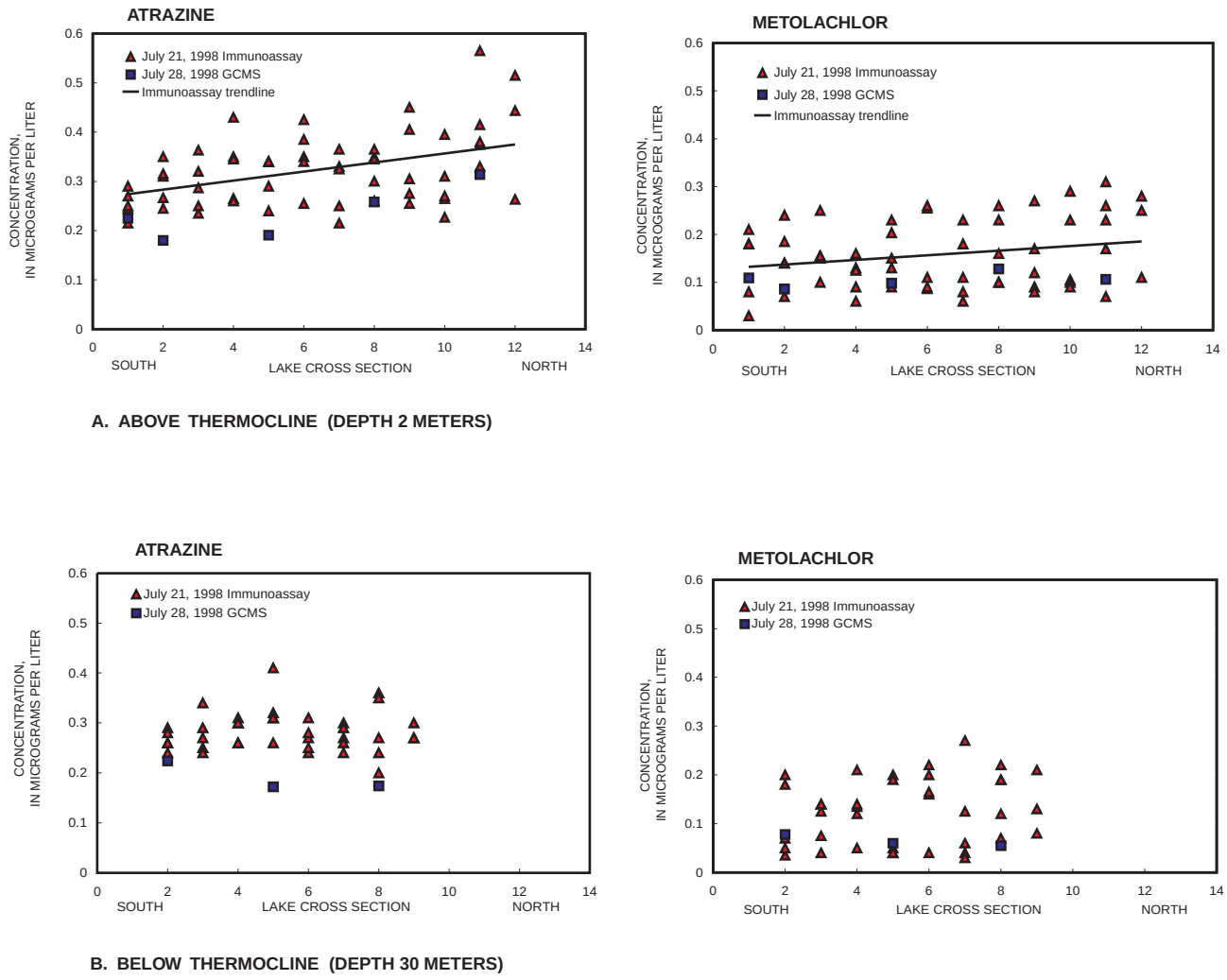


Figure 3. Concentrations of atrazine and metolachlor above and below thermocline at selected cross sections of Cayuga Lake, N.Y., July 1998. (Locations are shown in fig. 1.)

the herbicide and metabolite concentrations in the tributaries might not be representative of all water flowing into the lake. For example, metabolite-enriched ground water that enters the lake directly from adjacent agricultural land might have contributed to the high ratios observed in the lake; this could be especially true in areas such as the Yawger Creek basin, where the karstic limestone provides direct flowpaths to the lake. Also, the long water-retention period for Cayuga Lake (about 12 years; Oglesby, 1978) could provide sufficient time for transformation of the parent compounds in the lake.

A lake volume of 9.4×10^9 m^3 (Birge and Juday, 1914) and an average atrazine concentration of 0.30 µg/L (from the data in fig. 3) indicate that the amount of atrazine present in the lake in 1998 was 2.8 metric tons. The amount of metolachlor, based on an average metolachlor concentration of 0.15 µg/L, was 1.4 metric tons. The ratios given in table 2 indicate that the metabolite mass in the lake were about 18 metric tons of metolachlor-ESA, 7.0 metric tons of metolachlor-OA, and 2.3 metric tons of deethylatrazine. As mentioned previously, the GCMS results for water samples collected at Ithaca's public-water supply at Bolton Point, which

takes water from below the thermocline near the southern end of the lake, has shown no time trend in pesticide concentrations (1996 to present). The lake's long retention time implies that at least a decade of continued monitoring would be required for a determination of trends in herbicide and metabolite concentrations.

SUMMARY AND CONCLUSIONS

An appraisal of pesticide occurrence in Cayuga Lake and its major tributaries was conducted in 1998 as part of a program with the State of New York for monitoring pesticides in water. The work included (1) collection of stormflow samples in three major tributaries during June 1998, shortly after herbicide applications to agricultural land, and (2) collection of water samples from Cayuga Lake at 12 cross sections on 2 consecutive weeks 1 month later. Results are presented for two pesticides that are widely used in corn and soybean agriculture (atrazine and metolachlor) and their main metabolites.

The highest metolachlor concentrations in all three tributaries occurred during peak flow, which indicates that the bulk of metolachlor is transported in stormflow. The metabolites persisted at high concentrations during streamflow recession as the soils drained, and as interflow and ground-water discharge contributed more to the streamflow than direct surface runoff after the rain had ceased. Concentrations of the atrazine metabolite (deethylatrazine), by contrast, increased only slightly during stormflow and were never more than half the values of the parent compound. Deethylatrazine concentrations remained relatively low compared to those of the parent compound and to the metolachlor metabolites, probably because atrazine degrades at a much slower rate than metolachlor. Significantly more metolachlor-ESA was transported than any other herbicide residue; this indicates that it is relatively stable and mobile in the aquatic environment.

The ratios of one metabolite to another metabolite, and to the parent compound, in streamflow samples indicated that base flow in the three tributaries before the June 1998 storm was more highly enriched with metolachlor-ESA than with metolachlor or metolachlor-OA. These ratios decreased during peak flow, when the concentrations of the parent compound were highest from the rapid flush in overland runoff, but increased during the recession period. The most marked increase during recession was in the ratio of metolachlor-OA to metolachlor, which were more than three times the base-flow values. Apparently, metolachlor-OA that is formed in the soils after pesticide application and is mobile during stormflow does not persist in ground water.

In general, concentrations of herbicides in Cayuga Lake were fairly uniform throughout the lake — from 0.2 to 0.6 µg/L for atrazine and from 0.05 to 0.3 µg/L for metolachlor. Seasonal loadings cause slightly higher concentrations in the epilimnion in parts of the lake near outlets of tributaries that drain areas of extensive agricultural activity in the northern part of the lake's basin. Water in the hypolimnion was well mixed from the previous winter turnover of the lake, and herbicide concentrations were less varied and did not show the effect of seasonal loadings that were seen in the epilimnion. Identification of temporal trends in herbicide concentrations will require at least a decade of continued monitoring because the lake's water-retention time can exceed 12 years.

Metolachlor-ESA concentrations in the lake were from 8 to 18 times greater than those of the parent metolachlor; metolachlor-OA concentrations were from 3.2 to 7 times greater than those of metolachlor, and deethylatrazine concentrations were about 17 percent lower than those of atrazine. These ratios were significantly higher in lake water than in tributary stormflow. The difference may be due in part to (1) the inflow of metabolite-enriched ground water that enters the lake directly from adjacent agricultural land, and (2) the transformation of the parent compounds during their residence in the lake.

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