Seasonal Variability and Effects of Stormflow on Concentrations of Pesticides and their Degradates in Kisco River and Middle Branch Croton River Surface Water, Croton Reservoir System, New York, May 2000-February 2001

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Samples from two streams in the Croton Reservoir system – Kisco River and the Middle Branch Croton River– were sampled 52 and 31 times, respectively, from May 2000 through February 2001. Samples from the Kisco River contained over 30 pesticides or pesticide degradates, and samples from Middle Branch Croton River contained over 20 pesticides or pesticide degradates. Many of the pesticides detected most commonly in this study are generally used in developed areas, and are frequently used on turfgrass.

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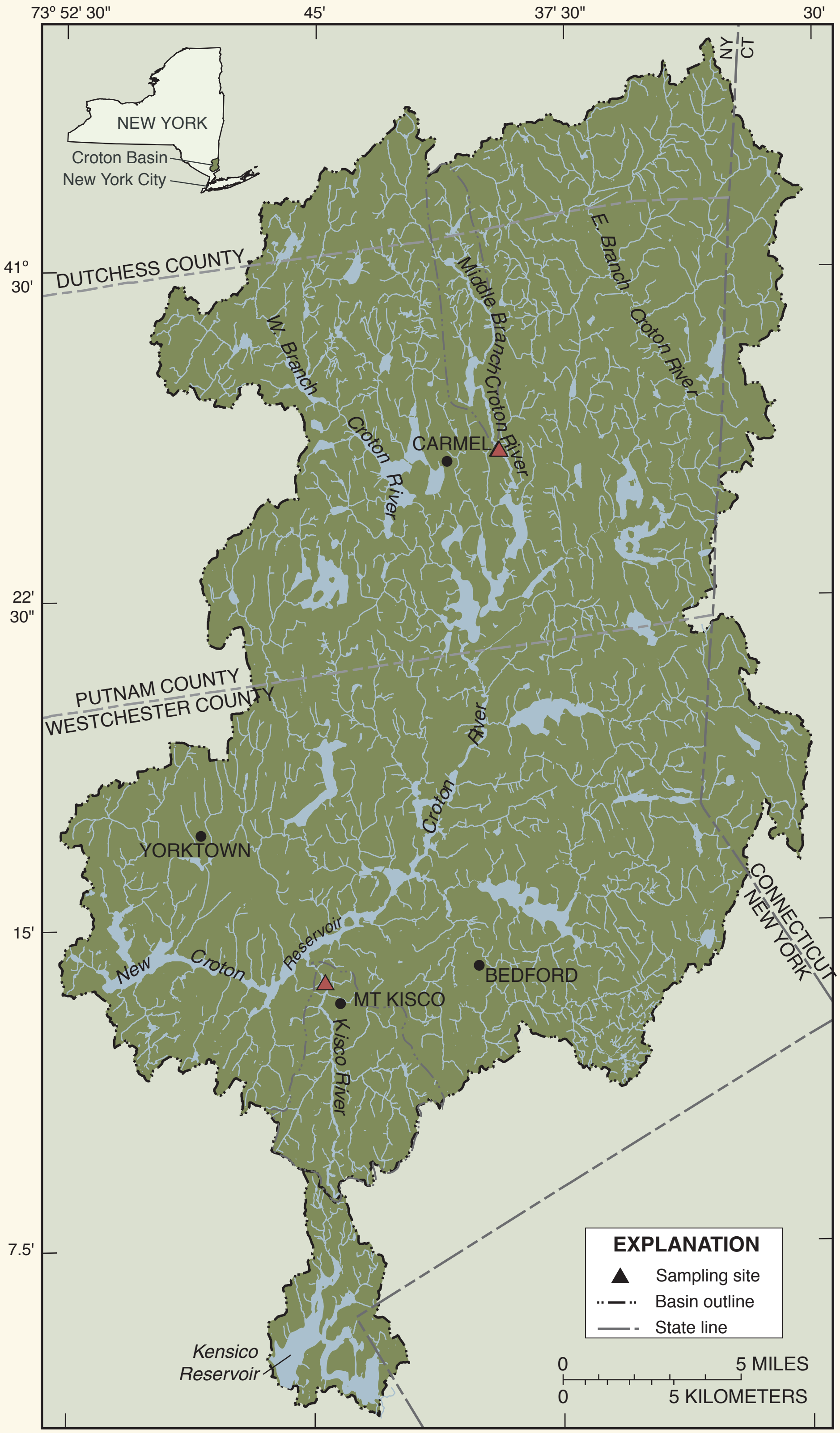

Base from U.S. Geological Survey digital data, 1:100,000, 1983

Figure 1. Geographic features of Croton River basin, Westchester and Putnam Counties New York, and location of sampling sites.

Seven herbicides (2,4-D, 2,4-D methyl ester, bromacil, dicamba, diuron, imazaquin, and sulfometuron), four insecticides (carbaryl, diazinon, imidacloprid, and malathion), two fungicides (metalaxyl and myclobutanil), and caffeine (an indicator of wastewater) were detected in at least one sample from the Kisco River at concentrations above 0.1 µg/L (micrograms per liter). Four of these compounds – 2,4-D, 2,4-D methyl ester, dicamba, and metalaxyl – were detected in at least one sample from the Kisco River at a concentration above 1 µg/L. Only three herbicides (2,4-D, imazethapyr, and prometon) and caffeine were detected at concentrations above 0.1 µg/L in one or more of the Middle Branch Croton River samples, and no compounds were detected above 0.4 µg/L in Middle Branch Croton River samples. No samples contained concentrations of pesticides that exceeded human health-based water-quality standards. However, samples from the Kisco River contained four insecticides (carbaryl, chlorpyrifos, diazinon, and malathion) and one herbicide (2,4-D) in concentrations that exceeded water-quality criteria for the protection of aquatic life. Aquatic-life protection criteria were generally exceeded only in stormflow samples collected in June, September, and December 2000. No samples from the Middle Branch Croton River contained target compounds that exceeded water-quality criteria for the protection of aquatic life.

Pesticide concentrations were generally higher, and the numbers of compounds generally larger in samples from the Kisco River than in samples from the Middle Branch Croton River, probably because the Kisco River watershed has a greater population density and is more extensively developed. The highest concentrations of most compounds in both streams were detected in stormflow samples collected in June, September, and December 2000. This indicates that stormflow sampling is essential in assessments of pesticide occurrence in streams that drain developed lands. The lowest concentrations of most compounds at both sites were detected in baseflow samples collected from October 2000 through February 2001, although the concentrations of several compounds increased substantially during stormflows at the Kisco River site in November and December, 2000.

Introduction

The New Croton Reservoir in southeastern New York is directly north of New York City and provides about 10 percent of the city's water supply. The 374-mi^2 Croton River basin above the reservoir (fig. 1) is predominantly (69 percent) forested; about 14 percent is developed, and 17 percent is forest, wetland or water. The forested land in the watersheds of several streams that feed the reservoir is undergoing rapid development; therefore, concern has arisen as to whether pesticides used in these areas are entering these streams (Phillips and Bode, 2002).

Past research on pesticides in surface waters of New York State has generally focused on streams that drain agricultural lands (Phillips and others, 1998; 1999; 2000; Eckhardt and Burke, 1999), but pesticides are also are used in a variety of settings in developed areas, such as on turfgrass, lawns and gardens, and golf courses; in buildings and parking lots; along roads, power-transmission right of ways, and railways; and in areas with ponded water for mosquito control.

The types, rates, and timing (season) of application of pesticides used in developed areas differ from those used in agricultural areas, as do the pathways of pesticide migration to streams. For example, the chlorophenoxy herbicide compounds, including 2,4-D, which are used for weed control, are likely to be used more heavily in developed areas than in agricultural areas (Templeton and others, 1998). Although quantitative estimates of pesticide use in urban areas are generally unavailable, greater amounts are probably used (per acre) by homeowners than on the most commonly grown agricultural crops (Templeton and others, 1998). Pesticide applications in agricultural areas generally occur only in the spring, whereas those in developed areas occur throughout the growing season; some pesticides used in developed areas such as imazaquin, which is used for weed control on turfgrass, can also be applied after the first frost. Pesticide migration to streams in urban areas is generally more rapid and direct than in undeveloped and agricultural areas. The extensive impervious surfaces route pesticides washed by stormwater from lawns, ornamental plantings, and golf courses directly to storm drains and streams, whereas stormwater in undeveloped and agricultural areas generally infiltrates the soil, where its movement downwards to the water table or overland is retarded.

Previous Studies

Only a few studies have addressed the occurrence of pesticides in streams that drain developed areas or the factors that control their concentrations in these streams. A recent study of pesticide occurrence in eight streams draining small, developed watersheds throughout the United States (Hoffman and others, 2000) found that most samples contained at least one herbicide or insecticide and, unlike the samples from agricultural watersheds, contained higher total insecticide concentrations than total herbicide concentrations. A recent study of pesticides in base-flow samples from 47 streams within the Croton River basin in the summer of 2000 (Phillips and Bode, 2002) detected nine compounds at concentrations greater than 0.10 μg/L; three of these were insecticides (diazinon, carbaryl, and imidacloprid), one was a fungicide (myclobutanil), and five were herbicides (simazine, 2,4-D, diuron, hexazinone, and 2,4-D methyl esther). Only two of these compounds (simazine and 2,4-D) were detected at concentrations above 1 μg/L. That study probably did not detect the maximum pesticide concentrations, however, because it did not include stormflow samples, which reflect the wash-off of pesticides from lawns and other areas and thus contain elevated concentrations of these compounds.

Few studies to date have examined instantaneous concentrations of commonly used pesticides in storm runoff from developed areas. Instantaneous-concentration data collected during storms provide an indication of the short-term concentration increases to which aquatic life is exposed; these data also may help indicate the sources of pesticides or the processes that affect their movement. For example, field and modeling studies have indicated that little herbicide runoff occurs from well-maintained turf (Harrison and others, 1993). A study of 2,4-D, dicamba, and mecoprop in runoff from an experimental turfgrass plot, however, indicated that about 10 percent of applied herbicide mass was transported from the plot, and that about 75 percent of the herbicide transport occurred during the first storm after application (Ma and others, 1999).

An urban stream study in Minnesota by Wotzka and others (1998) indicated that event mean concentrations (EMC) of herbicides in streams that drain developed areas were as high as 70 μg/L, and that triazine and acetanilide compounds (including atrazine and metolachlor), which are commonly associated with agriculture use, had lower EMCs than chlorophenoxy herbicides (including 2,4-D, MCPA, and MCPP). That study also found that maximum herbicide EMCs in developed areas occurred during midsummer storms, not those in spring or early-summer; in contrast, maximum EMCs in adjacent agricultural areas occurred during early spring storms (Wotzka and others, 1998).

Approach and Objectives

In 2000, the U.S. Geological Survey (USGS), in cooperation with the New York State Department of Environmental Conservation (NYSDEC), began a monitoring program to assess the occurrence of pesticides in surface waters of the Croton River basin. A part of that study entailed sampling at the mouths of two tributaries – the Kisco River and the Middle Branch Croton River (fig. 1 and table 1) – to identify which pesticides and pesticide degradates were present and to document the variability in their concentrations with respect to stream discharge and season. The objectives of the study were to (1) relate the presence of pesticides and their degradates in samples from the two sites to (a) the land-use characteristics (developed or agricultural) of the two watersheds and the inferred pesticide-application times, and (b) Federal and State water-quality criteria; (2) evaluate and interpret temporal changes in pesticide concentrations in relation to seasons and flow (stormflow and baseflow) conditions.

Table 1. Drainage area, population, and land use represented by sampling sites on Middle Branch Croton River and Kisco River , N.Y., May 2000 through February 2001.

[mi^2, square miles Locations are shown in fig. 1.]

Site name	Drainage area (mi^2)	Population[1] (per mi^2)	Percentage of watershed[2]		
			Developed	Agricultural	Forest
Middle Branch Croton River	13.7	630	12.9	3.1	80.0
Kisco River below Mt. Kisco	17.6	940	23.8	5.5	70.2

[1] Population density values calculated from 1990 U.S. Census data (Bureau of the Census, 1991a,b).

[2] Values in each category do not add to 100 because other categories are omitted. Land-use characteristics were identified through satellite-imagery data collected in 1994 (U.S. Geological Survey, 1998).

The two sites were chosen because their drainage areas contain forested, agricultural and developed land, but differing population densities, and because their developed lands reflect land use throughout the Croton River basin. The Kisco River watershed has a higher population density (940/mi^2) and greater amount of developed land (23.8 percent) than the Middle Branch Croton River (hereafter referred to as Middle Branch) watershed (table 1) and thus, probably has greater pesticide use. The Middle Branch sampling site, 12 mi to the north of the Kisco River site, is 1.5 mi downstream from Lake Carmel, and Lake Carmel regulates flow at the Middle Branch site.

This report (1) describes the study area, (2) presents the concentrations of all pesticides detected in stormflow and baseflow samples, (3) discusses the relations of pesticide occurrence and concentrations to land use and water quality standards, (4) explains the seasonal patterns of pesticide occurrence and concentrations, and (5) interprets the effect of stormflow on pesticide concentrations.

Methods

Samples were collected from both sites (fig. 1, table 1) during base-flow and stormflow conditions from May 2000 through February 2001; the stormflow samples were collected to discern whether stormflows produce the maximum pesticide concentrations. Stormflow samples were collected at the Kisco River site throughout the period of study; however, the largest storms sampled included storms in June, September, and December, 2000. These storms represent three of the four largest flows during the period May 2000 through February 2001, and daily flows during these storms are exceeded less than 10 percent of the time. Stormflow samples were also collected at Middle Branch during these three storms. Although the flow at the Middle Branch site is highly regulated, so the effect of rainfall on streamflow at this site is highly variable, the storms sampled include 2 of the three largest flows recorded at this site between May 2000 and February 2001.

Land-use characteristics of the watersheds above each sampling site were identified through satellite imagery collected in 1994 (U.S. Geological Survey, 1998: table 1). Population density data were obtained from 1990 census data (Bureau of the Census, 1991a,b).

Sample Collection

Baseflow samples and some stormflow samples were collected through standard equal-width interval (EWI) stream-sampling techniques (Shelton, 1994). Most of the stormflow samples were collected as a point sample by an automatic sampler in glass bottles that had been cleaned according to procedures described in Shelton (1994). All tubing in the automatic sampler was Teflon[2] lined, except for short (less than 1-ft) sections in the pump head and distributor arm. The non-Teflon tubing sections were changed after every storm. The automatic samplers were programmed to collect samples after a prescribed rate of stage increase during the rising phase, near the peak, and during the falling stage of the stormflows.

Analytical Methods and Quality Control

Samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., by three analytical procedures: 1) the SH2010 method for 47 pesticides and degradates; (2) the SH2060 method for 63 pesticides and degradates; and (3) the SH2002 method for 76 pesticides and degradates. The SH2010 and SH2002 methods use gas chromatography/mass spectrometry and are described in Zaugg and others (1995) and Sandstrom and others (2001), respectively. The SH060 method uses liquid chromatography/mass spectrometry and is described in Furlong and others (2001). A complete list of analytes with method detection limits is given in reference cited above for each method. All methods use a 1-liter filtered sample extracted on a solid-phase cartridge; thus, the values represent filtered pesticide and pesticide-degradate concentrations. The detection limits provided by these methods range from 0.001 to nearly 0.2 µg/L (micrograms per liter), which is much lower than that obtained by analytical methods typically used in public-water-supply-monitoring programs, and provide much higher rates of detection. Fifty-two samples were collected from the Kisco River site and analyzed by the SH2010 method, 25 samples from this site were analyzed by the SH2060 method, and 15 samples by the SH2002 method. Thirty-one samples were collected from

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the Middle Branch site and analyzed by the SH2010 method, 16 samples from this site were analyzed by the SH2060 method, and 8 samples by the SH2002 method. The constituents detected in samples from each site, and the methods used for each constituent, are summarized in tables 2A (Kisco River) and 2B (Middle Branch).

Some of the concentrations reported for certain compounds analyzed by the SH2060 method (including some sufonylurea, imidazolinone, and sulfanomide herbicides), may reflect the tendency of the method to overestimate concentrations of some compounds by as much as a factor of 2 (Furlong and others, 2001). Matrix enhancement may cause elevated recovery of such compounds as imazaquin, sulfometuron, imazethapyr, fluometuron, metalaxyl, and imidacloprid. The concentrations reported here are not adjusted for potential overestimation. The concentrations listed for some compounds in tables 2A and 2B are indicated as estimated values for one of three reasons: because 1) they are reported below the detection limit, 2) they exceed the highest concentration on calibration curves, or 3) the compound has a high variability in reported method recoveries.

Blank and replicate samples were collected for quality control samples. Blank samples were produced by exposing organic-free water supplied by the NWQL to sample intakes, pump-head tubing, and glass sample jars. No target analytes were detected in any of the 14 blanks (10 for SH2010, 2 for SH2060 and 2 for SH2002). Surrogate compounds added to the samples for the three analytical methods showed median recoveries of 74 to 104 percent for all samples; 90 percent of the recoveries for most surrogates were between 64 and 124 percent. Concentrations of analytes were not adjusted for reported analytical recoveries.

Two duplicate samples were collected for each of the three analytical methods at the Kisco River site, and two duplicates for the SH2010 method were collected at the Middle Branch site. One duplicate pair consisted of a sample collected using the EWI technique that was divided into two aliquots, and the second duplicate pair consisted of a sample collected using the equal-width technique paired with a point sample collected concurrently by automatic sampler. These duplicate samples yielded 21 comparisons between analytes. Comparisons were made only if the same analyte was detected in both samples of a replicate pair. Concentration differences in these 21 comparisons ranged from 0 to 48 percent; the difference in 67 percent of these comparisons was less than 10 percent and exceeded 20 percent in only one comparison. Seven comparisons indicated a target compound in only one of the two samples paired for replicate analysis; the concentrations of the detected compound in all of these comparisons were near the detection limit. The comparison between samples collected by the EWI method with point samples collected by automatic sampler did not indicate any systematic bias in the latter samples; therefore, no correction was made to any point-sample concentrations.

Concentrations of Pesticides and Selected Degradates

Of the more than 155 compounds for which the samples were analyzed, 38 were detected in samples collected from the Kisco River (table 2A), and 24 were detected in samples from the Middle Branch (table 2B). Of the 38 compounds detected in Kisco River samples, 25 were herbicide or herbicide degradates, 9 were insecticides or insecticide degradates, and 3 were fungicides. Of the 24 compounds detected in Middle Branch samples, 17 were herbicides or herbicide degradates, 5 were insecticides or insecticide degradates, and one was a defoliant. Caffeine (an indicator of wastewater) was detected in samples from both sites. The Kisco River samples contained four pesticides whose maximum concentrations exceeded 1 µg/L; the Middle Branch samples contained none.

The Kisco River samples contained 14 compounds at a concentration of 0.1 µg/L or greater in at least one sample (table 2A). Seven of these compounds are herbicides (2,4-D, 2,4-D methyl ester, bromacil, dicamba, diuron, imazaquin, and sulfometuron), four are insecticides (carbaryl, diazinon, imidacloprid, and malathion), and two are fungicides (metalaxyl and myclobutanil). Caffeine was detected in at least one Kisco River sample at a concentration of 0.1 µg/L or greater. Four compounds (2,4-D, 2,4-D methyl ester, dicamba, and metalaxyl) were detected in at least one sample from this site at a concentration of 1.0 µg/L or greater.

The Middle Branch samples contained only three herbicides (2,4-D, imazaquin, and prometon) at concentrations of 0.1 µg/L or greater. Two of these (2,4-D and prometon) had maximum concentrations greater than 0.3 µg/L, but no pesticide or degradate had a concentration greater than 0.4 µg/L. The Middle Branch samples also contained two insecticides and three insecticide degradates, but at concentrations less than 0.1 µg/L, and the defoliant, also at a concentration less than 0.1 µg/L. Caffeine was detected in some Middle Branch samples at a concentration of 0.1 µg/L or greater.

Together the two sites contained eight pesticide degradates – four were detected only in Kisco River samples, two only in Middle Branch samples, and two in samples from both sites (tables 2, 3). The maximum concentration of each of these compounds was less than 0.03 µg/L. The parent compounds of each degradate except 2,5-dichloraniline was detected in at least one sample from each site (table 2A, 2B). The presence of the 3,4-dichloroaniline, 1,4-napthoquinone, and 1-naphthol is difficult to interpret because these degradates can be formed through thermal degradation of the parent compound during analysis; therefore, it could have been either present in the sample initially, or created during the analysis.

Table 2A. Data on pesticides detected in waters samples collected from Kisco River, N.Y., May 2000 - February 2001

[µg/L, micrograms per liter; dash indicates no sample; E, estimated concentration. Sampling location is shown in figure 1. Frequency of detection limit and exceedence of specified concentrations cannot be directly compared between compounds not analyzed by the same method (52 samples were analyzed by SH2010 method, 25 samples by SH2060 method, and 15 samples by SH2002 method).]

Compound	Analytical Method: Type	Analytical Method: Detection limit (µg/L)	Percentage of samples: With a compound detection†	Percentage of samples: Detected at concentration > 0.10 µg/L	Water-quality criterion (µg/L)	Maximum concentration (µg/L)	Month of maximum concentration
Herbicides and Herbicide Degradates							
2,4-D	SH2060	0.077	64	32	4[a]	E24	September
2,4-D methyl ester	SH2060	0.087	28	8	4[a]	2.4	September
3,4-Dichloroaniline*	SH2002	0.008	13	0	-	E0.0069	June
Atrazine	SH2010	0.007	48	0	1.8[a]	0.031	May
Bromacil	SH2060	0.081	4	4	5[a]	E0.17	November
Bromoxynil	SH2060	0.057	4	0	5[a]	E0.003	December
Deethylatrazine*	SH2010	0.006	38	0	-	E0.026	May
Deethyldeisopropylatrazine*	SH2060	0.060	16	0	-	E0.02	June
Dicamba	SH2060	0.096	4	4	10[d]	E2.1	September
Dichlorprop	SH2060	0.050	24	0	-	0.085	November
Diphenamid	SH2060	0.058	16	0	-	E0.012	December
Diuron	SH2060	0.079	48	12	-	0.11	May
Fluometuron	SH2060	0.062	24	0	-	E0.012	December
Hexazinone	SH2002	0.008	67	0	-	0.025	June
Imazaquin	SH2060	0.10	48	24		E0.85	December
Imazethapyr	SH2060	0.088	8	0	-	E0.074	May
MCPA	SH2060	0.059	12	0	2.6[d]	0.076	June
Metolachlor	SH2010	0.013	5.8	0	7.5[a]	0.011	May
Pendimethalin	SH2010	0.010	3.8	0	-	0.039	December
Prometon	SH2010	0.015	79	0	-	0.057	September
Siduron	SH2060	0.093	36	0		E0.02	June
Simazine	SH2010	0.011	23	0	0.5[b]	0.013	May
Sulfometuron	SH2060	0.039	12	4	-	0.45	May
Tebuthiuron	SH2010	0.016	1.9	0	1.6[a]	E0.0064	September
Trifluralin	SH2010	0.009	9.6	0	0.2[a]	E0.0017	December
Insecticides and Insecticide Degradates							
1,4-Napthoquinone*	SH2002	0.008	40	0	-	E0.0074	November
1-Naphthol*	SH2002	0.005	33	0	-	0.012	December
2-[(2-ethyl-6-methylphenyl)-amino]-1-propanol*	SH2002	0.016	20	0	-	0.012	July
Carbaryl	SH2010	0.041	87	13	0.2[a]	E0.66	December
Chlorpyrifos	SH2010	0.005	9.6	0	0.041[d]	0.06	September
Diazinon	SH2010	0.005	71	1.9	0.08[c]	0.24	July
Diclorvos	SH2002	0.005	40	0	-	0.023	June
Imidachlorprid	SH2060	0.106	40	4	-	0.13	June
Malathion	SH2010	0.027	23	1.9	0.1[d]	0.13	September
Methomyl oxime	SH2060	0.01	4	0	-	E0.0059	December
Fungicides							
Benomyl	SH2060	0.022	4	0	-	E0.011	August
Metalaxyl	SH2060	0.057	24	4	-	3.93	August
Mycolbutanil	SH2002	0.008	73	6.7	-	0.749	June
Other							
Caffeine	SH2060	0.081	80	24	-	E0.98	December

* degradate.

† includes samples with a concentration reported below method detection limit.

[a] Canadian or Canadian Interim standards for the protection of aquatic life (Canadian Council of Resource and Environment Ministers, 1997;Environment Canada, 1999);

[b] New York State Surface water Standard (New York State Department of Health, 1998);

[c] Great Lakes standard for the protection of aquatic life (International Joint Commission Canada and United States, 1977);

[d] U.S. Environmental Protection Agency standard for the protection of aquatic life (U.S. Environmental Protection Agency, 1999).

Table 2B. Data on pesticides detected in water samples collected from Middle Branch Croton River, May 2000 - February 2001

[µg/L, micrograms per liter; dash indicates no sample; E, estimated concentration. Sampling location is shown in fig. 1. Frequency of detection limit and exceedence of specified concentrations cannot be directly compared between compounds not analyzed by the same method (31 samples were analyzed by SH2010 method, 16 by SH2060 method, and 8 by SH2002 method.

Compound	Analytical Method: Type	Analytical Method: Detection limit (µg/L)	Percentage of samples: With a compound detection†	Percentage of samples: Detected at concentration > 0.10 µg/L	Water-quality criterion (µg/L)	Maximum concentration (µg/L)	Month of maximum concentration
Herbicides and Herbicide Degradates							
2,4-D	SH2060	0.077	50	13	4 [d]	E0.39	May
2,4-D methyl Ester	SH2060	0.087	13	0	-	E0.058	May
Atrazine	SH2010	0.007	58	0	1.8[a]	0.0115	May
Bromacil	SH2060	0.081	6.3	0	5 [d]	E0.016	June
Deethylatrazine*	SH2010	0.006	42	0	-	E0.0093	May
Deethyldeisopropylatrazine*	SH2060	0.06	13	0	-	E0.019	June
Deisopropylatrazine*	SH2060	0.074	13	0	-	E0.0067	May
Dinoseb	SH2060	0.043	6.3	0	0.05 [a]	E0.004	May
Diphenamid	SH2060	0.058	6.3	0	-	E0.018	December
Diuron	SH2060	0.079	31	0	-	E0.0312	September
Fluometuron	SH2060	0.062	25	0	-	E0.014	December
Imazaquin	SH2060	0.103	19	6.3	-	E0.11	December
Imazethapyr	SH2060	0.088	25	0	-	E0.096	May
Metolachlor	SH2010	0.013	32	0	7.8 [a]	0.0066	May
Prometon	SH2010	0.015	74	6.5	-	0.311	July
Simazine	SH2010	0.011	3.2	0	0.5 [b]	E0.0044	June
Triclopyr	SH2060	0.101	19	0		E0.0895	December
Insecticides and Insecticide Degradates							
1,4-Napthoquinone*	SH2002	0.008	13	0	-	E0.0005	December
2,5-Dichloroaniline*	SH2002	0.005	13	0		E0.0019	December
2-[2-Ethyl-6-methylphenyl) amino]-1-propanol*	SH2002	0.016	13	0	-	0.0218	July
Carbaryl	Sh2010	0.041	19	0	0.2 [a]	0.0143	November
Diazinon	SH2010	0.005	45	0	0.08 [c]	0.0439	July
Defoliant							
Tribuphos	SH2002	0.016	13	0	-	E0.0054	December
Other							
Caffeine	SH2060	0.081	69	13	-	0.27	September

* degradate

† includes samples with a concentration reported below method detection limit

[a] Canadian or Canadian Interim standards for the protection of aquatic life (Canadian Council of Resource and Environment Ministers, 1997; Environment Canada, 1999)

[b] New York State Surface Water Standard (New York State Department of Health, 1998)

[c] Great Lakes standard for the protection of aquatic life (International Joint Commission Canada and United States, 1977)

[d] U.S. Environmental Protection Agency standard for the protection of aquatic life (U.S. Environmental Protection Agency, 1999)

Table 3. Pesticide degradates detected and their parent compounds detected in samples from Kisco River and Middle Branch Croton River, N.Y., 2000-2001.

Common name	Sample source	Parent compound
Deethylatrazine	Kisco River, Middle Branch	Atrazine
Deethyldeisopropylatrazine	Kisco River	Atrazine
Deisopropylatrazine	Middle Branch	Simazine, Atrazine
3,4-Dichloroaniline*	Kisco River	Diuron, Propanil, Linuron, Neburon
1,4-Napthoquinone*	Kisco River	Carbaryl
1-Napthhol*	Kisco River	Carbaryl
2-[(2-ethyl-6methylphenyl)amino]-1-propanol	Kisco River, Middle Branch	Metolachlor
2,5-Dichloroaniline	Middle Branch	Chloramben

* degradate that might also be formed from one or more of the parent pesticides through thermal degradation of parent pesticide in injection port of gas chromatograph during gas chromatography/mass spectrometry analysis (Sandstrom and others, 2001)

Effects of Land Use and Timing of Application on Pesticide Concentrations

The Kisco River samples generally contained pesticides in greater numbers and at higher concentrations than the Middle Branch samples because the Kisco River watershed has a higher population density and greater percentage of developed land (table 1). The concentrations of most of the commonly detected herbicides, including 2,4-D, diuron, 2,4-D methyl ester, dichlorprop, and imazaquin, exceeded 0.1 µg/L more frequently in samples from the Kisco River than in samples from Middle Branch (tables 2A, 2B) and had higher maximum concentrations. The only herbicide to be detected at a concentration greater than 0.1 µg/L more frequently in samples from Middle Branch than in samples from Kisco River was prometon (table 2A, 2B). Diazinon and carbaryl were detected in more than 70 percent of the samples from the Kisco River (table 2A), but in fewer than half of the samples from Middle Branch. The insecticides malathion and imidacloprid were detected in one or more samples from the Kisco River at concentrations greater than 0.1 µg/L, but not in any samples from the Middle Branch.

The interpretation that the higher detection frequency and higher maximum concentrations in the Kisco River samples than in the Middle Branch samples results from this watershed's greater population density is supported by Hoffman and others (2000). Hoffman and others (2000) detected the insecticides carbaryl, diazinon, malathion, and chlorpyrifos more frequently in samples from urban streams than in nonurban streams throughout the United States, and also noted that peak insecticide yields could be expected in developed watersheds with population densities ranging from 2,600 to 4,000 per square mile. This interpretation is also consistent with a comparison of pesticide concentrations throughout the Croton River basin in the summer of 2000 (Phillips and Bode, 2002), who found the highest baseflow summer pesticide concentrations in watersheds with population densities greater than 1,000 per square mile.

Little quantitative information on pesticide applications in developed areas is available from the literature, but some of the pesticides that can be expected to be used most commonly in developed areas were among those detected most frequently in this study. For example, the chlorophenoxy herbicides 2,4-D, 2,4-D methyl ester and dichlorprop which are heavily used in developed areas (Templeton and others 1998), were frequently detected in samples from the Kisco River, as were the herbicides diuron and imazaquin, which also are used in a variety of developed settings, including lawns, golf courses, and rights of way (Pesticide Action Network, 2002). Diazinon and carbaryl, which are commonly used in developed areas for control of insects on turfgrass and in gardens, and malathion, which is used on ornamental plants and for mosquito control in developed areas (Hoffman and others, 2000), were among the most frequently detected compounds in Kisco River. The herbicide 2,4-D methyl ester, the insecticide imidacloprid, and the fungicide metalaxyl, which were not included in the national study by Hoffman and others (2000), were frequently detected at elevated concentrations in samples from the Kisco River; this indicates that they may also be present in other urban streams across the United States.

Pesticides that are associated with agricultural use, but not commonly used in urban areas, were detected infrequently in the Kisco River and Middle Branch samples. The herbicides atrazine and metolachlor, which are commonly used in agricultural settings, and the atrazine degradate 2-Chloro-4-isopropylamino-6-amino-s-triazine (also known as deethylatrazine) are frequently found in urban streams at low concentrations (Hoffman and others, 2000). These compounds were not detected in the Kisco River and Middle Branch samples at concentrations above 0.1 µg/L, and only rarely at concentrations above 0.01 µg/L. In contrast, these three compounds were detected at concentrations above 0.01 µg/L in nearly all samples collected during 1994-96 from Canajoharie Creek, a central New York stream that drains an agricultural area. The concentrations of atrazine and metolachlor commonly exceeded 0.1 µg/L during storms in June during the three year study at Canajoharie Creek. (Wall and Phillips, 1998). The national study by Hoffman and others (2000) concluded that the most likely source of these agricultural pesticides in streams that drain developed non-agricultural areas is atmospheric drift from nearby agricultural lands. Neither the Kisco River nor the Middle Branch watersheds contain much farmland; therefore, these three compounds are probably derived either from minor applications within these watersheds or from atmospheric drift from agricultural areas outside the watershed.

Pesticide Concentrations in Relation to Established Water-Quality Standards and Guidelines

No compounds detected in this study exceeded any human-health-based water-quality standards, but four insecticides and one herbicide in samples from the Kisco River exceeded water-quality guidelines for the protection of aquatic life (fig. 2, tables 2A, 2B). No pesticides in samples from the Middle Branch exceeded any water-quality criteria (fig. 2, tables 2A, 2B). No health-based standards or aquatic-life-based water-quality guidelines have been established for at least half of the compounds detected in this study, however.

The insecticides diazinon, carbaryl, malathion, and chlorpyrifos were detected at least once in Kisco River samples at concentrations that exceeded an aquatic-life-protection guideline (fig. 2). Diazinon concentrations exceeded the aquatic-life-protection guideline in two of the Kisco River samples (4 percent), carbaryl, chlorpyrifos, and malathion exceeded the aquatic-life-protection guideline in one of these samples (2 percent); the 2,4-D concentrations exceeded the aquatic-life-protection guideline in two (8 percent), of these samples. Diazinon and carbaryl concentrations were greater than or equal to half of the aquatic-life-protection guideline in more than 13 percent of the Kisco River samples. All exceedences of aquatic-life-protection guidelines occurred during stormflows.

The stormflow concentrations of some insecticides approached the aquatic-life-protection guidelines from June through December 2000 (fig. 2) and exceeded them in June (diazinon), September (chlorpyrifos and malathion), and December (carbaryl); 2,4-D concentrations exceeded the guideline in September stormflows. These results further indicate that effective monitoring of runoff quality in urban or residential areas requires stormflow data from the growing season through the Fall (May through December).

Seasonal Variability in Pesticide Concentrations

The highest concentrations of most pesticide and pesticide degradates at both sites occurred during storms. Unlike agricultural areas, watersheds with a large amount of development can produce elevated pesticide concentrations in storms after, as well as during, the growing season, primarily because of multiple applications of pesticides.

Kisco River

The highest concentrations of most herbicides and insecticides in the Kisco River samples were in stormflow samples collected in June, September, and December 2000. In general, the highest baseflow concentrations of most pesticides were in samples collected during May and June; few pesticides were detected in baseflow samples after September.

Herbicides

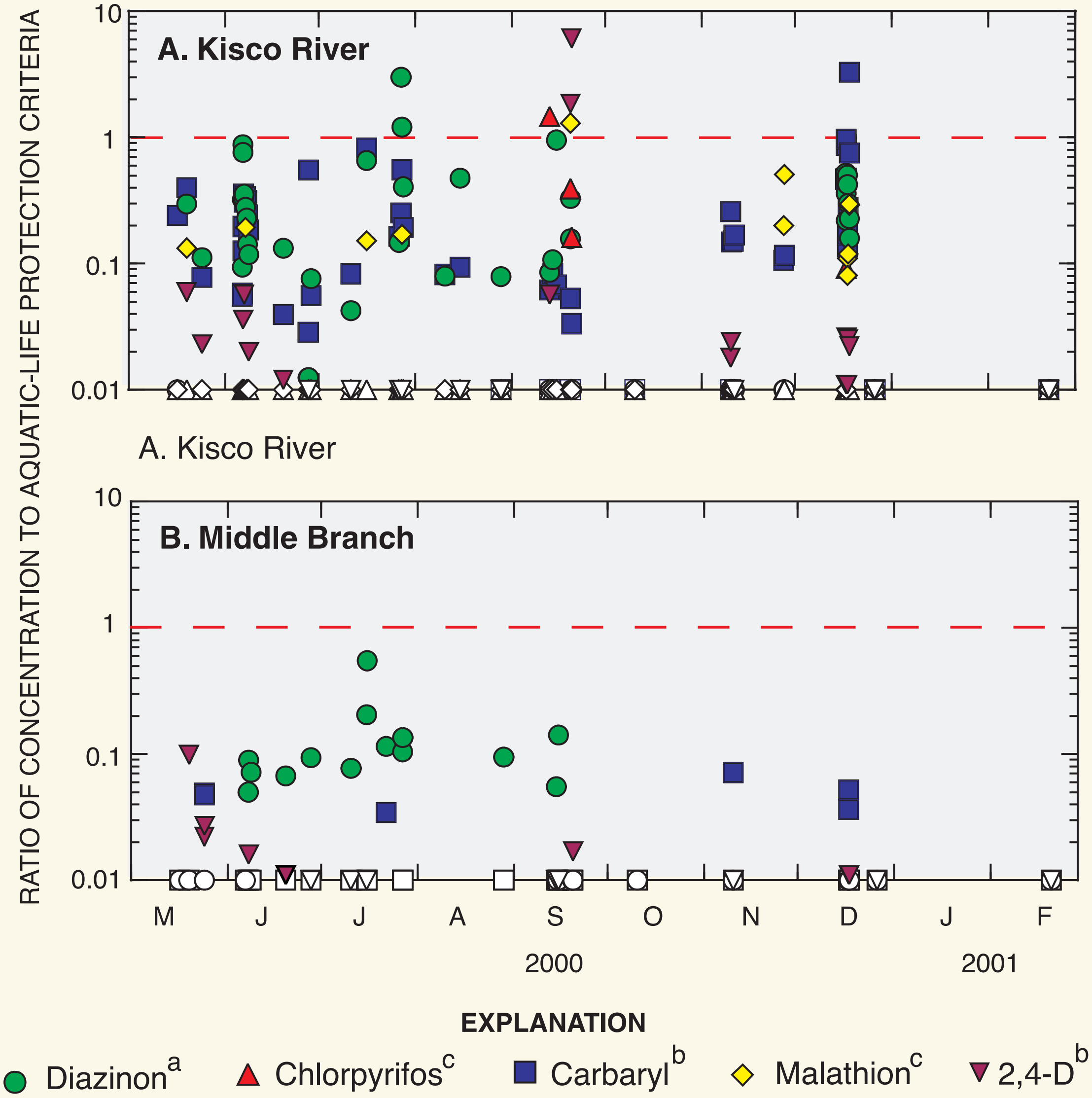
The highest concentrations of the most frequently detected herbicides were found in samples collected during large storms in June, September, and December 2000. An exception was atrazine, which reached its maximum concentration during a small storm in May and showed a smaller response to stormflows than other herbicides that were found at higher concentrations. Peak concentrations of herbicides can sometimes be related to the frequency of application indicated by the manufacturer.

2,4-D, Imazaquin, and Diuron

The herbicides 2,4-D, imazaquin and diuron were commonly detected during low flows as well as stormflows in late May and early June, but were detected only during stormflows thereafter. 2,4-D and diuron were detected only during storms in September, November, and December, and imazaquin was only detected in stormflows in late July, August, and December (fig. 3A). Maximum concentrations of 2,4-D and imazaquin were detected in stormflow samples from September and December, respectively. The highest concentration of diuron was found in a stormflow sample collected in May, but elevated concentrations also were detected in late summer and early fall stormflow samples. Other herbicides that were detected at high concentrations, including dicamba and 2,4-D methyl ester (not shown in fig. 3A), showed seasonal patterns similar to that of 2,4-D and imazaquin – with maximum concentrations in September, November, or December, and detections after August only in stormflow samples.

Not all stormflows contained elevated concentrations of 2,4-D, imazaquin, or diuron. For example, the concentrations of 2,4-D and diuron in September stormflow samples exceeded 1 µg/L, yet no imazaquin was detected; conversely, imazaquin and diuron were detected in late July and August stormflow samples, but no 2,4-D was found (fig. 3A).

The observed pattern of peak concentrations of some herbicides in June and September stormflow samples can be related to the manufacturer's recommended pesticide-application patterns. The periods of peak 2,4-D concentrations (June and September 2000) in Kisco River samples are consistent with the application instructions on a widely used turfgrass formulation that is marketed for homeowner use and commonly sold at home and garden stores. The label for a frequently used herbicide containing both 2,4 D and dicamba recommends two applications 3 to 4 months apart during the growing season; this is consistent with the 3-month lag between the June and



Notes:

Open symbol denotes concentration below detection limit.

a. Great Lakes aquatic life criteria (International Joint Commission, 1977)

b. Canadian aquatic life criteria (Environment Canada, 1999)

c. U.S. Environmental Protection Agency aquatic life criteria
(US Environmental Protection Agency, 1999)

Figure 2. Ratio of pesticide concentration to aquatic–wildlife protection standards in Kisco River and Middle Branch Croton River samples, Westchester and Putnam Counties, N.Y., May 2000-February 2001.

September peaks in 2,4-D concentrations (fig. 3A). Dicamba was detected only in samples from the small September storm, during which 2,4-D concentrations exceeded 0.3 µg/L. Elevated concentrations of both compounds during this storm probably reflect the timing of the application of these widely used herbicides in the Kisco River watershed.

The elevated pesticide concentrations in late fall and winter stormflow samples from the Kisco River site reflect a delay in the flushing of pesticides applied, possibly as repeated applications much earlier. For example, the elevated concentrations of herbicides such as 2,4-D in the late December stormflow samples probably reflect the delayed flushing of these compounds from the soil after late summer or early fall applications. The fall of 2000 was dry, with no storms in October and only a few small storms in November (fig. 3A); the storm in late December was the largest since late September and probably reflected transport of pesticides applied since October. Similarly, the 2,4-D in samples collected during a small November storm probably represents a minor flushing of this compound that was followed by the major flushing in December. Conversely, the peak imazaquin concentrations in the December stormflow samples probably reflect relatively late applications in the fall because imazaquin is sometimes applied to turfgrass after the first frost (Crop Data Management Systems, 2001).

The results from Kisco River sampling suggest that the nationwide urban-stream study by Hoffman and others (2000), which predicted peak herbicide concentrations in urban and other developed areas of the Northeast to occur during spring and early summer and decreasing concentrations thereafter through the fall, does not fully reflect the occurrence of herbicides during the late summer and fall, because it did not include stormflow sampling. Of the 25 herbicides or herbicide degradates detected in Kisco River samples, 12 showed maximum concentrations in stormflow samples from May or June samples, 5 from September, and 8 from November or December. Of the seven herbicide or herbicide degradates with maximum concentrations greater than 0.1 µg/L, five showed maximum concentrations in September, November, or December (table 2A). Again, the main reason for this discrepancy between the two studies is probably that the study by Hoffman and others (2000) did not target stormflow samples.

Atrazine

Seasonal patterns of atrazine concentrations in the Kisco River samples did not parallel those of 2,4-D or imazaquin; they were highest in May stormflow samples and decreased through July (fig. 3A), after which atrazine was detected only in samples collected during a small September storm and the large December storm. The decrease in atrazine concentrations at this site from late spring through late summer parallels the reported seasonal pattern of herbicide concentrations in streams that drain corn-growing areas in central New York – with peak herbicide concentrations in late spring and a steady decline thereafter (Wall and Phillips, 1998). This pattern indicates that the atrazine detected in the Kisco River is derived mainly from spring applications in agricultural areas, either upstream within the watershed or outside the watershed and deposited through atmospheric drift. The presence of atrazine in the December stormflow sample probably reflects either the storage of atrazine in the soil and subsequent flushing several months after application, or direct flushing after a late application in the fall. Fall application of atrazine, if it occurred, would probably have been for some purpose other than agriculture because atrazine is mostly applied on cropland in New York in the spring.

Prometon

Concentrations of prometon in Kisco River samples remained nearly constant from May through September (fig. 3A), with a peak concentration during a small September storm. Prometon is frequently mixed with paving materials; therefore, the constant concentrations at the Kisco River site probably are derived from a steady migration of this herbicide from paved surfaces.

Insecticides

The three most commonly detected insecticides (diazinon, carbaryl, and imidacloprid) were found in all Kisco River samples collected from May through August, regardless of flow conditions, and in stormflow collected from September through December (fig. 3A). After mid-August, imidacloprid was detected only during the December storm. Unlike many of the herbicides detected in this study, the insecticides diazinon, carbaryl, and imidacloprid were detected mostly in base-flow samples collected from June through August, and the base-flow concentrations sometimes approached stormflow concentrations (fig. 3A). The occurrence of these insecticides at elevated concentrations throughout the growing season could reflect a nearly constant application in a variety of settings, including lawns, ornamental plantings, and home pest control.

Of the 9 insecticides and their degradates found in Kisco River samples, one had peak concentrations in June, three had peak concentrations in July, two had peak concentrations in September, and three had peak concentrations in November or December (table 2A); the peak concentrations generally occurred during stormflows. Although a study of urban streams throughout the Northeast by Hoffman and others (2000) found that total insecticide concentration was highest in midsummer and early fall, the Kisco River results indicate that elevated insecticide concentrations can persist into the late fall. This discrepancy could reflect the absence of stormflow samples in the study by Hoffman and others (2000).

Middle Branch

Samples from Middle Branch show some of the seasonal patterns in herbicide and insecticide concentrations seen in the Kisco River data. However, the lower detection frequency and lower peak concentrations (a reflection of the lower population density and smaller amounts of developed land), along with streamflow regulation at the Lake Carmel outlet 1.5 mi above the Middle Branch site, make it difficult to assess the effect that changes in streamflow have on pesticide concentrations.

Herbicides

2,4-D was commonly detected in samples collected in May and June; imazaquin was detected less frequently, and diuron was not detected at all during this period. After July, 2,4-D and diuron were detected only in stormflow samples collected in September, November, and December (fig. 3B). Although the storm in late September did not cause a substantial increase in stream discharge in Middle Branch (although it did in the Kisco River), the concentrations of diuron and 2,4-D increased during these storms. After June, imazaquin was detected only in a stormflow sample collected in December.

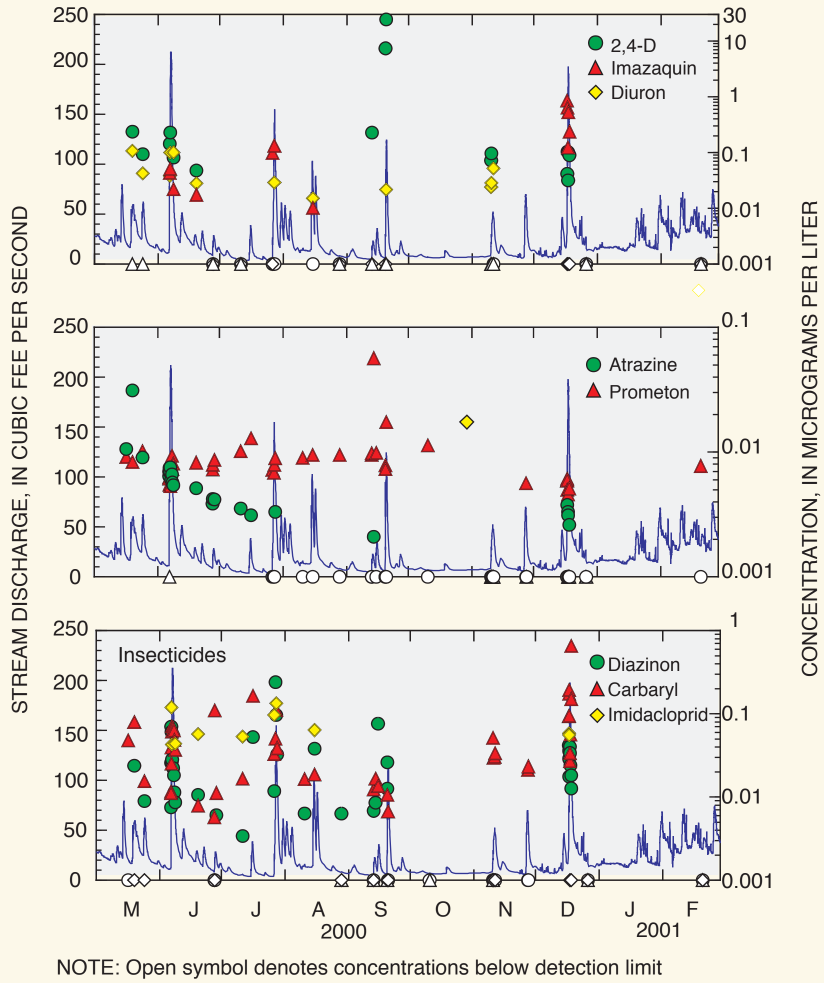
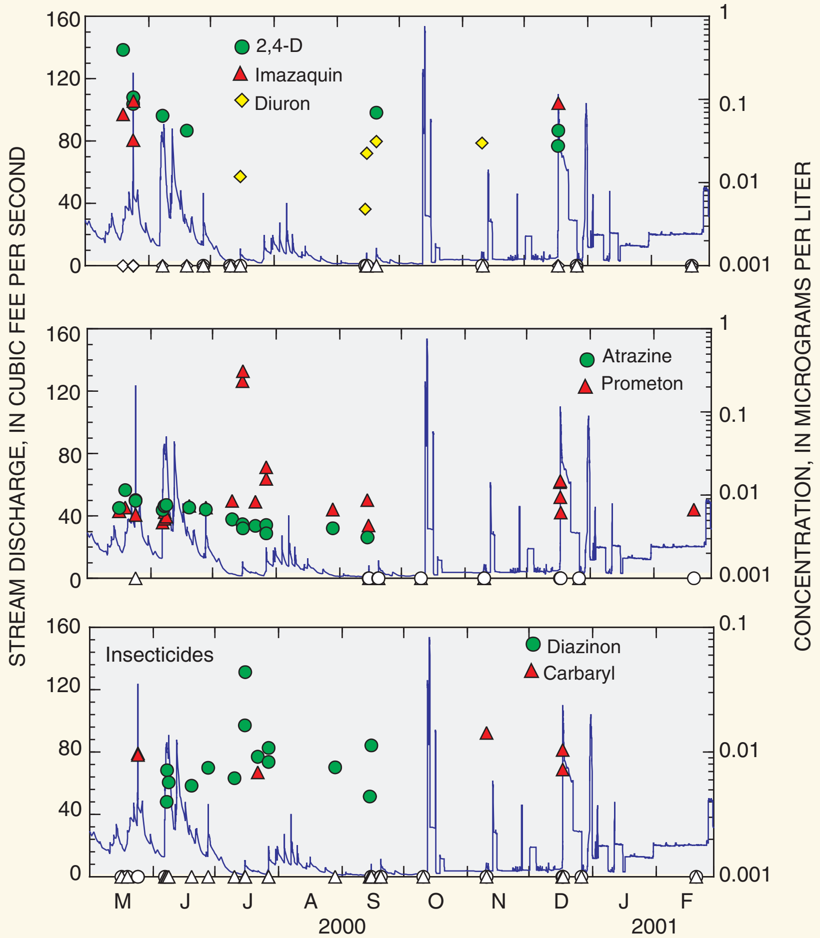


Figure 3A. Concentration of eight pesticides in Kisco River samples collected May 2000-February 2001, Westchester County, N. Y. [Sampling location is shown in fig. 1.].

Concentrations of atrazine in the Middle Branch were highest in May and decreased slightly through August (fig. 3B), and the concentration patterns observed in samples from this site were generally similar to those observed in Kisco River samples. After August, atrazine was detected only in samples collected during a small storm in September and was not detected during the December storm. This may indicate a lack of atrazine application in the Middle Branch watershed during the fall, unlike the Kisco River watershed. Concentrations of prometon remained nearly constant from May through September (fig. 3B), although a peak concentration occurred during a small July storm. Of the 17 herbicides or herbicide degradates detected in Middle Branch samples, 11 had peak concentrations in May or June, unlike the peak concentration of herbicides in Kisco River samples, half of which occurred during September, November, or December.

Insecticides

As in the Kisco River samples, diazinon was often detected in Middle Branch samples collected from July through September (fig. 3B), regardless of flow conditions, but was not detected in any samples collected from this site after October 1. Carbaryl was detected infrequently; the few detections were in stormflow samples from May, October, and November. Imidacloprid was not detected in any Middle Branch samples. Peak insecticide concentrations in Middle Branch samples occurred in July or later; one insecticide and one insecticide degradate had peak concentrations in July, and the three other insecticides or degradates had peak concentrations in November or December.



NOTE: Open symbol denotes concentrations below detection limit

Figure 3B. Concentration of seven pesticides in Middle Branch Croton River samples collected May 2000-February 2001, Putnam County, N. Y. [Sampling location is shown in fig. 1.]

Effects of Stormflow on Pesticide Concentrations in Kisco River Samples

Streamflow above the Middle Branch sampling site is regulated by Lake Carmel, 1.5 mi upstream; therefore, data from this site are not discussed in this section.

Concentrations of many herbicides and insecticides at the Kisco River site increased during some of the stormflows, as described below.

Herbicides

The Kisco River data indicate that the relation between storm discharge and herbicide concentrations varies among compounds and differs from storm to storm, and that not all stormflows produced increased concentrations of herbicides. Concentrations of 2,4-D and diuron increased with increasing discharge during the September storm (fig. 4), and peaked during the maximum stream discharge. This was presumably the result of surface washoff of these herbicides from lawns and other areas to which they had been applied. Concentrations of these compounds increased only slightly during the June storm, however, and 2,4-D concentrations during the December storm at this site did not correlate with stream discharge (fig. 4). During the December storm, some herbicides, such as imazaquin, showed peak concentrations on the rising limb of the hydrograph, and decreasing concentrations during the peak discharge and on the recession limb.

Atrazine concentrations increased during the stormflows of June and December, but this compound was not detected in any September stormflow samples. Atrazine concentrations during the June and December storms were highest during the rising limb of the hydrograph; the peak concentrations occurred near the initial discharge peak on the rising limb.

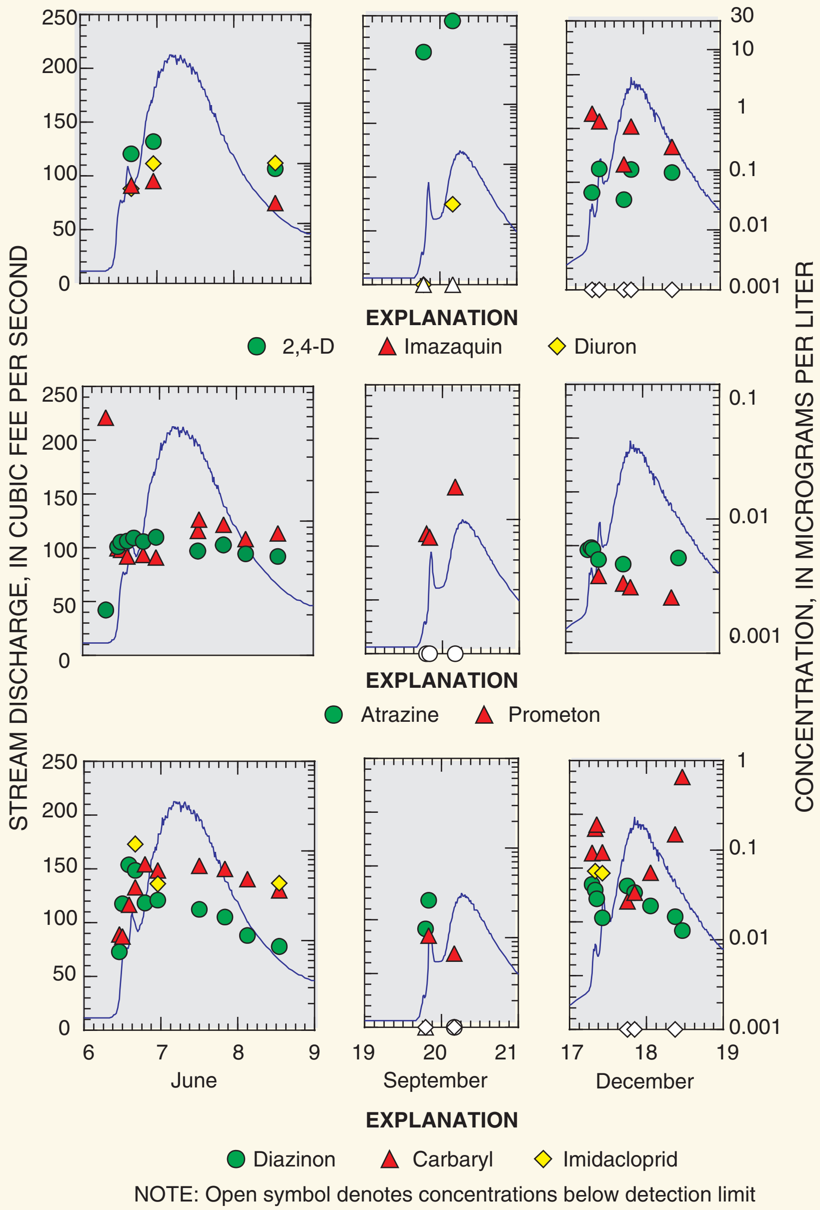


Figure 4. Concentration of selected compounds in Kisco River samples collected during storms in June, September, and December 2000. [Sampling location is shown in fig. 1.]

Prometon concentrations did not change during any stormflows. This steady pattern indicates a relatively slow but constant inflow of prometon from within the watershed.

Insecticides

Concentrations of insecticides in the Kisco River did not always increase with increasing stream discharge during storms (fig. 4). Typically, a storm hydrograph for the Kisco River site has two discharge peaks – an initial peak on the rising limb, followed by a decrease for a few hours, then a second peak that normally exceeded the initial peak. The peak concentration of diazinon coincided with the initial discharge peak of the June and September storms, and, to a lesser degree, with the initial peak of the December storm. In contrast, peak concentrations of carbaryl occurred later, just before the second discharge peak in the June storm, and after the second peak discharge of the December storm. Peak concentrations of imidacloprid, like those of diazinon, coincided with the initial discharge peak during the June and December storms. The carbaryl concentrations were anomalous in that they declined after the initial discharge peak in the December storm, then rose on the falling limb.

The occurrence of peak pesticide concentrations during the initial discharge peak rather than the main discharge peak could reflect a variety of factors. The initial discharge peak of the Kisco River hydrographs probably represents runoff from extensively paved areas, which presumably contribute greater amounts of runoff during the initial part of a storm than pervious (unpaved) areas. A peak pesticide concentration during the initial discharge peak could therefore reflect the runoff of pesticides inadvertently applied to, or spilled on, paved areas and, possibly, a greater use of pesticides in highly developed (extensively paved) areas. The occurrence of peak pesticide concentrations on the second peak or falling limb of the hydrograph may indicate washoff of pesticides from areas with little pavement, or the arrival of pesticides from parts of the watershed far from the sampling site.

SUMMARY AND CONCLUSIONS

Two tributaries to the Croton watershed (the Kisco River and Middle Branch) were sampled as part of a cooperative project between the USGS and New York State Department of Environmental Conservation to assess the occurrence of pesticides in surface waters of the Croton watershed. Pesticide sampling of stormflow and base-flow samples from the Kisco River and Middle Branch from May 2000 through February 2001 resulted in detection of over 30 pesticides or pesticide degradates in Kisco River samples and 20 pesticides or pesticide degradates in Middle Branch samples. Four compounds (the herbicides 2,4-D, 2,4-D methyl ester, dicamba, and the fungicide metalaxyl) were detected at concentrations above 1 µg/L in at least one sample from the Kisco River; no compounds were detected at concentrations above 0.4 µg/L in Middle Branch samples, and only two compounds (the herbicides 2,4-D and prometon) were detected at concentrations above 0.3 µg/L in one or more Middle Branch samples. No human-health-based water-quality standards were exceeded in any samples from either site, but four insecticides (carbaryl, diazinon, malathion, and chlorpyrifos) and one herbicide (2,4-D) in Kisco River samples exceeded guidelines for the protection of aquatic life. No guidelines for the protection of aquatic life were exceeded in any Middle Branch samples.

Concentrations were generally higher, and the number of compounds detected were greater, in samples from the Kisco River than in samples from Middle Branch, probably because the Kisco River watershed contains a higher population density and a larger percentage of developed land than the Middle Branch watershed. The chlorophenoxy herbicides 2,4-D, 2,4-D methyl ester and dichlorprop, the herbicides diuron and imazaquin, and the insecticides diazinon and carbaryl, all of which are used in a variety of developed settings, were frequently detected in Kisco River samples.

The maximum concentrations of some of the most commonly detected herbicides occurred in the Kisco River during large storms in June, September, and December. Not all stormflows showed increased concentrations of all compounds, but the peak concentrations of some compounds, including 2,4-D and imazaquin, were detected during storms that occurred shortly after the recommended months of application. Three commonly detected insecticides (diazinon, carbaryl, and imidacloprid) were frequently detected in stormflow and baseflow samples collected from May through August, but were not detected in any baseflow samples collected after August. The detection of insecticides throughout the growing season could be a result of a near-constant rate of application of these compounds throughout this period. The elevated pesticide concentrations in late fall and winter samples could have been caused by a drought-induced delay in the flushing of pesticides applied much earlier in the fall, or they could result from late applications (after the first frost).

The relation between stream discharge and pesticide concentration during Kisco River stormflows varied among compounds and from storm to storm. The concentrations of 2,4-D and diuron increased with increasing discharge during the September storm and peaked during the maximum stream discharge. The 2,4-D concentrations during the December storm at this site, however, did not correlate with discharge. Peak concentrations of diazinon during the June storm occurred during an initial discharge peak, whereas peak concentrations of carbaryl peaked later in this storm, just before peak discharge. The occurrence of peak pesticide concentrations during the initial discharge peak could reflect the washoff of pesticides inadvertently applied to or spilled on paved areas in the watershed, or the wide use of pesticides within this highly developed watershed. The occurrence of peak pesticide concentrations during the latter part of the storm may reflect pesticide use in areas with little pavement or in parts of the watershed that are far from the sampling point.

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