

Prepared in cooperation with the NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

# Pesticide Concentrations in Surface Waters of New York State in Relation to Land Use - 1997

## Abstract

*Analyses of water samples collected from 64 streams and rivers across New York State in June 1997 indicate that patterns of pesticide detection are largely related to the predominant upstream land use and pesticide-application patterns. Of the 47 pesticides for which the samples were analyzed, 25 were detected. Concentrations of most pesticides detected were low and generally did not exceed 0.1 µg/L (microgram per liter). Herbicides used on cornfields, including atrazine, metolachlor, cyanazine, alachlor, and the atrazine degradate deethylatrazine, were detected in samples from 41 to 97 percent of the 64 sites sampled. The highest concentrations (greater than 0.10 µg/L) of these compounds were in streams in western New York State, where corn production is the greatest. Two insecticides—carbaryl and diazinon—were detected in 20 and 14 percent of the samples, respectively. Carbaryl was detected most frequently in streams whose drainage basins either contain extensive vineyards or orchards, or are widely urbanized. Diazinon was detected most frequently in streams that drain urban or residential watersheds. Concentrations of four insecticides—azinphos-methyl, p,p'-DDE, diazinon, and dieldrin- and one herbicide-simazine—exceeded some New York State water-quality criteria. Some Federal or State criteria were exceeded at 10 sites. These results represent an initial assessment of the status of pesticide concentrations in surface waters of New York State and, when combined with data collected in the future, will help water managers to assess the status, trends, and health impacts of pesticide contamination of ground and surface waters of New York State including Long Island. This information also will be useful to researchers and water managers who require such data to define the health and environmental effects of pesticide use in the State.* ♦

## INTRODUCTION

In 1997, the State of New York and the U.S. Geological Survey (USGS) began a cooperative effort to monitor pesticides in State waters as required under the New York State Pesticide Reporting Law (Environmental Conservation Law Section 33-0714). The initial monitoring phase entailed a statewide survey of pesticide concentrations in surface waters, particularly in areas where pesticides are applied and in areas where surface water is used for water supply. Samples were analyzed for 47 pesticides, including herbicides, insecticides, and their degradation products. Herbicides are used to control weeds in agricultural fields as well as lawns, commercial land, and other open areas in urban and residential settings. Insecticides are used to control insects in agricultural and urban settings.

*In general, concentrations of most pesticides detected in this statewide survey did not exceed 0.10 µg/L.*



**Table 1.** Site-identification number, land-use classification, and names of stream sites at which water samples were collected in June and July 1997 for pesticide analysis.

[URB = Urban/residential, FOR = Forested, ORV = Orchard/Vineyard, LAG = Low Intensity Row-Crop agricultural site, HAG = High Intensity Row-Crop agricultural site. Locations are shown in fig. 1]

Site No.	Site Class-ification	USGS Station Number	Site name	1997 Sampling Date	Drainage area (in square miles)
01	URB	01304500	Peconic River at Riverhead	June 12	75
02	URB	01309500	Massapequa Creek at Massapequa	June 16	38
03	FOR	04268000	Raquette River at Raymondville	June 19	1130
04	LAG	01372043	Hudson River near Poughkeepsie	June 09	11700
05	FOR	04275500	Ausable River near Au Sable Forks	June 18	448
06	URB	01375000	Croton River at New Croton Dam near Croton-on-Hudson	June 16	378
07	URB	01376500	Saw Mill River at Yonkers	June 09	25.6
08	LAG	01361200	Claverack Creek at Claverack	June 10	60.6
09	LAG	04280450	Mettawee River near Middle Granville	June 12	167
10	LAG	01371500	Wallkill River at Gardiner	June 16	695
11	LAG	01351450	Schoharie Creek at Esperance	June 11	875
12	LAG	01351270	West Creek near Warnersville	June 10	53
13	FOR	01434025	Biscuit Brook above Pigeon Brook at Frost Valley	June 09	3.72
14	LAG	01434000	Delaware River at Port Jervis	June 17	3070
15	URB	01356220	Stony Creek at Vischer Ferry	June 12	12
16	LAG	04260500	Black River at Watertown	June 19	1860
17	LAG	01423000	West Branch Delaware River at Walton	June 17	332
18	HAG	04249000	Oswego River at Lock 7, Oswego	June 09	5100
19	LAG	04247000	Oneida River near Euclid	June 09	1439
20	LAG	03011020	Allegheny River at Salamance	June 18	1610
21	LAG	01513831	Susquehanna River at Owego	June 10	4220
22	HAG	04235000	Canadaigua Outlet at Chapin	June 16	195
23	HAG	04235820	Grout Brook tributary southeast of Fair Haven	June 17	0.27
24	HAG	04235276	Black Brook at Tyre	June 16	19
25	HAG	04235250	Flint Creek at Phelps	June 11	102
26	HAG	04231000	Black Creek at Churchville	June 16	130
27	HAG	01529500	Cohocton River near Campbell	June 10	470
28	HAG	04218000	Tonawanda Creek at Rapids	June 10	349
29	HAG	04216418	Tonawanda Creek at Attica	June 10	76.9
30	LAG	01510000	Otselic River at Cincinnatus	June 17	147
31	HAG	04230500	Oatka Creek at Garbutt	June 16	200
32	HAG	04245200	Butternut Creek near Jamesville	June 17	32.2
33	HAG	04213500	Cattaraugus Creek at Gowanda	June 18	436
34	ORV	04232100	Sterling Creek at Sterling	June 09	44.4
35	ORV	04219650	Fourmile Creek near Youngstown	June 17	19.7
36	ORV	04232070	Salmon Creek near Sodus	June 16	26.0
37	ORV	04232060	Salmon Creek at Pultneyville	June 16	18.1
38	ORV	04219726	Lake Ontario Tributary No. 150 near Wilson	June 17	4.58
39	ORV	423034077092601	Unnamed tributary to Keuka Lake	June 09	0.75
40	ORV	0423241755	Bullhorn Creek at McGrath Point	June 09	1.21
41	ORV	424104077180001	Unnnamed tributary to Canadaigua Lake	June 09	0.25
42	ORV	0421337640	Beaver Creek near Cordova	June 17	4.02
43	ORV	0421332805	Spring Creek at mouth near Westfield	June 17	2.4
44	HAG	423939077465201	Unnamed stream near Shakers Crossing	June 10	17.5
45	HAG	425540078140101	Unnamed stream near Alexander	June 10	0.080
46	LAG	04228915	Reynolds Brook at Canandice Lake Rd.	June 12	3.48
47	FOR	03011505	Red House Brook south of Red House Lake	June 17	3.78
48	LAG	422950076305901	Cayuga Lake near Bolton Point	July 02	786
49	LAG	425549076250201	Skaneateles Lake near Skaneateles	July 02	72.7
50	LAG	424618077364701	Hemlock Lake near Hemlock	July 02	45.4
51	HAG	04229500	Honeoye Creek at Honeoye Falls	June 11	196
60	URB	01304000	Nissequogue River near Smithtown	June 16	27
61	URB	01305000	Carmans River at Yaphank	June 18	71
62	URB	01305500	Swan River at East Patchogue	June 18	8.8
63	URB	01306495	Connetquot River near Oakdale	June 17	24.3
64	URB	01308000	Sampawams Creek at Babylon	June 17	22.7
65	URB	01308500	Carmans River at Yaphank	June 17	35.4
66	URB	01309100	Santapogue River (Highway 27A) at Linde	June 17	5.42
F1	HAG	01349150	Canajoharie Creek near Canajoharie	June 11	59.7
F2	LAG	01357500	Mohawk River at Cohoes	June 11	3450
F3	HAG	04237500	Seneca River at Baldwinsville	June 11	3140
F4	HAG	04234000	Fall Creek near Ithaca	June 11	126
F5	HAG	04228500	Genesee River at Avon	June 10	1670
F6	HAG	04227000	Canaseraga Creek at Shakers Crossing	June 10	335

This report presents the results of the June-July 1997 statewide pesticide survey of 64 streams and rivers across New York State, and discusses the methods used to collect and analyze the data. Detection rates for several pesticides are presented, and pesticide concentrations are discussed in relation to (1) Federal and State water-quality standards, (2) results of previous water-quality investigations in New York State, and (3) predominant land-use and pesticide-use patterns in the watersheds investigated.

## Methods

Water samples were collected from a statewide network of 64 sites (table 1, fig. 1) from early June through early July 1997, by which time most agricultural pesticides had been applied. Each site was sampled once, and samples were collected under base-flow (dry-weather) conditions except at five sites, where they were collected during periods of stormflow runoff. In general, concentrations of pesticides in streams in June and July are highest during stormflow conditions (Wall and Phillips, 1997), but inclusion of these few samples in the analysis had negligible effect on the results. Samples from six sites on Long Island were collected as part of the USGS Long Island/New Jersey National Water-Quality Assessment program. Together, the 64 sites represent a wide range of land uses—forested, agriculture (cropland, orchards, and vineyards), urban, and residential. The watersheds represented by these sites range in size from less than 1 mi<sup>2</sup> (square miles) to more than 10,000 mi<sup>2</sup>.

Water samples were collected and filtered in accordance with methods described by Shelton (1994) and were analyzed for 47 pesticides through methods described by Zaugg and others (1995). Detection limits (technically known as Method Detection Limits) for pesticides analyzed ranged from 0.001 to 0.018 µg/L. Analyses of quality-assurance samples indicate that these laboratory results accurately represented concentrations in the streams. The laboratory methods used in this study resulted in low and (or) inconsistent recovery for five pesticides (carbaryl, carbofuran, deethylatrazine, terbacil, and azinphos-methyl). Thus concentrations reported for each of these compounds are considered estimates (Chris Lindley, U.S. Geological Survey, written commun., 1994). Detection rates are reported as a percentage of the total number of samples analyzed, and include samples in which concentrations were reported as being below the method detection limit. This reporting is common when a compound can be conclusively identified (Jeffrey W. Pritt, U.S. Geological Survey, written commun., 1994). These concentrations indicate the presence of pesticides in the sample; these concentrations are considered estimates. The data discussed in this report are available in Butch and others (1998) and on the

Internet at <http://ny.usgs.gov/htmls/pub/nypesticides/index.html>.

Each site was classified in one of five categories, depending on the predominant land use in the watershed. These categories were Forested, Urban/Residential, Orchard/Vineyard, Low intensity row-crop agricultural and High intensity row-crop agricultural. Watershed boundaries were overlain on mapping-data imagery generated from satellite data collected in 1994 (U.S. Geological Survey, 1997). Forested watersheds were defined as those in which forests and wetlands cover more than 88 percent of the watershed area. Urban/residential watersheds are those in which more than 13 percent of the land is urban (including residential, commercial and industrial land, parks, lawns, and golf courses). Low intensity row-crop agricultural watersheds were those in which row crops occupy less than 20 percent of the land, and high intensity row-crop watersheds are those in which more than 20 percent of the land is planted in row crops. The remote-sensing data were inadequate for delineation of orchards and vineyards. Therefore, these watersheds were not classified according to remote-sensing data, but through field reconnaissance, as having substantial orchard or vineyards.

## PESTICIDES IN SURFACE WATERS OF NEW YORK

The most commonly detected pesticides were the herbicides that are frequently applied to cornfields. The herbicides atrazine, metolachlor, and the atrazine-degradation compound deethylatrazine were detected in 80 percent of the streams (figs. 1 and 2). Other frequently detected herbicides that are commonly used on cornfields include alachlor and cyanazine, which were detected in 50 and 41 percent of the streams sampled, respectively. The highest concentrations of these compounds were found in western New York streams that drain areas with the greatest corn production in the State. These four herbicides also are frequently found in streams and rivers of the Midwest, which drain the nation's major corn-producing regions (Goolsby and Battaglin, 1993). Atrazine was detected in all but two of the streams; yet the concentrations of atrazine in the four forested watersheds were extremely low. The presence of atrazine in streams draining forested watersheds is probably due to atmospheric transport and deposition. The herbicide EPTC, which is commonly used on corn and dry beans, was detected in slightly more than 10 percent of the streams, most of which are high intensity row-crop watersheds in western New York.

The herbicide simazine was detected in 72 percent of the streams sampled. This compound is commonly used in orchards and vineyards, and many of the streams and rivers with the highest concentrations of simazine drain watersheds in western New York that are classified as orchard/vineyard.

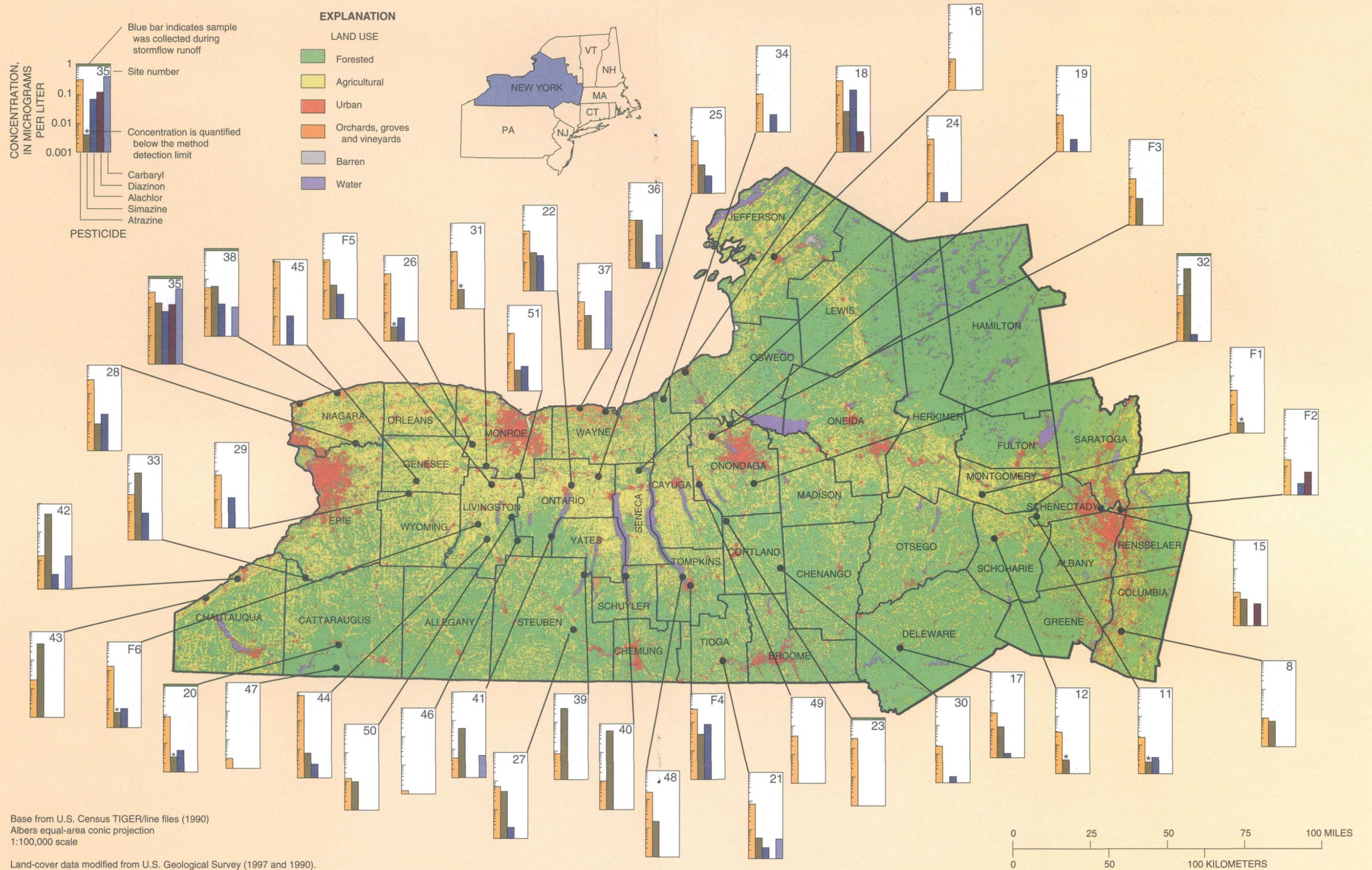
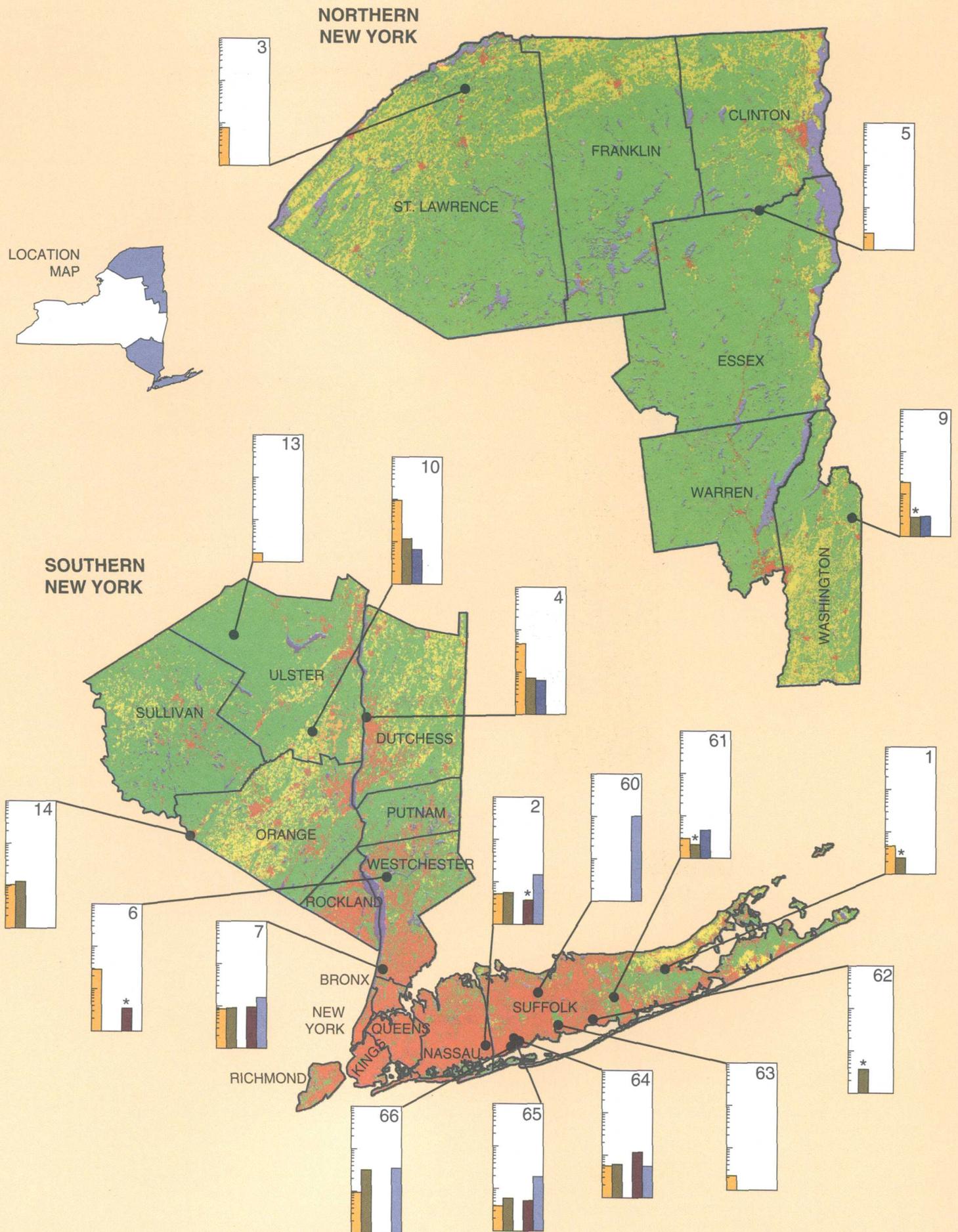
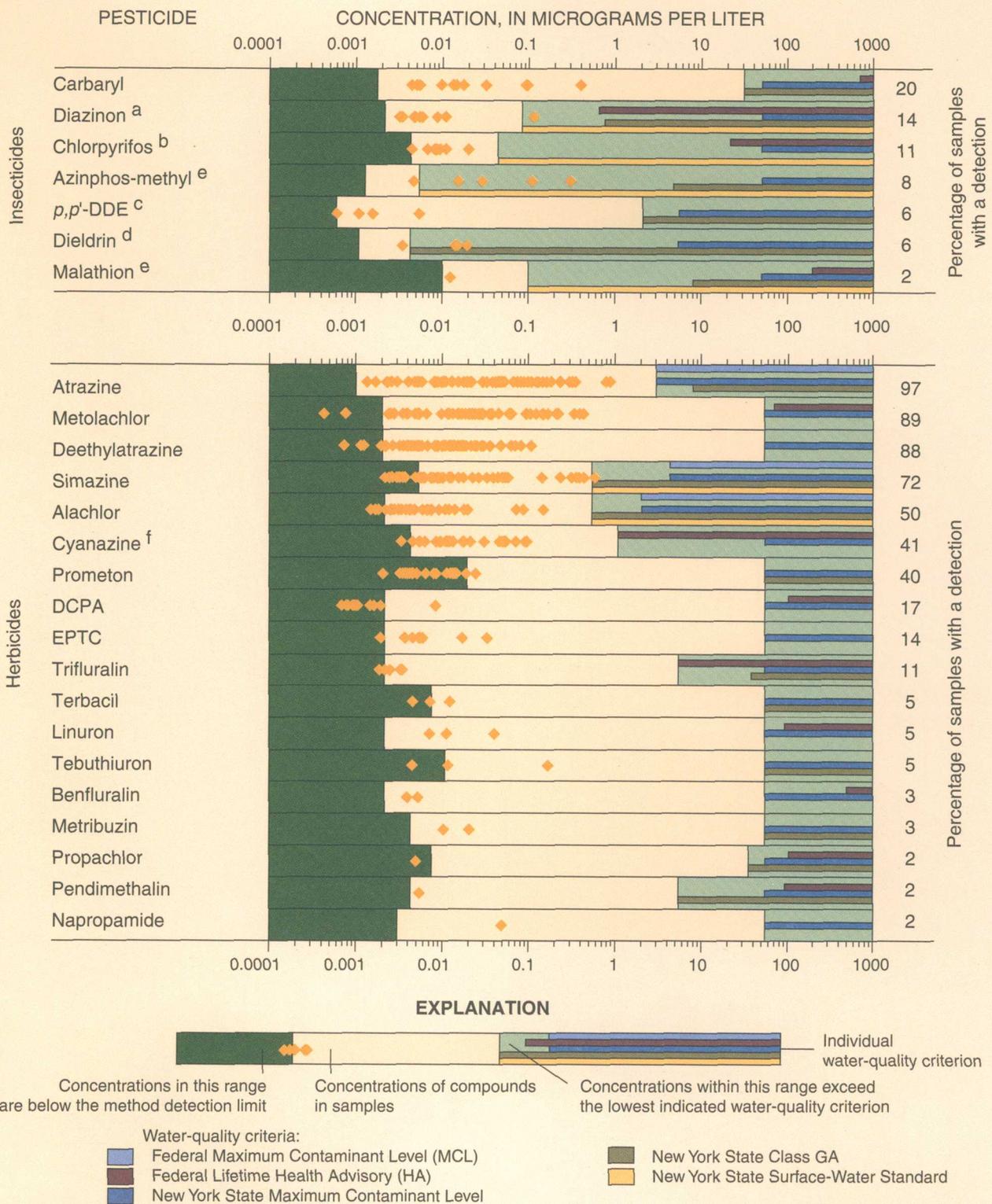


Figure 1. Land-use/land-cover categories in New York and statewide network of pesticide-sampling sites, with measured concentrations of five selected pesticides.



**Figure 1.** (Continued) Land-use/land-cover categories in New York and statewide network of pesticide-sampling sites, with measured concentrations of five selected pesticides.



NOTE: Percentage values and constituent range include quantifiable detections below method detection limits. Percentage values may not be comparable between pesticides due to different detection limits and the number of quantifiable detections below the method detection limit.

Footnotes

- <sup>a</sup> New York State Surface-Water Standard based on New York State Aquatic Life Criteria
- <sup>b</sup> New York State Surface-Water Standard based on U.S. Environmental Protection Agency Freshwater No Observable Effects Limit
- <sup>c</sup> All *p,p'*-DDE detections exceeded the New York State Surface-Water Standard for consumption of fish ( $7 \times 10^{-6}$   $\mu\text{g/L}$ )
- <sup>d</sup> All Dieldrin detections exceeded the New York State Surface-Water Standard for consumption of fish ( $6 \times 10^{-7}$   $\mu\text{g/L}$ )
- <sup>e</sup> New York State Surface-Water standard based on New York State Aquatic Chronic Criteria
- <sup>f</sup> Draft Federal Lifetime Health Advisory (HA)

**Figure 2.** Concentrations of 25 pesticides detected in New York stream samples collected in June - July 1997, and percentage of samples in which each pesticide was detected. New York State water-quality criteria are based on New York State(1998); Federal water-quality criteria are based on U.S. Environmental Protection Agency (1986, 1996).

*Concentrations of only a few compounds exceeded applicable State or Federal Water-Quality standards.*



Two insecticides—carbaryl and diazinon—were detected in 20 percent and 14 percent of the samples, respectively. These compounds were most often detected in streams draining areas in which these compounds are commonly applied—carbaryl in orchard/vineyard watersheds, and diazinon in urban/residential watersheds. The highest carbaryl concentrations were found in streams draining two types of watersheds—orchard/vineyard and urban/residential watersheds in western New York, and urban/residential watersheds in southeastern New York (including Long Island). The highest concentrations of diazinon were found in urban/residential watersheds in southeastern New York, including Long Island.

In general, concentrations of most pesticides detected in this statewide survey were low, and few exceeded 0.1 ug/L. The largest exceptions to this generalization were atrazine, metolachlor, cyanazine, and simazine; more than 10 percent of the streams contained these compounds in concentrations greater than 0.1 ug/L. Of the 47 pesticides studied, 22 were not detected in any sample (table 2).

The pesticide concentrations measured in this survey probably do not reflect maximum annual concentrations because most of the samples were collected during base-flow (low-flow)

conditions. Previous sampling for pesticides in a small agricultural watershed in the Hudson River Basin during 1994-96 indicated that concentrations of pesticides are lower in base flow than in stormflow (Wall and Phillips, 1996a, 1997). Base flow consists mostly of ground water that discharges from the underlying aquifer to streams. Thus, the presence of pesticides in base flow samples suggests that these pesticides may be present in ground water.

The similarity of results from the 1997 survey to results from a 1994 survey of pesticides at 46 sites in the Hudson River Basin (Wall and Phillips, 1996b)

**Table 2.** Pesticides not detected in surface-water samples from statewide survey, June-July 1997, and their detection limits. [Detection limits are in micrograms per liter.]

Constituent	Detection limit	Constituent	Detection limit
Acetochlor	0.002	Molinate	0.004
$\alpha$ -HCH	0.002	Parathion	0.004
Butylate	0.002	Pebulate	0.004
Carbofuran	0.003	<i>cis</i> -Permethrin	0.005
2,6-Diethylalanine*	0.003	Phorate	0.002
Disulfoton	0.017	Propanil	0.004
Ethalfuralin	0.004	Propargite	0.013
Ethoprop	0.003	Pronamide	0.003
Fonofos	0.003	Terbufos	0.013
Lindane	0.004	Thiobencarb	0.002
Methyl Parathion	0.006	Triallate	0.001

\* Degradation product

indicates that most of these pesticides have been present in New York streams for at least 3 years. Both surveys used identical sample-collection and analytical methods; therefore, the results of the two surveys can be compared directly. The most commonly detected pesticides in both surveys were atrazine, metolachlor, and deethylatrazine. Other compounds that were commonly detected in both years were simazine, cyanazine, and alachlor. The most commonly detected insecticides in both years were carbaryl and diazinon.

## Water-Quality Criteria

Concentrations of only a few compounds exceeded applicable State or Federal water-quality standards. Concentrations, detection limits, and water-quality criteria are summarized in figure 2. No pesticides exceeded Federal MCL (maximum contaminant levels) or health advisory levels (HA), and four insecticides (azinphos-methyl, *p,p'*-DDE, diazinon, and dieldrin) and only one herbicide (simazine) exceeded a New York State water-quality criterion. (New York State water quality criteria are given in New York State, 1998; Federal standards are given in United States Environmental Protection Agency, 1996). Three types of State criteria were exceeded—those for consumption of fish (for the persistent organochlorine compounds *p,p'*-DDE and dieldrin), those for the protection of aquatic life (azinphos-methyl and diazinon) and for surface water (simazine). One or more State criteria were exceeded in samples from 10 sites.

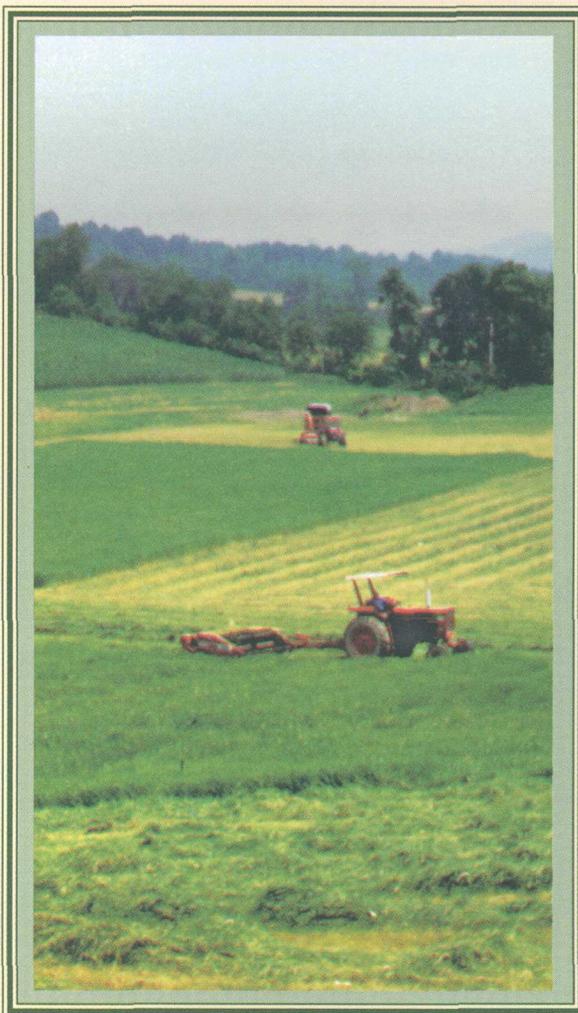
The State criterion for consumption of fish ( $6.0 \times 10^{-7}$  ug/L) was exceeded at four sites (sites 11, 37, 38, and 42, see table 1) for *p,p'*-DDE; most of these sites are in orchard/vineyard watersheds in western New York. The State criterion for consumption of fish ( $7 \times 10^{-6}$  ug/L) was exceeded at four sites (sites 2, 38, 64, 66) by dieldrin. Three of these sites are on Long Island in urban/residential watersheds; the other (38) is in western New York in orchard/vineyard watershed. Use of DDT (the parent compound of *p,p'*-DDE) and dieldrin is prohibited in New York State.

The State criterion for protection of aquatic life (0.005 ug/L) for azinphos-methyl was exceeded at four sites (35, 36, 37, and 38). All of these sites are in western New York in orchard watersheds. The state criterion for protection of aquatic life (0.070 ug/L for diazinon) was exceeded at three sites (sites 7, 35, and 64). Two of these sites are in urban/residential watersheds on Long Island or southeastern New York, and the other (site 35) is in an orchard/vineyard watershed in western New York. The State guideline for surface water and class GA ground water (0.50 ug/L for simazine) was exceeded at one site (site 40). This site is in an orchard/vineyard watershed in western New York.

## Use of Low Detection Limits

This study used detection limits that are generally (1) much lower than Federal or State water-quality criteria, and (2) below those used in most other studies and monitoring programs. The reasons, paraphrased from Ryker and Williamson (1996) are explained below:

1. Use of low detection limits (for pesticides) allows detection of temporal trends and identification of streams that need protection to prevent concentrations of pesticides from increasing to levels that could threaten the water quality or the ecological health of a stream. Although detection limits close to the established water quality-criteria are suitable for compliance monitoring, they would provide less useful data than do low detection limits for early warning of increasing pesticide concentrations. Use of low detection limits over a long period can help indicate whether pesticide concentrations are increasing, decreasing, or remaining constant.
2. Low detection limits allow researchers to discern correlations between pesticide exposure and human health or ecological health. If detection limits were higher, most pesticide concentrations would be



*The most commonly detected pesticides were the herbicides that are frequently applied to agricultural fields*

reported as below those limits and could not be used in statistical correlations between pesticide exposure and human health.

3. Low detection limits maximize the number of samples that can be used to relate pesticide concentrations to environmental factors. Large numbers of samples decrease the uncertainty in predicting pesticide contamination.

4. Low detection limits can increase the likelihood that pesticides not detected in analyses are truly absent from waters sampled.

## SUMMARY AND CONCLUSIONS

Results of an initial assessment of the status of pesticide concentrations in surface waters of New York State indicate that, of the 47 pesticides studied in a statewide survey of 64 streams and rivers in New York State in June-July 1997, 25 pesticides were detected, and most detected pesticides were at concentrations below 0.10 ug/L. The most commonly detected pesticides (detected at more than 80 percent of the sites sampled) were herbicides that are commonly applied to cornfields, including atrazine, metolachlor, and the atrazine-degradation compound deethylatrazine. The highest concentrations (between 0.1 and 1.0 ug/L) for these three compounds were found in streams in western New York that drain areas with the greatest corn production in the State. Two insecticides—carbaryl and diazinon—were detected in 20 percent and 14 percent of the samples, respectively, and were most frequently detected in streams draining watersheds dominated by orchards or vineyards or in watersheds dominated by urban or residential land use. Insecticides, that were detected, were mostly at concentrations below 0.01 ug/L. In general, patterns of pesticide detections corresponded to patterns of use.

Concentrations of only a few compounds exceeded applicable State water-quality standards, and no concentrations exceeded federal health advisory or maximum contaminant levels. New York State water-quality criteria were exceeded at 10 sites by four insecticides (azinphos-methyl, *p,p'*-DDE, diazinon, and dieldrin) and one herbicide (simazine).

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