

Pesticides and Their Metabolites in Three Small Public Water-Supply Reservoir Systems, Western New York, 1998-99



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Twenty five pesticides or pesticide metabolites were detected in samples collected from May, 1998 through January, 1999 in three small public-supply reservoirs in western New York. Samples were collected at tributaries and reservoir outlets for comparison with samples from the water-supply intakes. No samples

from public-water-supply intakes exceeded any Federal or State water-quality standards, although some samples from tributaries did exceed a few standards. The maximum concentrations of the most frequently detected pesticides in water-supply intake samples were between 10 and 50 percent of the lowest applicable

water quality standard. Pesticides that exceeded water-quality standards at the tributary sites were the herbicides atrazine, alachlor, and cyanazine, and the insecticide *p,p'*-DDE. Land use in the watersheds that surround these reservoirs is largely agricultural; thus, the results do not necessarily represent conditions in other water-supply reservoirs in New York State.

The most frequently detected pesticides or pesticide metabolites were the corn herbicides atrazine and metolachlor, and two metabolites of metolachlor - metolachlor ethanesulfonic acid (ESA) and metolachlor oxanilic acid (OA). More than half of the samples from the three water-supply intake sites contained at least one of these compounds at concentrations greater than 0.2 $\mu\text{g/L}$ (micrograms per liter); the concentrations ranged from 0.01 to nearly 10 $\mu\text{g/L}$. Many samples contained metabolites of other commonly used herbicides at concentrations greater than those of their parent compounds. Only two insecticides or insecticide metabolites were detected (carbofuran and *p,p'*-DDE) and concentrations of these compounds were less than 0.1 $\mu\text{g/L}$.



The total concentration of pesticides and metabolites at the three water-supply intake sites are correlated with land use. The highest concentrations were in the watershed with the greatest percentage of row-crop land use, and the lowest concentrations were in the watershed with the smallest amount of row-crop land use. Total median concentration of all pesticides and metabolites at the water-supply-intake sites (median sum of detected pesticide and metabolite concentrations in all samples) was 10.0 µg/L for the LeRoy intake (25 percent row-crop land use), 2.99 µg/L for the Perry intake (21

percent row-crop land use), and 1.28 µg/L for the Hornell intake (12 percent row-crop land use). The decline in concentrations and numbers of pesticides and metabolites detected after the first storm runoff following pesticide application (the spring flush) was generally much greater in the tributaries than at the water-supply intakes, particularly for the LeRoy site. The lower variability at the intake sites is attributed to storage within the reservoir and may also be the result of sustained release of pesticides and metabolites from ground water that discharges to the reservoirs.

INTRODUCTION

In 1997, the U.S. Geological Survey (USGS), in cooperation with the New York State Department of Environmental Conservation (NYSDEC) began a statewide monitoring program to assess the occurrence of pesticides in ground water and surface waters of New York State, including Long Island. A part of that study addressed pesticides and their metabolites in three small public-water-supply reservoirs in western New York that receive agricultural runoff. These three reservoirs supply the city of Hornell and the villages of LeRoy and Perry (fig. 1). These reservoirs were selected for study because results of a study by the New York State Department of Health (NYSDOH) indicated that these reservoirs contained higher concentrations of pesticides than many other water-supply reservoirs in New York. In 1997, NYSDOH detected atrazine at concentrations ranging from 0.2 µg/L to 0.8 µg/L at these three sites. Concentrations of metolachlor at the Hornell and LeRoy reservoirs were around 1.0 µg/L, and concentrations of cyanazine at the LeRoy reservoir ranged from 0.1 to 0.3 µg/L (Paul Kaczmarczyk, NYSDOH, personal communication, 2000). Although the

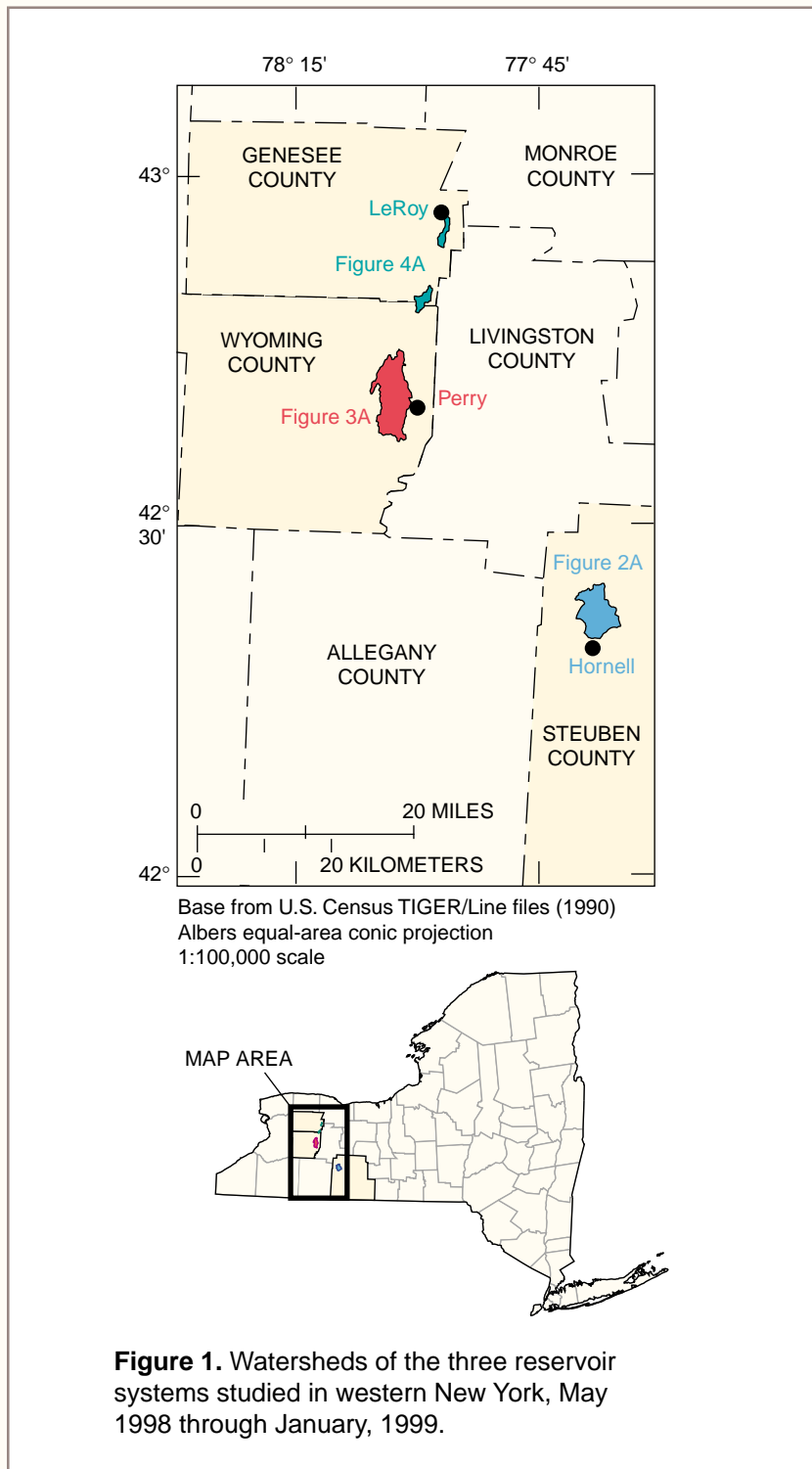


Figure 1. Watersheds of the three reservoir systems studied in western New York, May 1998 through January, 1999.

concentrations observed in this study are not necessarily representative of those in other public-supply reservoirs in the State, the seasonal trends, and the relations between concentrations in tributaries and those at the water-supply intakes, could apply to reservoirs in other small watersheds in areas with large amounts of row-crop land use.

The purpose of this study was to investigate the occurrence of pesticides and their metabolites within the three watersheds, and to relate the concentrations of these compounds to (1) Federal and State water-quality standards; (2) differences in the amount of row-crop land within the three watersheds; and (3) season of sampling. The study entailed sampling at 11 sites between May 1998 and January 1999. Three of the sites were at water-supply intakes, where water is withdrawn for public supply; five were on tributaries that feed the reservoirs, and three were at reservoir outlets. The sites, and the amount of agricultural land use (including row crop) within the

drainage area of each sampling site are summarized in table 1.

The study addressed a greater number of pesticides and metabolites and used far lower analytical detection limits than those typically used in routine pesticide monitoring in public water supplies. Of particular interest in this study were two metabolites of the commonly used herbicide metolachlor - metolachlor ESA (ethanesulfonic acid) and metolachlor OA (oxanilic acid). These two metabolites have frequently been detected in agricultural areas of New York and other States (Phillips and others, 1999; Eckhardt and others, 1999; Kahlkoff and others, 1998). Concentrations of these metabolites are frequently much higher than those of the parent compounds from which they are derived.

METHODS

Locations of sampling sites in the Hornell, Perry, and LeRoy reservoir watersheds are shown in 2A, 3A, and 4A, respectively. Each sampling site

was classified as one of three types - intake, tributary, or outflow - depending on location within the watershed or use of the site for water supply. Intake sites were those used for water-supply withdrawal. Data from the intake sites do not represent treated (finished) water that is provided to consumers. Tributary sites were on streams that discharge to either the reservoir or to lakes upstream of the reservoir. Outlet sites were on reservoirs at locations not directly used for public water supply. Samples were collected at one intake and one or more tributary site in each of the three watersheds, and at outlet sites in the Hornell and LeRoy watersheds.

The Hornell system contains two reservoirs upstream from the public-supply reservoir; they are known as reservoirs 2 and 3, and the sampling sites on their outlets are designated H-02 and H-03 (fig. 2A, table 2). The intake for the village of Perry draws water from Silver Lake (fig. 3B), which is the only lake or reservoir in that watershed. The LeRoy system consists of two lakes (Lake LaGrange

Table 1. Land use in the 11 sampling-site drainage areas in western New York, May 1998 through January 1999.

[Land-use data based on USGS satellite imagery data (1998). Drainage-areas are in square miles.]

Site	Symbol in figs. 2A, 3A, 4A	Drainage Area	Land use, as percentage of drainage area			
			Row Crop	Agriculture*	Residential	Fores
Hornell						
Intake	H-I	13.0	12	41	0.19	58
Reservoir 3 Outlet	H-03	11.2	11	41	0.16	58
Reservoir 3 Tributary	H-T3	7.12	8.7	37	0	63
Reservoir 2 Outlet	H-02	3.75	17	51	0.12	47
Reservoir 2 Tributary	H-T2	3.25	16	51	0	48
Perry						
Intake	P-I	17.4	21	73	2.0	17
Tributary	P-T1	9.90	23	80	0.93	19
LeRoy						
Intake	L-I	3.33	26	83	0.10	12
Lake LeRoy Tributary	L-T1	0.79	40	85	0	15
Lake LaGrange outflow to LeRoy Reservoir	L-01	1.88	20	84	0.093	10
Lake LaGrange Tributary	L-T2	1.45	19	90	0.024	9.3

* Includes dairy, row crop, and other cultivation

and LeRoy Reservoir, fig. 4A). A pipeline conducts water from Lake LaGrange to LeRoy Reservoir; samples that represent this water were collected at the Lake LaGrange outlet (site L-01 in fig. 4A and table 2).

All intake sites and most other sites were sampled at least once in May, June, July, and September 1998. Samples were collected during stormflow on June 26 at most of the tributary sites, but not from the intake sites. Samples were collected from the intake and outlet sites on January 5, 1999, but not from the tributary sites (table 2). Additional samples were collected from the Lake Lagrange outlet on May 18, 1998 and June 22, 1998. The dates of sampling at all sites are summarized in table 2.

Samples were analyzed in USGS laboratories for 60 pesticides and metabolites through methods described by Zaugg and others (1995), Zimmerman and Thurman (1999), and Ferrer and others (1997) (table 3). The analytical method described by Zaugg and others (1995) was developed in cooperation with the U.S. Environmental Protection Agency and was designed to include some of the most commonly used pesticides in the nation. The laboratory methods used in this study resulted in low and (or) inconsistent recovery for five pesticides (carbaryl, carbofuran, deethylatrazine, terbacil and azinphos-methyl). Concentrations reported for each of these compounds are considered estimates, and may

underestimate the true concentration (Chris Lindley, U.S. Geological Survey, written commun., 1994). The detection limits for the compounds monitored in this study, which ranged from 0.001 to 0.2 µg/L (table 3), are much lower than those achieved by analytical methods typically used in public-water-supply monitoring programs, and are far below federal and state public health standards. Therefore, much higher rates of detection were obtained than would have been possible with less sensitive analytical methods.

Land-use characteristics for each sampling site were determined by overlaying watershed boundaries on satellite imagery data collected in 1994 (U.S. Geological Survey, 1998).

WHAT ARE METABOLITES?

Metabolites are formed through the metabolic degradation of a parent compound and can be present in water at concentrations higher than those of the parent compound. Some metabolites can form through the degradation of more than one compound. For example, deisopropylatrazine can form from the degradation of either atrazine or simazine (Thurman and others, 1994). Other metabolites are specific to only one parent compound. For example, metolachlor ESA and OA are derived solely from the parent compound metolachlor.

Sampling for herbicide metabolites in this study was motivated in part by (1) findings in the midwestern United States that the concentrations of many metabolites in surface and ground water often equaled or exceeded those of the parent compound (Kahlkoff and others, 1998; Thurman and others, 1994; Clark and others, 1999), and (2) by similar findings in New York State (Eckhardt and others, 1999; Phillips and others, 1999). At present, little is known about the health effects of these metabolites, and few, if any, Federal water-quality standards for these metabolites have been established. Metabolites represented more than half of the total mass of pesticides plus metabolites detected in many samples collected in this study.

CONCENTRATIONS OF PESTICIDES AND THEIR METABOLITES

Of the 60 pesticides and pesticide metabolites for which samples were analyzed, 23 were detected (fig. 3). Of the 23 that were detected, 21 were herbicides or herbicide metabolites, and 2 were an insecticide or an insecticide metabolite. Pesticide and metabolite concentrations are summarized in figures 2B, 3B, and 4B, in which they are identified as representing either intake sites or reservoir tributary and outlet sites.

Herbicides and their Metabolites

Eight herbicides or herbicide metabolites were detected in intake samples at concentrations of 0.2 µg/L or more (figure 5). Two were the herbicides atrazine and metolachlor. The remaining six were the atrazine metabolites deethylatrazine and hydroxyatrazine,

the metolachlor metabolites metolachlor ESA and OA, and the alachlor metabolites alachlor ESA and OA. These metabolites are frequently present at concentrations higher than those of the parent compounds. The following sections discuss the herbicides and herbicide metabolites detected in decreasing order of frequency.

Atrazine, deethylatrazine, metolachlor, metolachlor ESA, and metolachlor OA.

Both atrazine and metolachlor, and the parent compounds of these metabolites, are used on corn and other row crops. All five compounds were detected in all samples from the Perry and LeRoy systems (fig. 3B and 4B), but only atrazine, metolachlor, and deethylatrazine were detected in all samples from the

Hornell system (fig. 2B). Within the Hornell system, metolachlor ESA was detected in 80 percent of the intake samples, and in all of the tributary and outlet samples. Metolachlor OA was detected in 60 percent of the intake samples, but in only 20 percent of the tributary and outlet samples. Except for

deethylatrazine, the concentrations of these five compounds, when detected, were generally higher than those of the other compounds detected in this study. Concentrations of these five compounds ranged from less than 0.01 µg/L to more than 10 µg/L in the three systems.

Alachlor ESA, cyanazine, deisopropylatrazine, simazine, and alachlor.

Cyanazine, simazine, and alachlor and the parent compounds of these metabolites are used on corn and other row crops. Simazine commonly is used in orchards, vineyards, and rights-of-way. Deisopropylatrazine is a metabolite of both simazine and atrazine. Within the Perry and LeRoy systems, these

five compounds were detected in 40 to 100 percent of the samples from the intake sites and in 23 to 100 percent of samples from tributary and outlet sites (figs. 3B, 4B). Within the Hornell system, alachlor ESA and cyanazine were detected in 40 and 20 percent, respectively, of the samples from the intake site (fig. 2B). None of

the other compounds were detected in samples from this site. Alachlor, simazine, alachlor ESA, and deisopropylatrazine were detected in 7 to 19 percent of the samples from the Hornell tributary and outlet sites. Concentrations of these compounds in all three systems ranged from less than 0.01 µg/L to nearly 5 µg/L.

EPTC, hydroxyatrazine, cyanazine amide, prometon, and alachlor OA.

EPTC and the parent compounds of these metabolites are used on corn and other crops. Prometon is generally used along rights-of-way and as an additive in asphalt, as well as for other nonagricultural purposes. Cyanazine amide is a metabolite of cyanazine. All of these compounds

were detected in at least one intake sample at LeRoy (fig. 4B), and all but cyanazine amide were detected in an intake sample from Perry (fig. 3B). All of these compounds were detected in 8 to 80 percent of the tributary and outlet samples from the LeRoy and Perry watersheds. None of

these compounds were detected in intake samples from Hornell, and only EPTC and prometon were detected in the tributary or outlet samples (fig. 2B) in the Hornell watershed. Concentrations of these compounds, when detected, ranged from less than 0.01 µg/L to just over 5 µg/L.

Pendimethalin, propazine, metribuzin, ethafluralin, linuron, and acetachlor.

Most of these herbicides are used on corn and other crops. They were detected only in

samples from tributary or outlet sites (fig. 2B 3B, 4B). Most of these compounds were only detected in

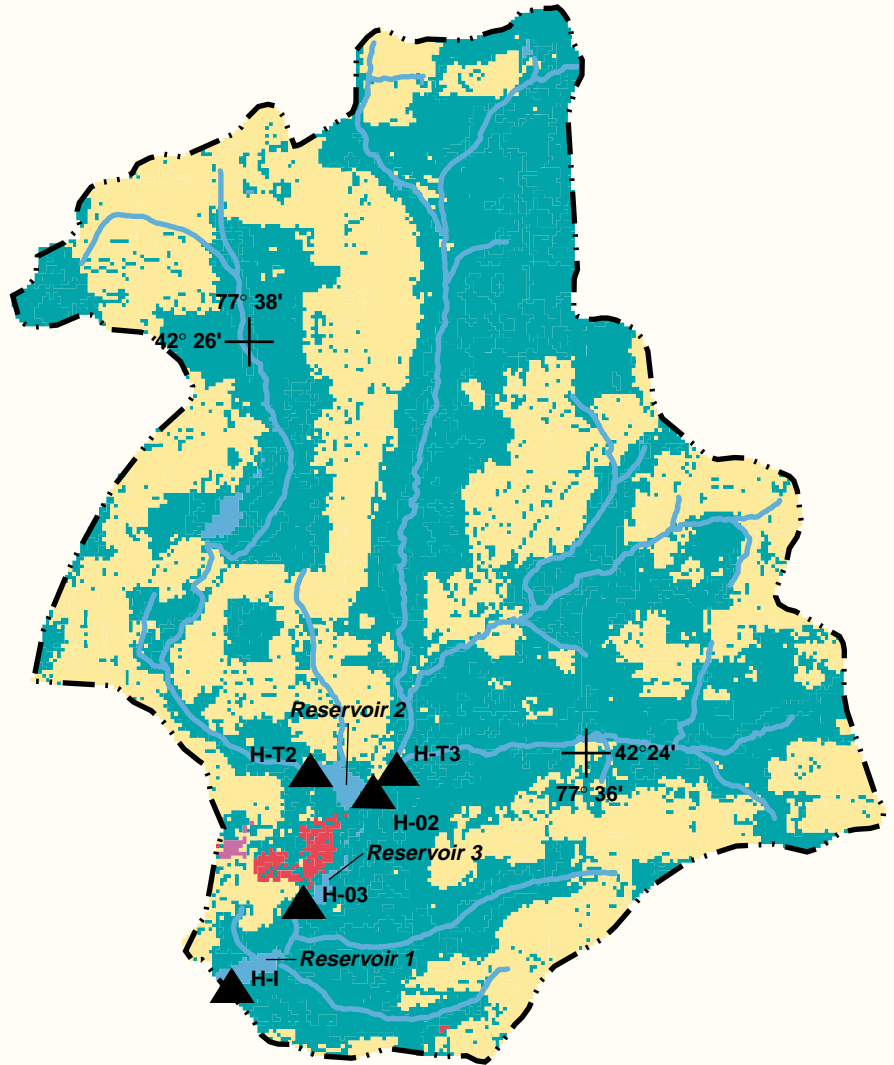
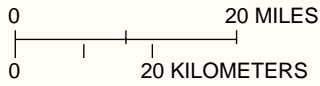
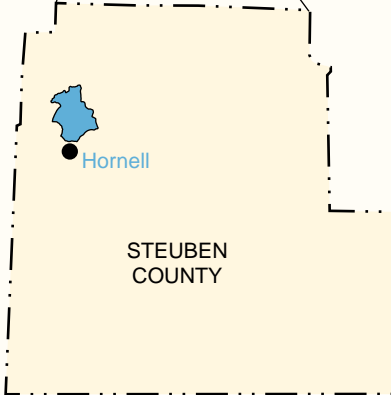
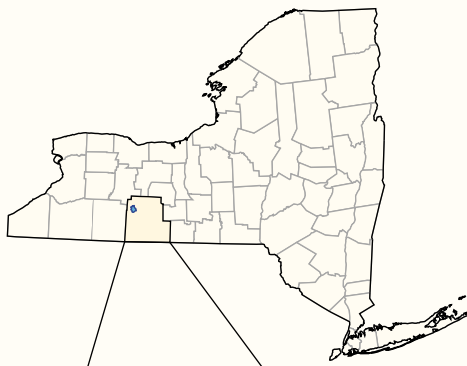
June 26 stormflow samples. Concentrations of these compounds were all below 0.5 µg/L.

Insecticides and their Metabolites

Only one insecticide (carbofuran) and one insecticide metabolite (*p,p'*-DDE) were detected during the study.

Carbofuran is used on corn and other crops. The use of DDT (the parent compound of *p,p'*-DDE) has been banned in New York State for over 20 years. These compounds were found only in samples from tributary sites.

Carbofuran was detected in one sample from Perry tributary P-T1, and *p,p'*-DDE was detected in one sample from Hornell tributary H-T2 (figs. 3A, 2A). Concentrations of these two compounds were less than 0.1 µg/L.



EXPLANATION

- DEVELOPED
- AGRICULTURAL
- FOREST
- OPEN WATER
- OTHER
- H-03 OUTLET- Sampling site
- H-I INTAKE- Sampling site
- H-T3 TRIBUTARY- Sampling site

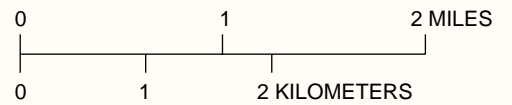
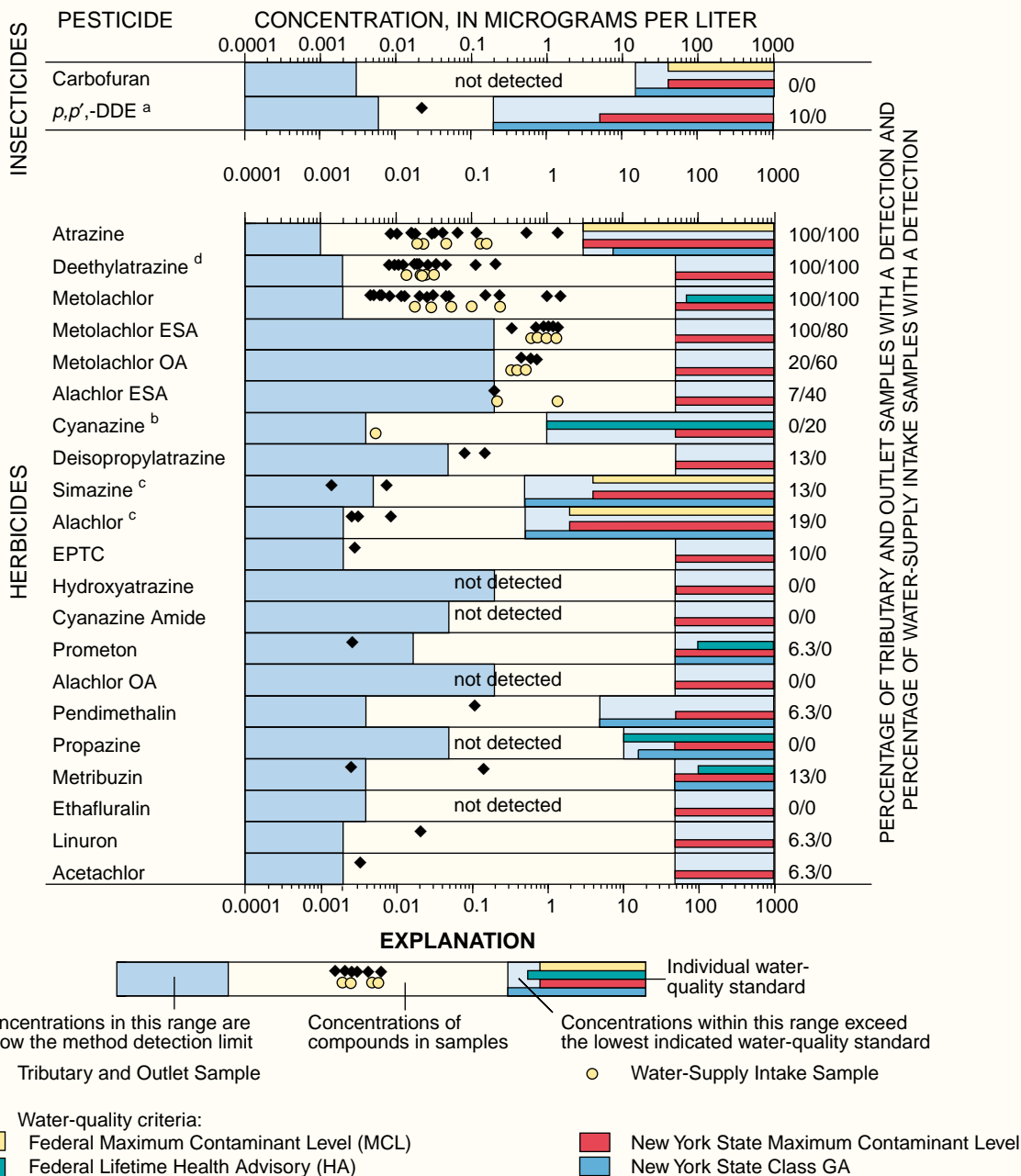


Figure 2A. Land use of the Hornell reservoir system, Steuben County, N. Y. (Data from the U.S. Geological Survey, 1998).

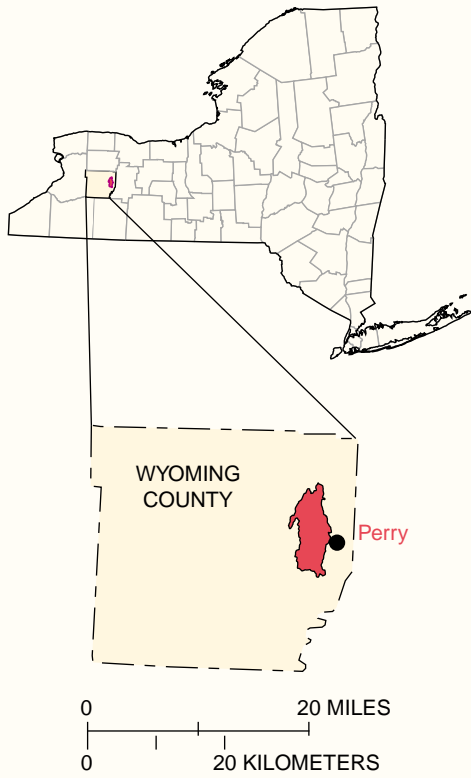
HORNELL - MAY 1998-JANUARY 1999



NOTE: Percentage values and constituent range include quantifiable detections below method detection limits. Percentage values may not be comparable between pesticides because (1) detection limits differ and (2) the number of quantifiable detections below the method detection limit differ. New York State regulations include general standards of 50µg/L for Unspecified Organic Contaminants and 5 µg/L for Principal Organic contaminants. New York State water-quality standards are based on New York State Department of Environmental Conservation (1998) and New York State Department of Health (1998). Federal water-quality standards are based on U.S. Environmental Protection Agency (1996). Federal MCL standards are based on a one-year average concentration of more than one sample.

Footnote
^a All *p,p'*-DDE detections exceed the New York State surface water standard for consumption of fish (7×10^{-6} µg/L).
^b Draft Federal Lifetime Health Advisory
^c New York State Surface Water Standard equals Class GA Standard.
^d Estimated concentration because of low and (or) inconsistent recovery

Figure 2B. Concentrations of pesticides and metabolites detected in water samples from the Hornell reservoir system, Steuben County, N. Y., the relation of detected concentrations to applicable water-quality standards, and percentage of samples in which each compound was detected.



78° 05'

42° 46'

EXPLANATION

- DEVELOPED
- AGRICULTURAL
- FOREST
- OPEN WATER
- P-I INTAKE- Sampling site
- P-T1 TRIBUTARY- Sampling site



42° 40'

78° 02'

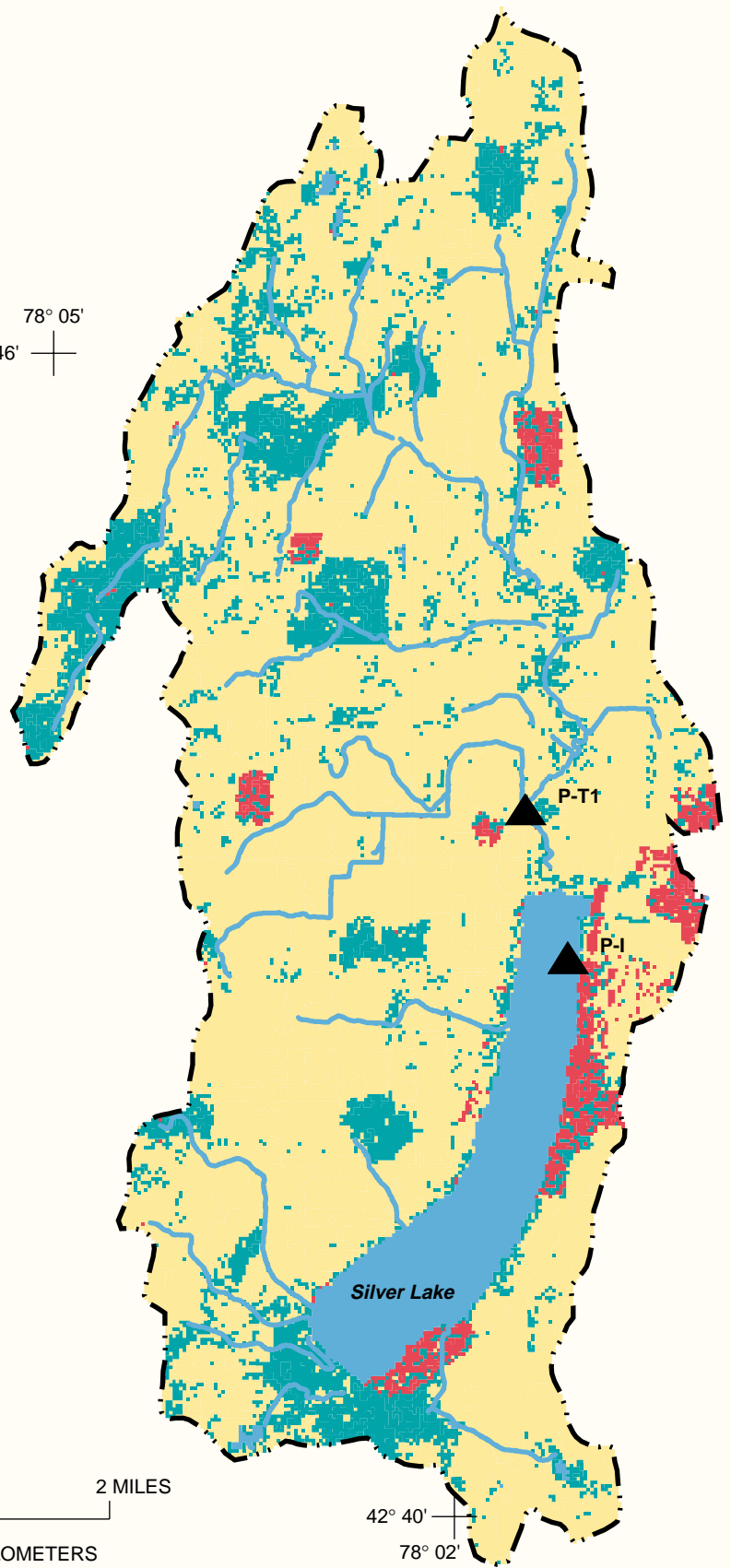
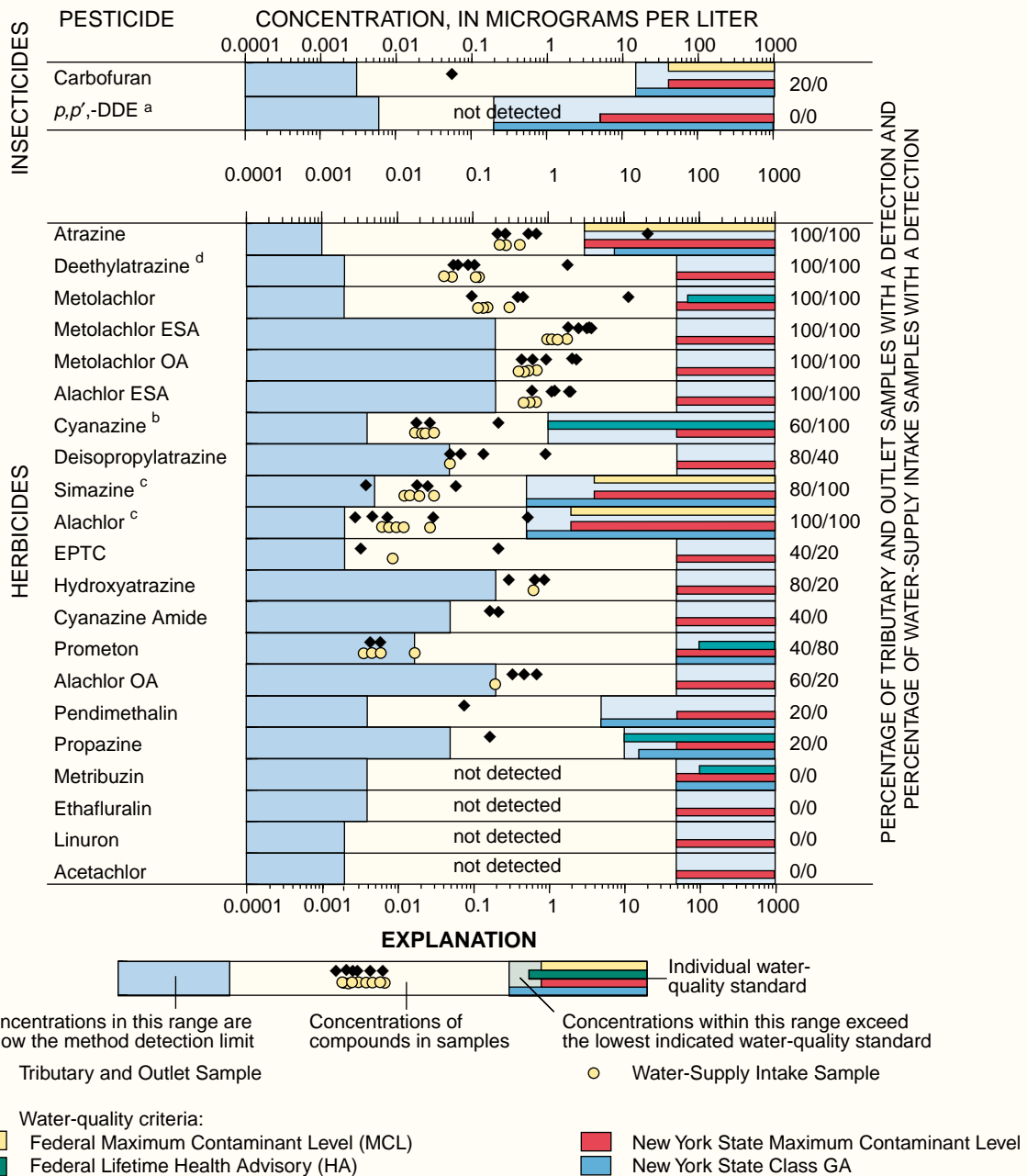


Figure 3A. Land use of the Perry reservoir system (Silver Lake), Wyoming County, N. Y. (Data from the U.S. Geological Survey, 1998).

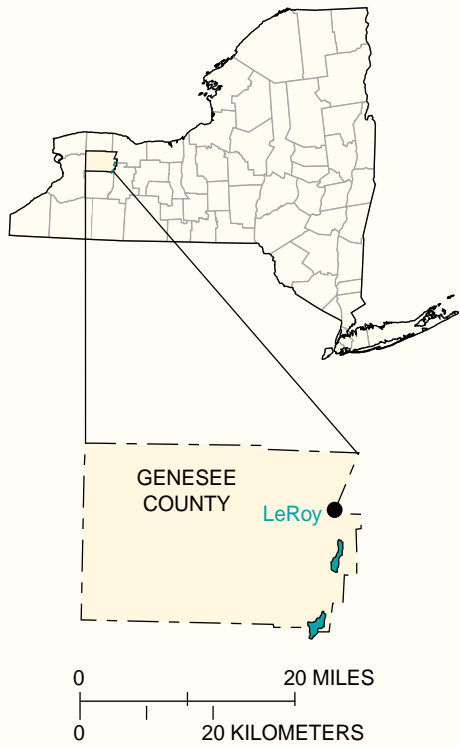
PERRY - MAY 1998-JANUARY 1999



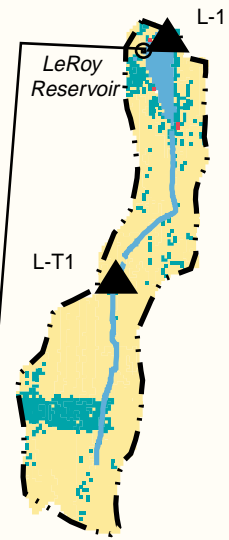
NOTE: Percentage values and constituent range include quantifiable detections below method detection limits. Percentage values may not be comparable between pesticides because (1) detection limits differ and (2) the number of quantifiable detections below the method detection limit differ. New York State regulations include general standards of 50µg/L for Unspecified Organic Contaminants and 5 µg/L for Principal Organic contaminants. New York State water-quality standards are based on New York State Department of Environmental Conservation (1998) and New York State Department of Health (1998). Federal water-quality standards are based on U.S. Environmental Protection Agency (1996). Federal MCL standards are based on a one-year average concentration of more than one sample.

Footnote
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^b Draft Federal Lifetime Health Advisory
^c New York State Surface Water Standard equals Class GA Standard.
^d Estimated concentrations because of low and (or) inconsistent recovery.

Figure 3B. Concentrations of pesticides and metabolites detected in water samples from the Perry reservoir system, Wyoming County, N. Y., the relation of detected concentrations to applicable water-quality standards, and percentage of samples in which each compound was detected.



78° 02'
42° 54'

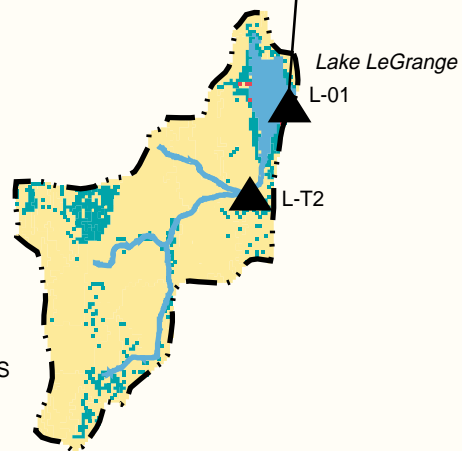


42° 50'
78° 00'

Pipeline

EXPLANATION

- DEVELOPED
- AGRICULTURAL
- FOREST
- OPEN WATER
- L-01 OUTLET- Sampling site
- L-1 INTAKE- Sampling site
- L-T2 TRIBUTARY- Sampling site

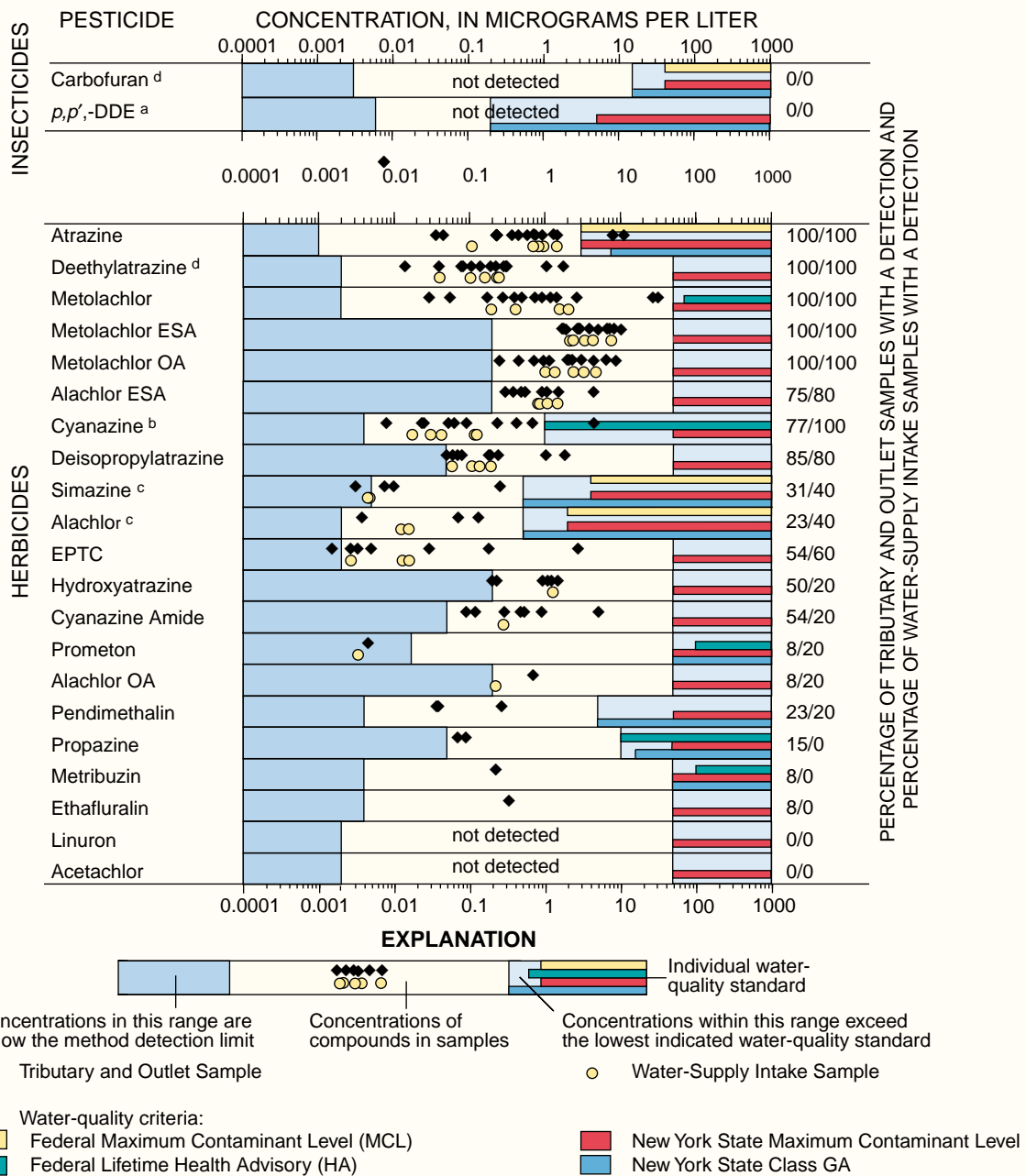


0 1 2 MILES
0 1 2 KILOMETERS

42° 46'
77° 58'

Figure 4A. Land use of the LeRoy reservoir system, (LeRoy Reservoir and Lake LaGrange), Genesee and Wyoming Counties, N. Y. (Data from the U.S. Geological Survey, 1998).

LEROY - MAY 1998-JANUARY 1999



NOTE: Percentage values and constituent range include quantifiable detections below method detection limits. Percentage values may not be comparable between pesticides because (1) detection limits differ and (2) the number of quantifiable detections below the method detection limit differ. New York State regulations include general standards of 50µg/L for Unspecified Organic Contaminants and 5 µg/L for Principal Organic contaminants. New York State water-quality standards are based on New York State Department of Environmental Conservation (1998) and New York State Department of Health (1998). Federal water-quality standards are based on U.S. Environmental Protection Agency (1996). Federal MCL standards are based on a one-year average concentration of more than one sample.

Footnote

- ^a All *p,p'*, -DDE detections exceed the New York State surface water standard for consumption of fish (7×10^{-6} µg/L).
- ^b Draft Federal Lifetime Health Advisory
- ^c New York State Surface Water Standard equals Class GA Standard.
- ^d Estimated concentration because of low and (or) inconsistent recovery

Figure 4B. Concentrations of pesticides and metabolites detected in water samples from the LeRoy reservoir system, Genesee and Wyoming Counties, N. Y., the relation of detected concentrations to applicable water-quality standards, and percentage of samples in which each compound was detected.

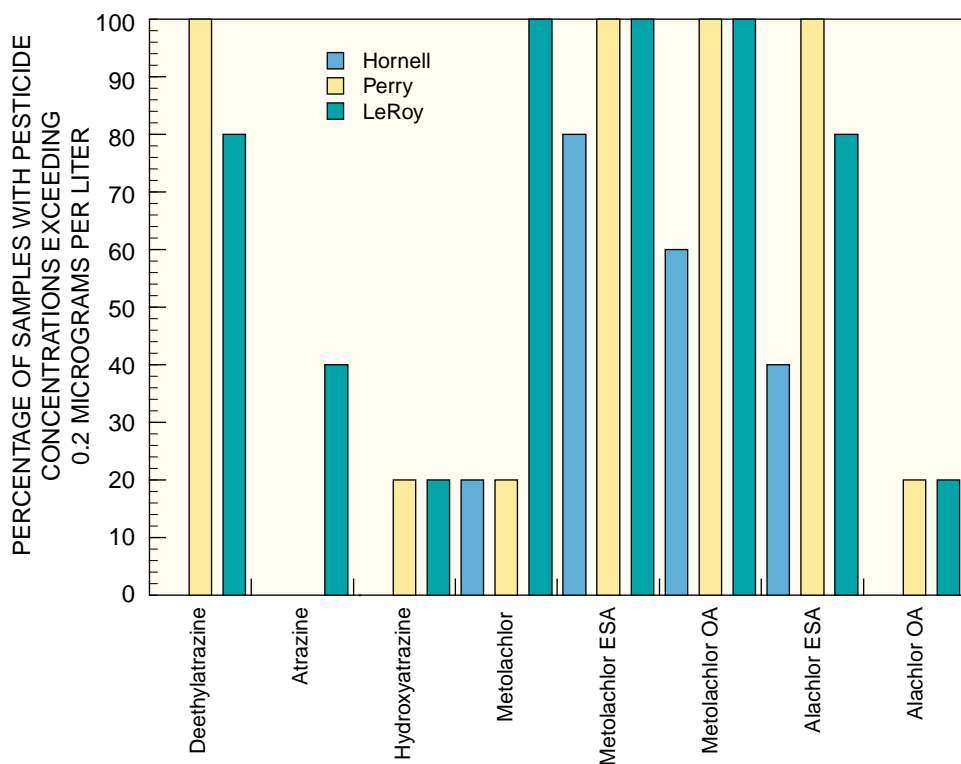


Figure 5. Percentage of samples from water-supply intake sites in the three reservoir systems in western New York containing pesticides in concentrations exceeding 0.2 micrograms per liter, May 1998 through January 1999. (Site locations are shown in fig. 1).

PESTICIDE CONCENTRATIONS IN THE THREE RESERVOIR SYSTEMS IN RELATION TO STATE AND FEDERAL WATER-QUALITY STANDARDS

The samples analyzed in this study contained few pesticides at concentrations that exceeded Federal or State water-quality standards. No samples from the water-supply-intake sites contained pesticides at concentrations that exceeded these standards (figs. 2B, 3B, 4B). The maximum concentrations of the most frequently detected pesticides in water-supply intake samples were between 10 and 50 percent of the lowest applicable water quality standard. No Federal drinking-water standards have been established, however, for many of the pesticide and pesticide metabolites that were detected. The water-quality standards referenced in this report are summarized in the box on page 14.

All samples in which these standards were exceeded were stormflow samples collected on June 26, 1998. Pesticides that exceeded any standards, and the sites at which these standards were exceeded, were as follows:

Atrazine: The Federal Maximum Contaminant Level (MCL) for atrazine (3 µg/L) was exceeded in three tributary stormflow samples—two from LeRoy tributary sites LT-1 and LT-3, and one from the Perry tributary site P-T1. (Locations are shown in figs. 3A and 2A.) The concentrations in samples from LeRoy sites LT-1 and LT-3 were 11.1 and 8.02 µg/L, and that in the sample from Perry site P-T1 was 20.7 µg/L.

Alachlor and cyanazine: The Federal Draft Health Advisory Limit for cyanazine (1 µg/L) and the New York State Surface Water Standard and Class GA Standard for alachlor (0.5 µg/L) were exceeded in the June 26 stormflow sample from the Perry tributary site P-T1. The cyanazine concentration was 4.48 µg/L, and the alachlor concentration was 0.547 µg/L. This sample also exceeded the MCL for atrazine.

p,p'-DDE: The New York State Surface-Water Standard for the consumption of fish (7 x 10⁻⁶ µg/L) was exceeded in a June 26 stormflow sample from Hornell tributary site H-T2 (table 1, fig. 2B). The concentration of p,p'-DDE in this sample was 0.021 µg/L.

Table 2. Dates of sample collection at public water-supply sites in western New York State, May 1998 through January 1999. [A dash indicates no sample was collected.]

Site	Symbol in figure. 2	Date of sample collection, 1998-99					
		May 18	June 22	June 26	July 20	Sep. 28	Jan. 5
Hornell							
Hornell Intake	H-I	x	x	--	x	x	x
Hornell Reservoir 3 Outlet	H-O3	--	--	--	x	x	x
Hornell Reservoir 3 Tributary	H-T3	x	x	x	x	x	--
Hornell Reservoir 2 Outlet	H-O2	--	--	--	x	x	--
Hornell Reservoir 2 Tributary	H-T2	x	x	x	x	x*	--
Perry							
Perry Intake	P-I	x	x	--	x	x	x
Perry Tributary	P-T1	x	x	x	x	x	--
LeRoy							
Intake	L-I	x	x	--	x	x	x
Tributary	L-T1	--	--	x	x	x*	--
Lake LaGrange Outflow to LeRoy	L-O1	x	x		x	x	x
Lake LaGrange Tributary	L-T2	x	x	x	x	x	

* Sample not analyzed by High Performance Liquid Chromatography at USGS Organic Research Laboratory in Lawrence, Kansas.

Table 3. Detection limits for the 60 pesticide and pesticide degradates for which samples from public water-supply sites in western New York State were analyzed, May 1998-January 1999. [ESA, ethanesulfonic acid. OA, oxanilic acid. Detection-limit concentrations (in parentheses) are in micrograms per liter.]

Detection	Pesticide limit	Detection	Pesticide limit	Detection	Pesticide limit	Detection	Pesticide limit
A. Gas Chromatography/Mass Spectrometry US Geological Survey National Water Quality Laboratory, Denver, Colo.							
Acetochlor (0.002)	Deethylatrazine* (0.002)	Metolachlor (0.002)	Pronamide (0.003)				
Alachlor (0.002)	Diazinon (0.002)	Metribuzin (0.004)	Propachlor (0.007)				
alpha-HCH (0.002)	Dieldrin (0.001)	Molinate (0.004)	Propanil (0.004)				
Atrazine (0.001)	Disulfoton (0.017)	Napropamide (0.003)	Propargite (0.013)				
Benfluralin (0.002)	EPTC (0.002)	<i>p,p'</i> -DDE* (0.006)	Simazine (0.005)				
Butylate (0.002)	Ethalfuralin (0.004)	Parathion (0.004)	Tebuthiuron (0.010)				
Carbaryl (0.003)	Ethopropos (0.003)	Parathion-methyl (0.006)	Terbacil (0.007)				
Carbofuran (0.003)	Fonofos (0.003)	Pebulate (0.004)	Terbufos (0.013)				
Chlorpyrifos (0.004)	Lindane (0.004)	Pendimethalin (0.004)	Thiobencarb (0.002)				
Cyanazine (0.004)	Linuron (0.002)	<i>cis</i> -Permethrin (0.005)	Tri-allate (0.001)				
DCPA (0.002)	Malathion (0.005)	Phorate (0.002)	Trifluarlin (0.002)				
2,6-Diethylaniline* (0.003)	Methyl azinphos (0.001)	Prometon (0.017)					
B. High Performance Liquid Chromatography USGS Organic Research Laboratory, Lawrence, Kansas							
Acetachlor ESA* (0.2)	Alachlor ESA* (0.2)	Hydroxyatrazine* (0.2)	Metolachlor OA* (0.2)				
Acetachlor OA* (0.2)	Alachlor OA* (0.2)	Metolachlor ESA* (0.2)					
C. Gas Chromatography/Mass Spectrometry USGS Organic Research Laboratory, Lawrence, Kansas							
Ametryn (0.05)	Deisopropylatrazine* (0.05)		Propazine (0.05)				
Cyanazine Amide* (0.05)	Prometryn (0.05)	Terbutryn (0.05)					

• degradation product

FEDERAL AND NEW YORK STATE WATER-QUALITY STANDARDS USED IN THIS STUDY

The concentrations of pesticides and pesticide metabolites detected in this study are compared with five different State and Federal standards. The standards are based on concentrations of individual pesticides and do not account for mixtures of pesticides. Web sites with additional information on the Federal Standards are included below.

-Federal Maximum Contaminant Levels (MCLs) are the maximum permissible level of a contaminant in water that is delivered to any user of a public water system under the Federal Safe Drinking Water Act (U. S. Environmental Protection Agency, 1996). MCLs are set as close as feasible to the level at which no known or anticipated adverse effects on health are expected to occur. <http://www.epa.gov/safewater/glossary.htm>

-Federal Health Advisory Levels (HALs) are established by U.S. Environmental Protection Agency under the Safe Drinking Water Act when adequate scientific information is available but an MCL has not yet been officially set. <http://www.epa.gov/OST/Tools/dwstds.html>

-New York State Maximum Contaminant Levels are established under the New York State Department of Health Public Water Systems Regulations (New York State, 1998). State MCLs are similar to Federal MCLs but they include (1) a standard of 50 µg/L for organic contaminants where adequate health data are not available to set specific standards, and (2) a standard for Principal Organic Contaminants of 5 µg/L.

- New York State Surface-water-quality standards have been established by the NYSDEC for (1) the protection of aquatic species, humans, and wildlife using the resource, and (2) preservation of the quality of water for use as a potential drinking-water source or for fishing. These standards are designed to protect these waters from health-based and aesthetic impacts.

-New York State Class GA Standards are set by NYSDEC on the basis of health-based or aesthetic-based procedures established in New York State (New York State, 1998) to protect ambient ground waters that are a potential source of drinking water. Class GA Standards are used for protection of the resource rather than as a limit for water consumption and use. Accordingly, these risk-based standards are typically more stringent than drinking-water MCLs.

Use of Low Detection Limits

The use of low detection limits for many pesticides for which samples were analyzed in this study resulted in a higher frequency of detection than would have been by using less sensitive methods. This is particularly important for monitoring insecticide concentrations, because many insecticides are present at extremely low concentrations. The use of analytical methods with such low detection limits not only aids in the identification of trace amounts of pesticides and metabolites in water and their trends, but also allows researchers to discern relations between pesticide exposure and human health. These low detection limits also increase the likelihood that pesticides not detected in the analysis are truly absent from the waters sampled.

Pesticide and Metabolite Concentrations at Intake Sites in Relation to Land Use

Total concentration of all pesticides and metabolites in samples from the three intake sites were directly related to the amount of cropland in the surrounding watershed. The highest concentrations were in the samples from the LeRoy reservoir watershed, which has the largest percentage of row-crop land (table 1). Total median pesticide and metabolite concentration (median of the sum of the concentrations of all detected pesticides and all detected pesticide metabolites in all samples collected from a given site during the study) for the LeRoy intake was 10 µg/L. The lowest total median intake-site concentration was in the Hornell reservoir (1.28 µg/L), whose watershed has the lowest percentage of row-crop land. The total median

concentration for the Perry intake site was intermediate between the others (2.99 µg/L), and the amount of row-crop land in the Silver Lake watershed at Perry is intermediate between the amounts in the other two watersheds.

Concentrations of the herbicides atrazine, cyanazine, and metolachlor and the metolachlor metabolites metolachlor ESA, and metolachlor OA also corresponded to land use. These were among the most frequently detected, and had some of the highest concentrations, of any compounds detected in this study. Together, these compounds generally constituted more than 80 percent of the total concentration of all pesticides and metabolites in samples from the intake sites. Their concentrations tended to be lowest in the Hornell intake samples, intermediate in the Perry intake samples, and highest in the LeRoy intake samples (fig. 6).

Seasonal Differences among Pesticide and Metabolite Concentrations at Intake Sites

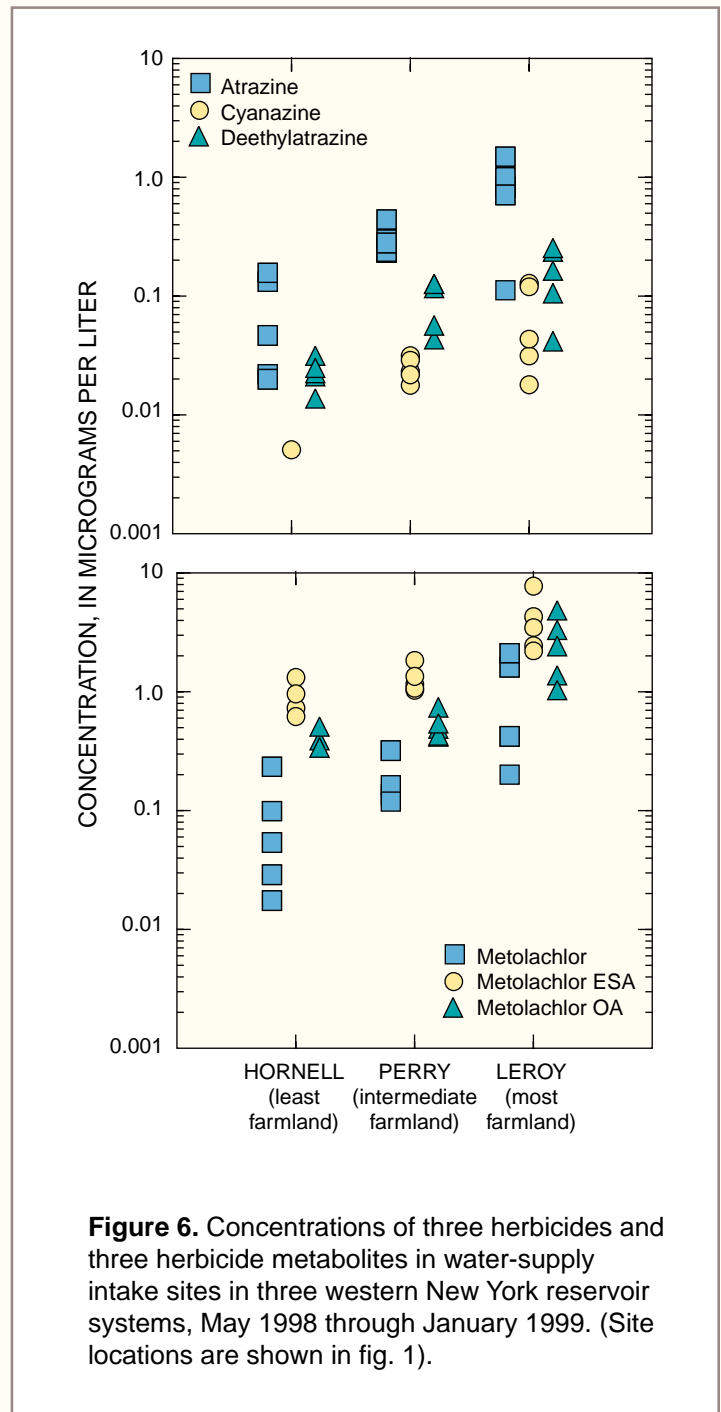
Total concentration of all detected pesticides and metabolites, and the numbers of pesticide and metabolite compounds detected at these sites varied seasonally. The patterns at the LeRoy and Perry intake sites differed from those at the Hornell intake site. In May 1998, total concentrations at the Perry and LeRoy intakes were about 3 and 5 $\mu\text{g/L}$, respectively. By July, after the spring pesticide applications (fig. 7), they increased to nearly 4 and 13 $\mu\text{g/L}$, respectively. Total concentration then declined through January 1999, although the January value was higher than that of the preceding May. The total concentrations at the Hornell intake peaked in June 1998 (at less than 3 $\mu\text{g/L}$), then declined to less than 0.7 $\mu\text{g/L}$ by January 1999 - a value much lower than that of May.

The numbers of pesticide and metabolite compounds detected also differed among the intake sites. Between 8 and 12 compounds were in the LeRoy and Perry intake samples. The fewest number of compounds were detected in summer (September at LeRoy, July at Perry), and greatest in January (fig. 7). The highest total concentration of all pesticides and metabolites detected in the intake samples did not coincide with the greatest number of pesticide and metabolite compounds detected for the LeRoy and Perry intake samples. Fewer compounds (between 3 and 7) were detected in the Hornell intake samples. The fewest number of compounds were detected at the Hornell site in September, and the most in June. Unlike the LeRoy and Perry intake samples, the highest total concentrations in Hornell intake samples coincided with the greatest number of compounds detected.

Previous studies in New York have found that concentrations of most herbicides measured in New York streams commonly peak in June storm runoff and decline to less than 10 percent of their June or July values in the winter months (Wall and Phillips, 1998). A similar pattern was found in samples from the Hornell intake, but the decline in the LeRoy and Perry intake samples from June 1998 to January 1999 was much less (fig. 7). The small number of samples collected in this study, and the short duration of the study, make the exact cause of the differences in seasonal patterns among the three watersheds difficult to identify. The persistence of elevated pesticide concentrations in the LeRoy and Perry intake

samples into January, however, suggest that pesticides and metabolites enter the reservoirs during and directly after the first storm after pesticide application. These compounds are stored in the reservoir and are likely also stored in the adjacent aquifer, which sustains elevated concentrations at the intake sites from the summer through early winter.

Differences among pesticide and metabolite concentrations in intake, outlet, and tributary sites in the LeRoy watershed are discussed in the following section through a comparison of concentrations of six commonly detected herbicides or herbicide metabolites.



HERBICIDE AND METABOLITE CONCENTRATIONS AT TRIBUTARY, OUTLET, AND WATER-SUPPLY-INTAKE SITES

Data from the LeRoy reservoir system are representative of the general relations among herbicide and metabolite concentrations at the tributary, outlet, and water-supply-intake sites and are used in this discussion to illustrate the seasonal differences in concentrations among the three types of sites. These comparisons can indicate the most likely migration paths of herbicides that reach the intake sites.

Concentrations of six of the most frequently detected herbicides and metabolites (atrazine, cyanazine, deethylatrazine, metolachlor, metolachlor ESA, and metolachlor OA) in the tributary to Lake LaGrange (site L-T2 in fig. 4A) fluctuated only slightly from May to mid-June, then increased sharply in the stormflow of June 26 (fig. 8), the first heavy rain since the application of pesticides earlier in the month. Concentrations in this tributary and also the tributary to LeRoy Reservoir (site L-T1) then decreased to less than 1 percent of the peak concentrations (site L-T1 was not sampled before June 26) by the end of September 1998. Concentrations of the two metolachlor metabolites in the tributary samples did not decline as much as the four herbicides after June 26. The likely source of the sustained metolachlor metabolite concentrations in the tributaries is ground water that is discharged to the streams.

The elevated concentrations of herbicides and metabolites in the June 26 tributary samples are consistent with those commonly observed in streams during spring stormflows that directly follow pesticide applications to agricultural land in New York (Eckhardt and others, 1999; Wall and Phillips, 1998). These and other studies generally have concluded that the maximum annual concentrations of many herbicides in streamflow occur during the spring flush in late June or early July. Thus, the elevated concentrations in the tributary stormflow of June 26 are probably attributable to the recent application of herbicides in that year.

Concentrations of these herbicides or metabolites at the water-supply-intake and the outlet sites between May and September generally fluctuated less than in the tributaries (fig. 8). The concentrations at the intake (site L-I) and at the Lake Lagrange outlet (site L-O1) gradually increased from May through late July, then mostly decreased, but nevertheless remained higher than in the May samples. No stormflow samples were collected at the intake or outlet sites in late June; therefore, a direct comparison among the tributary,

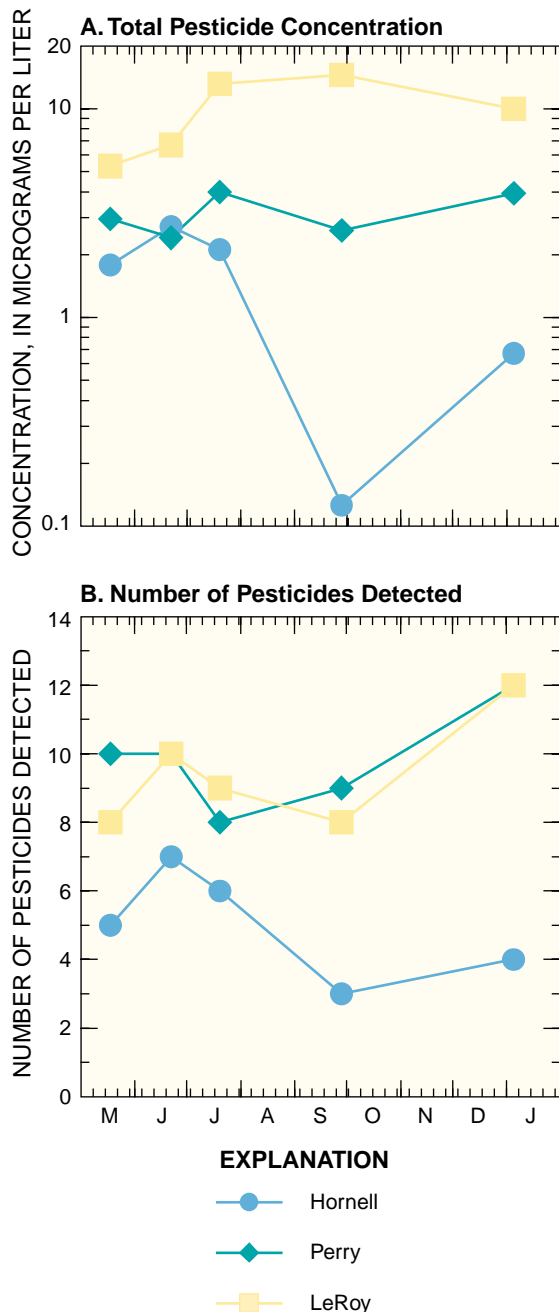


Figure 7. Concentration and detection of pesticides and metabolites in samples from water-supply-intake sites on the three reservoirs in western New York, May 1998 through January 1999. A. Total concentration of all pesticides and metabolites, B. Number of pesticides and metabolites detected.

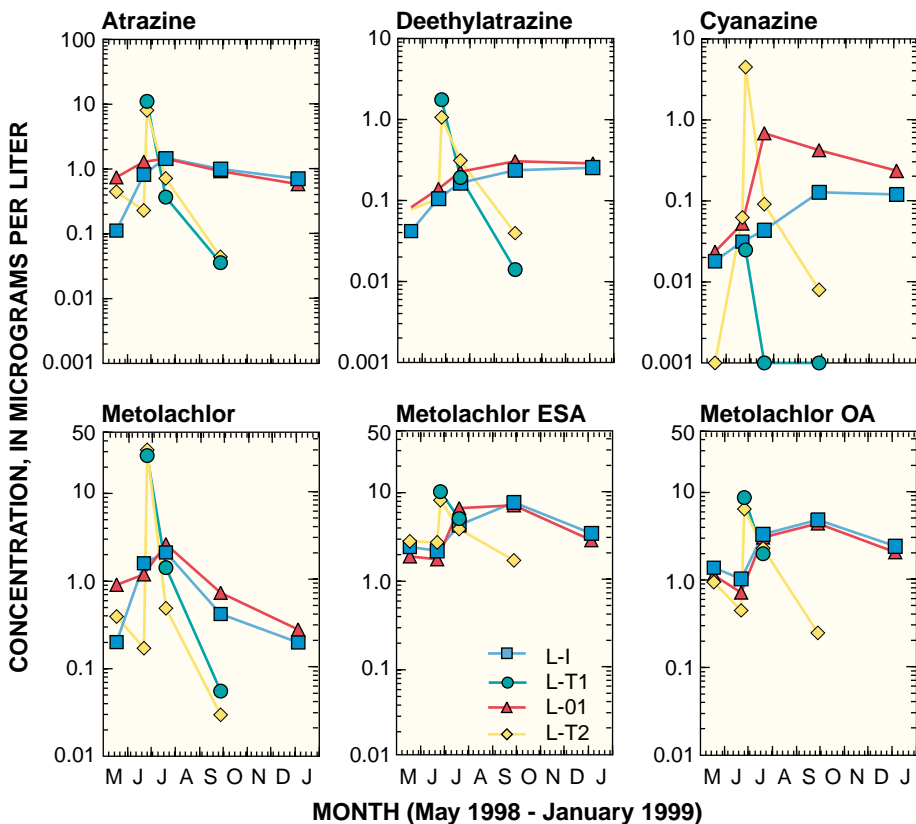


Figure 8. Concentrations of two herbicides and their metabolites in samples from tributaries, outlet, and water-supply intake in LeRoy reservoir system in western New York, May 1998 through January 1999. (Sampling-site locations are shown in fig. 4A.)

intake, and outlet concentrations of June 26 cannot be made, nor can the immediate effect of pesticide inputs from tributary stormflow on concentrations within the reservoirs be assessed.

Although the peak June concentrations of the six compounds in the two tributaries exceeded the peak concentration at the intake and the outlet, the concentrations in the two tributaries were lower than those at the intake and the outlet by September. Concentrations of these six compounds at the intakes and outlets in the Perry and Hornell reservoirs also generally exceeded those in the tributaries by September,

although the seasonal differences were not as great as those in the LeRoy watershed. The exception to this pattern was the concentrations of metolachlor ESA and metolachlor OA in the Perry tributary in September, when they exceeded those at the Perry water-supply intake.

The above observations indicate that herbicide and metabolite concentrations in surface-water inflow to the LeRoy and Perry watersheds gradually decrease throughout the year after the first flush following pesticide application in late spring or early summer. Although the concentrations at the water-supply-

intakes (and presumably in the reservoirs themselves) are probably never as high as in the tributaries during the spring flush, the concentrations at the intake do not decline from July through September, probably because the herbicides and metabolites are stable in the lakewater, and are probably replenished by herbicides and metabolites in ground water that enters these lakes. The greater decrease in herbicide and metabolite concentrations in the Hornell intake after the spring flush than in the Perry and LeRoy intakes indicates that herbicides and metabolites in the Hornell reservoir are either not stored to the same extent as in the other two reservoirs, or are degraded more rapidly, or become more diluted than in the other two watersheds.

The exact cause of the observed differences among tributary, intake, and outlet samples was not investigated in this study, but the data presented indicate that the concentrations of herbicides and metabolites at the water-supply intakes were higher than those in the tributaries well into the fall and early winter. The tributaries are a major source of herbicides and metabolites, but the concentrations do not remain elevated after June. The inflow from the tributaries does not directly account for the elevated herbicide and metabolite concentrations at the intake from July to September 1998; therefore, the elevated concentrations at the intakes are attributed to either storage in the reservoirs or in the ground-water flow system that discharges to the tributaries and reservoirs, or a combination of both. Herbicide and herbicide metabolite storage is probably greatest in the LeRoy watershed, which has the largest percentage of agricultural land, and is least in the Hornell watershed, which has the smallest percentage of agricultural land.

The small number of samples taken in this study make it difficult to determine the reasons for the differences in the concentrations and distribution of compounds observed in samples from the three watersheds. The differences seen, however, strongly suggest that sampling strategies to estimate the maximum annual pesticide concentrations in streams, lakes and reservoirs need to be specifically tailored to land use and hydrologic conditions of the monitored watershed.

SUMMARY

Concentrations of selected pesticides and metabolites in three largely agricultural watersheds in western New York were monitored from May 1998 through January 1999. Twenty three compounds, including one insecticide, one insecticide metabolite, and 21 herbicides or herbicide metabolites were detected. Samples were collected at three types of sites-tributaries, lake outlet, and water-supply intake. Water samples from some tributary sites exceeded Federal or State standards for atrazine, alachlor, cyanazine, and *p,p'*-DDE, but no samples from water-supply-intake sites exceeded water-quality standards. The maximum concentrations of the most frequently detected pesticides in water-supply intake samples were between 10 and 50 percent of the lowest applicable water quality standard. Results from this study probably are not representative of conditions in other water-supply reservoirs in New York

State, however, because the reservoirs were selected on the basis of their elevated pesticide concentrations and high percentage of agricultural land within the watersheds.

The most frequently detected herbicides were atrazine and metolachlor, which are used on corn and other row crops. Other frequently detected compounds were the metolachlor metabolites - metolachlor ethanesulfonic acid (ESA) and metolachlor oxanilic acid (OA). At least one of these four compounds was detected at a concentrations above 0.2 µg/L in half of the water-supply-intake samples.

Concentrations of the most frequently detected compounds ranged from less than 0.01 µg/L to 4 µg/L. Metabolites of herbicides detected in this study were often present at concentrations greater than that of their parent compounds. Maximum concentrations of the two insecticides detected (carbofuran and *p,p'*-DDE) were less than 0.1 µg/L.

Total concentration of all pesticides and metabolites at the three water-supply intakes are correlated with the amount of cropland within the watersheds. Total median concentration of pesticides and metabolites (the median sum of all concentrations of detected pesticides and metabolites for all samples taken at an intake) were 10 µg/L at the LeRoy intake (watershed is 26 percent cropland use); 2.99 µg/L at the Perry intake (21 percent cropland), and 1.28 µg/L in the Hornell intake (12 percent cropland). Herbicides or herbicide metabolites constituted over 90 percent of the

total pesticide and metabolite concentration in these samples.

Total concentration of all pesticides and metabolites in water-supply-intake samples from the LeRoy and Perry systems increased from May to July 1998 and decreased thereafter. The January 1999 concentrations at the LeRoy and Perry intakes exceeded those of May 1998, whereas the January 1999 concentrations at the Hornell intake did not. Concentrations of herbicides and herbicide metabolites in samples from tributaries varied more than those in the intake samples. Concentrations in the tributary samples peaked in late June after a rainstorm following the spring pesticide application, then by late September, declined to levels much lower than those at the water-supply intakes. This indicates that, in general, the tributaries did not contribute significant amounts of herbicides or metabolites to the reservoirs from July to September 1998. Therefore, herbicides and herbicide metabolites that enter the tributaries in the spring probably are stored in the reservoirs, where they become diluted and slowly move to the water-supply intakes throughout the year.

The differences in the concentrations and distribution of pesticides observed among the three watersheds in this study suggest that sampling strategies to estimate the maximum annual pesticide concentrations in streams, lakes and reservoirs need to be specifically designed to account for land use and hydrologic conditions in the watershed.

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