



Prepared in cooperation with New York State Department of Environmental Conservation
and New York City Department of Environmental Protection

Stream-Water Chemistry, Nutrients, and Pesticides in Town Brook, a Headwater Stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999

Water-Resources Investigations Report 01-4050

**U.S. Department of the Interior
U.S. Geological Survey**

Cover photo by Scott Foster (New York City Department of Environmental Protection)

Stream-Water Chemistry, Nutrients, and Pesticides in Town Brook, a Headwater Stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999

By Michael R. McHale and Patrick J. Phillips

U.S. Geological Survey
Water-Resources Investigations Report 01-4050

Prepared in cooperation with

New York State Department of Environmental Conservation

New York City Department Of Environmental Protection



Troy, New York

2001 (Revised June 2002)

U.S. DEPARTMENT OF THE INTERIOR
GAIL NORTON, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

For additional information write to:

District Chief
U.S. Geological Survey
425 Jordan Road
Troy, NY 12180

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225-0286

CONTENTS

Abstract.....	1
Introduction.....	2
Objectives.....	3
Purpose and scope.....	3
Study area.....	3
Previous studies.....	3
Acknowledgements.....	3
Data collection.....	5
Stream discharge.....	5
Water quality.....	5
Pesticides.....	5
Stream water chemistry.....	6
Nutrients.....	7
Nutrient export.....	8
Nutrient transport dynamics in stormflow.....	9
Pesticides and their metabolites.....	11
Concentrations in Town Brook.....	12
Atrazine, deethylatrazine, and metolachlor.....	13
Metolachlor ESA, metolachlor OA, and simazine.....	13
Pendimethalin and deisopropylatrazine.....	16
Federal and New York State water quality standards used in this study.....	16
Pesticides concentrations at Town Brook in relation to State and Federal water-quality standards.....	17
Pesticide concentrations in relation to hydrologic conditions.....	17
Summary.....	18
References cited.....	19

FIGURE

Figure 1. Pertinent geographic features of Delaware County, N.Y. and location of Cannonsville Reservoir and the Town Brook watershed study area.....	2
Figure 2. Geography and locations of sampling sites in Town Brook watershed, Delaware County, N.Y.....	4
Figure 3. Runoff rate and concentrations of ammonia, nitrate, total nitrogen, orthophosphate, total dissolved phosphorus, and total phosphorus in Town Brook, Delaware County, N.Y., 1999.....	11
Figure 4. Total export of six nutrients, total annual runoff, and percentage of nutrient export and total runoff represented by flow component, Town Brook, Delaware County, N.Y., 1999. Total annual nutrient loads are given as kilograms per unit area (1 hectare) per year. Total annual loads are also given as the percentage exported during each flow condition in the pie charts. Total annual runoff is given as a depth over the entire watershed in millimeters.....	12
Figure 5. Percent total export of six nutrients from Town Brook, Delaware County, N.Y., in 1999, by season. Total annual nutrient loads are given as kilograms per unit area (1 hectare) per year. Total annual loads are also given as the percentage exported during each season in the pie charts.	13
Figure 6. Hydrographs of stormflows with corresponding nutrient concentrations at Town Brook outlet, Delaware County, N.Y.: A. Storm of July 4, 1999. B. Storm of September 16, 1999. Nitrate is reported as NO_3^- -N, ammonia is reported as NH_3 -N, and orthophosphate is reported as PO_4^{3-} -P.....	14
Figure 7. Concentrations of pesticides and metabolites in baseflow and stormflow samples from Town Brook, Delaware County, N.Y., their relation to State and Federal standards, and the percentage of baseflow and stormflow samples in which each compound was detected.....	15

Figure 8. Runoff rate and concentrations of the eight detected pesticides and pesticide metabolites during the July 4, 1999 storm at Town Brook, Delaware County, N.Y. 17

TABLES

Table 1. Detection limit for the 60 pesticides and pesticide metabolites for which water samples from Town Brook watershed, Delaware County, N.Y. were analyzed, January through July 1999. 6

Table 2. Dates and methods used for collecting pesticide samples at Town Brook, Delaware County, N.Y., January through July, 1999. 7

Table 3. Chemical quality of Town Brook, Delaware County, N.Y., 1999, by flow component and season. 8

Table 4. Linear regression results for concentration of selected constituents as a function of runoff rate from Town Brook watershed, Delaware County, N.Y. 1999. 9

Table 5. Mean nutrient concentrations in Town Brook, Delaware County, N.Y., 1999 by flow component and season. 10

Table 6. Volume-weighted mean nutrient concentrations during storms and baseflow at Town Brook (1999) and Cannonsville Reservoir inlet at Beerston (1991-96). 10

Table 7. Percentage of baseflow and stormflow samples from Town Brook, Delaware County, N.Y., containing pesticides in concentrations exceeding 0.05 micrograms per liter, January through July 1999. 17

CONVERSION FACTORS AND VERTICAL DATUM

INTERNATIONAL SYSTEM (SI) TO INCH-POUND UNITS

Multiply	By	To Obtain
millimeter (mm)	0.0394	inch
meter (m)	3.28	foot
kilometer (km)	0.622	mile
hectare (ha)	2.47	acre
hectare (ha)	0.00386	square mile
square kilometer (km ²)	0.386	square mile
liter (L)	0.264	gallon
millimeters per hour	0.0394	inches per hour
kilograms per hectare per year	0.892	pounds per acre per year

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Temperature: degrees Celsius (°C) = 5/9 (degrees Fahrenheit (°F) minus 32)

Concentration of chemical constituents in water are given either in:

milligrams per liter (mg/L) >> micrograms per gram ($\mu\text{g}/\text{g}$) = parts per million (ppm); or

micrograms per liter ($\mu\text{g}/\text{L}$) >> micrograms per kilogram ($\mu\text{g}/\text{kg}$) = parts per billion (ppb)

Stream-Water Chemistry, Nutrients, and Pesticides in Town Brook, a Headwater Stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999

By Michael R. McHale and Patrick J. Phillips

ABSTRACT

Stream-water chemistry was monitored from January 1 through December 31, 1999, in the Town Brook watershed (TBW) in Delaware County, N.Y. to provide a basis for future evaluation of the effectiveness of Best Management Practices (BMPs) in decreasing agricultural nutrient and pesticide leaching to receiving waters. Total runoff from the watershed during 1999 was 664 millimeters (mm). Annual nutrient export (in kilograms per hectare) values were: ammonia (NH_3), 0.25; nitrate (NO_3^-), 4.3; total nitrogen (TN), 10.6; orthophosphate (OP), 0.26; total dissolved phosphorus (TDP), 0.30; and total phosphorus (TP), 1.2 during 1999. Stream-water samples were collected during baseflow, elevated baseflow, and stormflow conditions. Stormflow, which produced the greatest flow-weighted mean nutrient concentrations, represented only 41 percent of the annual runoff but accounted from 49 to 68 percent of the annual nutrient export. The highest seasonal flow-weighted mean concentrations were measured during the summer; the highest concentrations occurred during a large storm on July 4, 1999 with a recurrence interval greater than 100 years. The greatest seasonal export of dissolved nutrients (NH_3 , NO_3^- , OP, and TDP) occurred during the winter, whereas the greatest export of TN and TP was during the summer. Most of the TN and TP export during the summer occurred during the July 4 storm. That storm, together with

a second large storm on September 16, 1999, accounted for the following percentages of annual export: ammonia, 17 percent; NO_3^- , 21 percent; TN, 45 percent; OP, 21 percent; TDP, 21 percent; and TP, 56 percent. Although these results provide information on the quantity and timing of nutrient export, they do not indicate the nutrient source nor the transport mechanisms by which nutrients are delivered to the stream.

Baseflow and stormflow samples were collected for pesticide analyses at the Town Brook watershed outlet from January through July 1999. Eight pesticides and pesticide metabolites (degradation products) were detected in the samples. Four compounds (metolachlor, atrazine, metolachlor ESA, and metolachlor OA) were detected in concentrations greater than 1 micrograms per liter ($\mu\text{g/L}$) in one or more samples. Two of these compounds—the herbicide metabolites metalochlor ESA and metalochlor OA—were detected in concentrations higher than those of the parent compound metolachlor. Only one sample, collected during the July 4 storm, exceeded New York State surface-water-quality standards for any pesticide (simazine); its concentration of 0.53 $\mu\text{g/L}$ was 0.03 $\mu\text{g/L}$ higher than the New York State standard (0.50 $\mu\text{g/L}$). No concentrations exceeded Federal water-quality standards. Pesticide and metabolite concentrations were as much as 25 times greater during stormflow than during baseflow. Stormflow pesticide concentrations were indicative of a spring “flushing”, in which stream

pesticide concentrations are elevated from concentrations typical during the rest of the year during the first few storms after pesticide application. Pesticides and pesticide metabolites were detected in all stormflow samples. These results illustrate the need to include baseflow and stormflow in pesticide sampling routines.

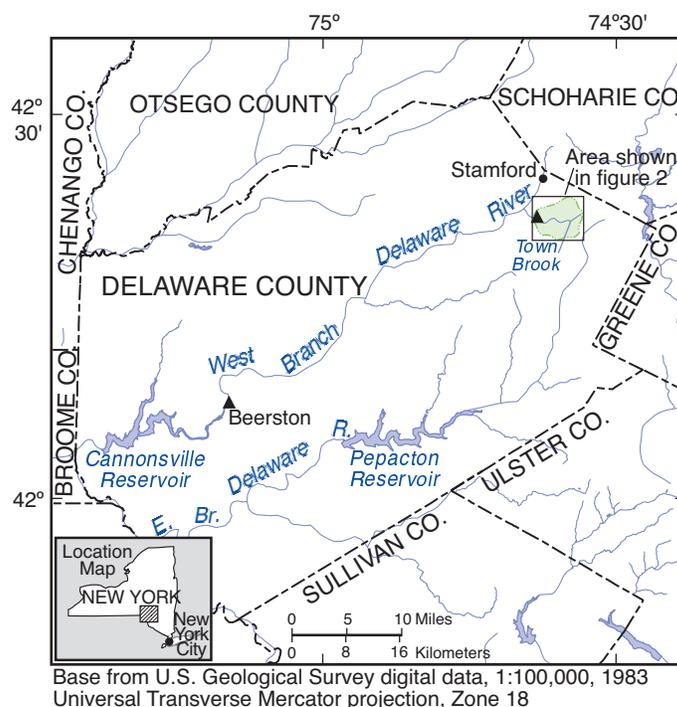
The results of this study emphasize the need for (1) baseflow and stormflow sampling to capture the range of nutrient and pesticide concentrations from agricultural watersheds, and (2) research to define the mechanisms of nutrient and pesticide export in agricultural watersheds.

INTRODUCTION

The Cannonsville Reservoir, a part of New York City's water-supply system (fig. 1), has shown signs of eutrophication (algal growth and decreased dissolved oxygen concentrations) (Effler and Bader, 1998; Effler and others, 1998). The Cannonsville watershed has been designated as phosphorus (P)-restricted to minimize eutrophication of the Cannonsville Reservoir. The P restriction, imposed by a memorandum of agreement between New York City and a coalition of towns in the watershed, limits P inputs to surface waters in the watershed until target P concentrations in the Cannonsville Reservoir are met (NYC MOA, 1997). The P restriction can limit land use and development within the watershed, although that is not its main intent. The Watershed Agricultural Program (WAP) (Walter and Walter, 1999) has designated the Cannonsville Reservoir watershed as an area of research for testing best management practices (BMPs) and other methods of P reduction within forested and agricultural ecosystems. The WAP is a partnership between farmers in the watershed and New York City that works to balance pollution prevention, economic viability, and public-health concerns to protect the quality of the New York City water supply. The WAP was begun in 1992 to decrease stream pollution from agricultural runoff through the adoption of BMPs on farms in an effort to decrease the transport of pathogens, nutrients, and other agricultural contaminants to streams and, ultimately, New York City reservoirs.

Development of an effective method for decreasing nutrient concentrations in stream water from agricultural watersheds requires the

identification of the sources of nutrients as well as the transport mechanisms (Gburek and Sharpley, 1998). Variables, including climate, presence of saturated soils, timing of manure application, presence of tile-drained fields, livestock access to streams, crop production, fertilizer use, and soil-nutrient concentrations, can affect the concentration and, ultimately, the rate of nutrient export. Definition of the seasonal patterns of nutrient export, total annual nutrient export, and the seasonal and stormflow patterns of stream-water chemistry and pesticide concentrations can help to quantify the amount of nutrients and pesticides entering streams and identify times of the year when nutrient and pesticide loading to streams is greatest. Knowledge of the characteristics of nutrient release during storms and how the various flow components contribute to nutrient export can help guide the design of future sampling strategies and research aimed at decreasing nutrient export from agricultural watersheds.



EXPLANATION

- ▲ Sampling Site
- Town Brook Watershed

Figure 1. Pertinent geographic features of Delaware County, N.Y. and location of Cannonsville Reservoir and the Town Brook watershed study area.

Objectives

From January through December 1999, the U.S. Geological Survey (USGS), in cooperation with New York State Department of Environmental Conservation and New York City Department of Environmental Protection, conducted a study to monitor stream-water chemistry and pesticide concentrations at the outlet of the Town Brook watershed as a preliminary step to more intensive research to evaluate BMP effectiveness within the watershed. Objectives of the study were to (1) provide an estimate of annual nutrient export from the watershed, (2) document the seasonal variability in nutrient export and identify times of the year when nutrient loading to streams is greatest, (3) investigate the relation between runoff rate and nutrient and pesticide concentrations, and (4) describe the processes that affect nutrient and pesticide release in stormflow, baseflow, and elevated baseflow, and calculate the contribution of each of the flow components to total annual nutrient export.

Purpose and Scope

This report describes the sampling procedures, analytical methods, and the results of stream-water quality monitoring and discusses the contributions of stormflow and baseflow to annual nutrient export and pesticide concentrations in relation to State and Federal standards.

Study Area

The 37-km² Town Brook watershed (fig. 2) is within the Cannonsville Reservoir watershed (fig. 1). Town Brook is a tributary of the West Branch Delaware River. It was chosen for water-quality monitoring because it drains mostly agricultural land and, therefore, is appropriate for research on the effectiveness of BMPs in decreasing the transport of agricultural contaminants. The watershed is about 54 percent agricultural (mostly family owned dairy farms) and 45 percent forest (fig. 2). The surficial geology is dominated by a poorly sorted till, the main axis of the valley contains some outwash sand and gravel in addition to kame deposits. The watershed is underlain by sedimentary bedrock of the Oneonta

Formation that is exposed or lies within 1 m of the surface on the ridgetops.

Previous Studies

Nutrient concentrations and export patterns in streams of the Mahantango Creek Agricultural Research watershed (MCR), in a similar climatic regime in central Pennsylvania, about 300 km from Town Brook watershed, have been described by Pionke and others (1996, 1999). MCR has been the subject of agricultural research by the U.S. Department of Agriculture Agricultural Research Service since 1968. The highest total dissolved phosphorus (TDP) concentrations, and 66 percent of TDP export during 1984-96, were detected during storms (Pionke and others, 1999). Total dissolved P concentration was positively correlated with discharge during large storms, whereas the majority of NO₃⁻ export were detected during baseflow and elevated baseflow conditions (Pionke and others, 1999). Summer discharge was smaller and contributed less TDP and NO₃⁻ than any other season, whereas winter and spring discharges were the largest and contributed the most TDP and NO₃⁻ (Pionke and others, 1999). The effect of seasonality on nutrient export was attributed mainly to differences in discharge rather than differences in nutrient concentration (Pionke and others, 1996).

Longabucco and Rafferty (1998) calculated P loads at the major inflow to the Cannonsville Reservoir. Phosphorous loads varied widely from year to year during 1991-96 because they were derived mainly from nonpoint sources (Longabucco and Rafferty, 1998). Longabucco and Rafferty (1998) emphasized the importance of storm-based sampling and noted that the timing and duration of storms can strongly affect the resulting nutrient loads. For example, a single storm during 1996 accounted for 74 percent, 34 percent, and 75 percent of the total annual loads of particulate P, TDP, and total suspended sediment, respectively.

Acknowledgments

Thanks are extended to Jason Martin and Alton Anderson for help with equipment installation and sample collection and to Hannah Ingleston for help with sample processing all of who work for the U.S.

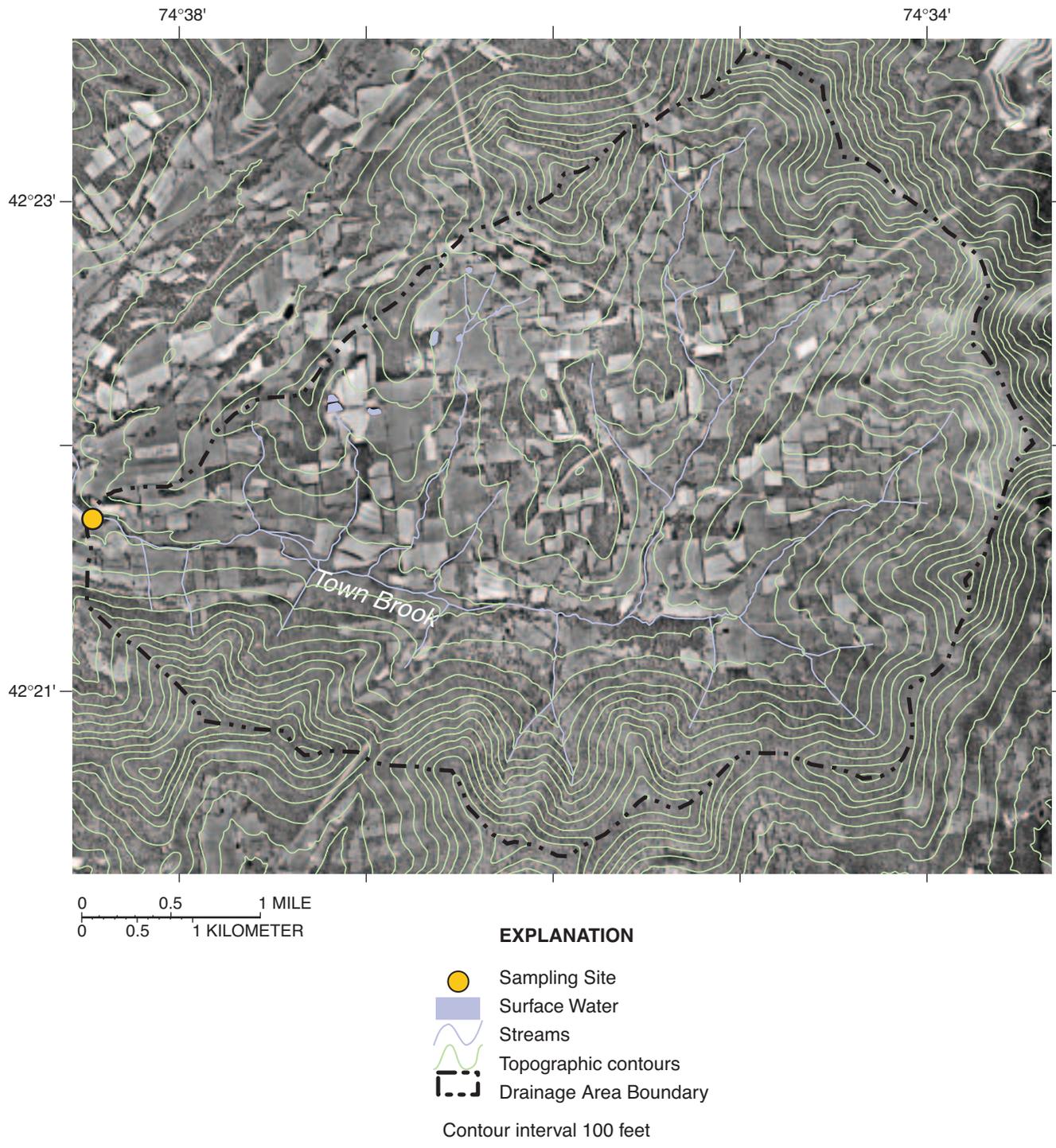


Figure 2. Geography and locations of sampling site in Town Brook watershed, Delaware County, N.Y. (Location is shown in fig. 1).

Geological Survey at the Troy N.Y. office. Thanks are also extended to the town of Hobart for permission to locate equipment and sample stream chemistry on town land. We would also like to thank the farmers who live within the Town Brook watershed for their cooperation during this study.

DATA COLLECTION

This study included manual and automated (for storms) stream water chemistry and pesticide sampling in addition to stream discharge measurements at the watershed outlet.

Stream Discharge

Stream discharge has been measured continuously at a USGS gaging station at the outlet of the Town Brook watershed (fig. 2) since October 1998. Two large storms within the watershed on July 4 and September 16, 1999, allowed evaluation of their effect on annual nutrient budgets. The July storm was a severe thunderstorm that stalled over the Town Brook valley; total rainfall for that storm at nearby Stamford, N.Y. (fig. 1) was 124.5 mm (National Oceanic and Atmospheric Administration, 2000) and caused a peak runoff rate of 12.1 mm/h. The September storm (Hurricane Floyd) dropped 66.3 mm of rain at Stamford (National Oceanic and Atmospheric Administration, 2000) and caused a peak runoff rate of 6.3 mm/h.

Water Quality

Water samples were collected weekly during the study for chemical analyses, and samples from nine storms were collected by an automated sampler. Samples were analyzed for pH, specific conductance, and concentrations of major ions and nutrients (nitrogen and phosphorus) at the USGS National Water-Quality Laboratory in Denver, Colo. All samples were chilled on ice immediately after collection and filtered through 0.45- μ polycarbonate filters within 48 hours (most within 24 hours) of collection. Samples were then stored at 4 °C until shipped to the laboratory for analyses. The sum of ammonium (NH_4^+) and solvated ammonia (NH_3 aqueous) are reported here as “ammonia” (NH_3) though these values typically are reported as

ammonium by other researchers. Nitrate and NH_3 are reported as NO_3^- -N and NH_3 -N, respectively; total nitrogen is the sum of all dissolved inorganic nitrogen (NH_4^+ , NO_3^- , NH_3 , and NO_2^-) plus dissolved and particulate organic nitrogen. Total P consists of particulate and dissolved organic P as well as all dissolved inorganic P. Total dissolved P refers to all organic and inorganic P that passes through a 0.45-micron polycarbonate filter. Orthophosphate is biologically available inorganic reactive P and is reported as PO_4^{3-} -P. Dissolved organic carbon (DOC) samples were filtered through 0.7- μ glass-fiber filters and analyzed at the USGS laboratory in Troy, N.Y.

Pesticides

Water samples were collected from January through July 1999, including two storms, for pesticide analyses at the USGS National Water-Quality Laboratory in Denver, Colo. Samples were collected by conventional and automated methods (table 1) and 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). The laboratory methods resulted in low and (or) inconsistent recovery for five pesticides (carbaryl, carbofuran, deethylatrazine, terbacil, and azinphos-methyl); thus, the concentrations reported for each of these compounds are considered estimates and may be lower than the true concentration (Christopher Lindley, U.S. Geological Survey, written commun., 1994). The detection limits for the compounds monitored in this study (0.001 to 0.2 $\mu\text{g/L}$) (table 1) are much lower than those achieved by analytical methods typically used in public-water-supply monitoring programs and are well below Federal and State public health standards (See “Federal and New York State Water-Quality Standards used in this study” insert on page 16). Therefore, much higher rates of detection were obtained than would have been possible with less sensitive analytical methods.

Samples were divided into two flow classes—baseflow (15 samples) and stormflow (7 samples) (table 2). All stormflow samples were collected during storms in early July 1999, after pesticide application. Eight baseflow samples and one storm sample were collected with glass bottles by standard equal-width sampling techniques across the stream channel (Shelton, 1994). Twelve samples were

Table 1. Detection limits for the 60 pesticide and pesticide metabolites for which water samples from Town Brook watershed, Delaware County, N.Y. were analyzed, January through July 1999.

[ESA, ethanansulfonic acid. OA, oxanilic acid. Detection-limit concentrations (in parentheses) are in micrograms per liter.]

Pesticide	Detection limit	Pesticide	Detection limit	Pesticide	Detection limit	Pesticide	Detection 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)	p,p -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)	cis-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, Denver, Colo.							
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, Denver, Colo.							
Ametryn	(0.05)	Deisopropylatrazine*	(0.05)	Propazine	(0.05)		
Cyanazine Amide*	(0.05)	Prometryn	(0.05)	Terbutryn	(0.05)		

* degradation product

collected with an automatic sampler in glass bottles cleaned according to procedures described in Shelton (1994). One storm sample was collected in an acid-washed polyethylene bottle.

Five quality-assurance samples were collected during the study. Two were equipment blanks that were used to assess whether pesticide or pesticide-metabolite compounds were present in plastic bottles cleaned by standard methods for nutrient sampling. These cleaning methods do not include a methanol rinse and, thus, are not identical to the cleaning methods used for pesticide-sampling bottles. No pesticides or pesticide metabolites were detected in the equipment blanks. For three samples collected by equal-width techniques duplicate samples were taken with an automated sampler. The difference in

concentrations of 12 pesticides in samples collected by the two sampling methods ranged from 0.3 to 12 percent, with an average difference of 3 percent. Metolachlor OA was detected in one sample duplicate at a concentration of 0.21 µg/L (just above the detection limit of 0.2 µg/L); no metolachlor OA was detected in the three samples collected by standard techniques.

STREAM-WATER CHEMISTRY

Flow conditions were defined in a manner similar to that used by Pionke and others (1999). Discharge was separated into three flow components—stormflow (from the initial rise in stage to the early recession

Table 2. Dates and methods used for collecting pesticide samples at Town Brook, Delaware County, N.Y., January through July, 1999.

[Asterisk denotes duplicate sample collected by automatic sampler within 0.5 hour of a sample collected by standard methods described in Shelton (1994)].

Date	Time	Sample Method	Type of Sample
January 24	1230	standard	baseflow
May 25	1300	standard	baseflow
June 9	1210	standard	baseflow
June 9*	1220	automatic	baseflow
June 15	1100	automatic	baseflow
June 15*	1110	standard	baseflow
June 28	1650	automatic	baseflow
June 29	1235	standard	baseflow
June 29*	1255	automatic	baseflow
June 29	2200	automatic	baseflow
June 30	1355	standard	baseflow
June 30	1550	automatic	baseflow
July 2	1020	standard	baseflow
July 3	2100	automatic	baseflow
July 4	0715	automatic	stormflow
July 4	0750	automatic	stormflow
July 4	0815	automatic	stormflow
July 4	0850	automatic	stormflow
July 6	1230	standard	baseflow
July 6	2300	automatic	stormflow
July 7	0540	automatic	stormflow
July 7	1400	standard	stormflow

greater than 30% of the total rise for each storm), elevated baseflow (the late recession from less than 30% of the total rise in stage to less than 2 days after the peak for each storm), and baseflow (stable nonstormflow periods or extended recessions more than 2 days after a stormflow peak). About 1 percent of flow was unclassified (small rises that were not related to rainfall or snowmelt).

All mean chemistry and nutrient values discussed here were weighted by discharge. Mean pH of Town Brook stream water was 7.0 during 1999 (table 3). Stormflow had the lowest mean pH value (6.9), and baseflow had the highest (7.3). Mean concentrations of acid-neutralizing capacity (ANC), Ca, Mg, Na, SO_4^{2-} , Cl and specific conductance were highest during baseflow, whereas the mean concentration of SiO_2 was highest during elevated baseflow. Potassium and DOC were highest during stormflow. A seasonal separation of concentrations indicates that SiO_2 concentrations were highest during winter

(December-February), whereas Na and Cl concentrations were highest during spring (March-May), probably as a result of salt-laden runoff from the road adjacent to the stream gage. Mean SO_4^{2-} concentrations were also highest during the spring. Specific conductance, pH, ANC, Ca, Mg, and K were highest during the summer (June-August), whereas DOC concentrations were highest during fall (September-November), probably as a result of the increase in organic matter associated with leaf-fall and crop harvest. Potassium and DOC were the only chemical constituents that showed significant relations with runoff, but the relations were not strong (table 4).

NUTRIENTS

Nutrient samples were collected from January through December 1999 to provide an estimate of annual nutrient export from the watershed, to document the seasonal variability in nutrient export, and to identify the times of the year when nutrient loading to Town Brook is highest. Concentrations of all nutrients were highest during stormflow (table 5). A seasonal separation of runoff-weighted mean concentrations indicated that the concentrations of NO_3^- and TN were highest during summer, NH_3 , was highest during winter (table 5). Ammonia concentrations typically were less than 0.2 mg/L; the lowest concentrations were below the detection limit of 0.002 mg/L and the highest occurred during a snowmelt on January 22, 1999 (fig. 3A). Although NH_3 concentrations increased during most storms, no strong relation between runoff rate and concentration was noted. Concentrations of NO_3^- also increased during storms; the highest (2.5 mg/L) occurred during the July 4 storm. Nitrate concentrations were characteristically high during the early spring, then decreased as the growing season began, but never were less than 0.22 mg/L (fig. 3B). The high NO_3^- concentrations during the July 4 storm caused the discharge-weighted mean summer NO_3^- concentrations to be high. Total N concentration varied widely and showed no distinct seasonal pattern (fig. 3C).

Total dissolved P and OP concentrations had similar ranges, and both increased during storms (figs. 3D, 3E). All mean P concentrations were greatest during the fall and lowest during the spring. Annual mean TP concentrations were more than six times

Table 3. Chemical quality of Town Brook, Delaware County, N.Y., 1999, by flow component and season.

[All values are flow-weighted means; standard deviations are in parentheses. ANC, acid-neutralizing capacity, DOC, dissolved organic carbon, n, number of samples. All values are in milligrams per liter except pH (pH units) and specific conductance (microsiemens per centimeter at 25°C). Location is shown in fig. 2.]

	pH	ANC	Ca ²⁺	Mg	Na	K ⁺	Cl ⁻	SO ₄ ²⁻	SiO ₂	DOC	Specific conductance	n
Flow component												
Baseflow	7.3 (0.3)	18.4 (13.3)	6.5 (2.8)	1.3 (0.50)	2.2 (0.84)	1.1 (0.41)	3.1 (1.4)	6.7 (2.6)	3.7 (0.98)	2.0 (0.3)	65.7 (21.7)	13-20
Elevated baseflow	7.2 (0.2)	13.5 (5.0)	5.7 (1.4)	1.1 (0.27)	2.0 (0.45)	1.4 (0.49)	2.2 (0.75)	6.3 (0.75)	4.0 (0.59)	4.0 (1.2)	56.4 (11.6)	14-16
Stormflow	6.9 (0.3)	14.3 (8.6)	5.3 (2.0)	1.1 (0.35)	2.1 (0.67)	2.5 (1.1)	3.0 (1.3)	5.7 (0.94)	2.9 (0.48)	5.4 (1.5)	59.0 (16.1)	48-61
Season												
Winter	6.9 (0.3)	9.7 (3.2)	4.9 (1.2)	1.1 (0.25)	2.2 (0.87)	1.8 (0.60)	3.7 (1.9)	6.7 (0.66)	3.3 (0.58)	3.5 (0.98)	57.9 (12.7)	15-16
Spring	7.1 (0.2)	14.4 (3.4)	6.1 (0.72)	1.3 (0.16)	2.7 (0.41)	1.7 (0.69)	4.3 (1.1)	6.8 (0.76)	3.1 (0.39)	3.5 (1.0)	68.7 (7.1)	33-36
Summer	7.3 (0.3)	23.8 (5.8)	7.4 (1.7)	1.4 (0.33)	2.3 (0.69)	2.8 (1.2)	3.0 (0.90)	4.9 (1.8)	3.2 (0.87)	5.0 (1.6)	74.8 (14.6)	16-29
Fall	6.9 (0.4)	14.8 (14.7)	4.9 (3.3)	1.0 (0.61)	1.7 (0.94)	2.7 (1.2)	2.0 (1.8)	5.2 (0.90)	2.9 (0.74)	6.5 (2.2)	52.7 (26.9)	11-16
Annual mean	7.0 (0.3)	14.3 (9.8)	5.4 (2.2)	1.1 (0.40)	2.1 (0.71)	2.3 (1.0)	2.9 (1.3)	5.8 (1.4)	3.1 (0.69)	5.2 (1.5)	58.9 (17.8)	75-97

greater than those of TDP, indicating that particulate P accounted for the majority of TP. No nutrients showed significant correlations with runoff rate (table 4).

Nutrient concentrations measured at Beerston, about 66 km downstream on the west branch of the Delaware River and close to the inlet to the Cannonsville Reservoir (fig. 1) were typically lower than those at Town Brook during stormflow and similar or higher than those at Town Brook during baseflow during 1991-96 (Longabucco and Rafferty, 1998) (table 6). The greater range in nutrient concentrations between flow conditions at the Town Brook watershed outlet than at the Beerston gage likely is due to the large difference in watershed size. The smaller Town Brook watershed would be expected to respond more rapidly to storm inputs than the much larger Cannonsville Reservoir watershed.

Nutrient Export

Nutrient export for the Town Brook watershed during 1999 were computed at a 15-minute time-step (the time interval for stage and discharge readings). Estimates were calculated as the product of the nutrient concentration (mg/L) and cumulative 15-minute flow (L). Concentrations were linearly interpolated between stream water samples. Nutrient export was partitioned by flow condition (fig. 4) and season (fig. 5). Total runoff for the year was 664 mm, 34 percent was baseflow, 24 percent was elevated baseflow, and 41 percent was stormflow (fig. 4).

Stormflow accounted for the majority (49 to 68 percent) of nutrient export (fig. 4). Baseflow at the Pennsylvania MCW accounted for a smaller percentage of OP, TDP, and NO₃⁻ than at Town Brook

Table 4. Linear regression results for concentration of selected constituents as a function of runoff rate from Town Brook watershed, Delaware County, N.Y., 1999

[TN is total organic nitrogen plus nitrite, nitrate, and ammonia]

Solute	r ²	P-value	Slope	n
Nutrients				
Total Phosphorus	0.004	0.53	1.45	96
Total dissolved phosphorus	0.03	0.09	0.43	96
Orthophosphate	0.04	0.04	0.48	96
NH ₃	0.006	0.47	0.37	96
NO ₃ ⁻	0.02	0.23	0.83	96
TN	0.002	0.65	7.25	95
Chemistry				
pH	0.0025	0.63	-0.02	94
Ca ²⁺	0.02	0.20	10.8	95
Mg ²⁺	0.035	0.07	4.4	95
Na ⁺	0.0012	0.74	1.5	95
K ⁺	0.11	< 0.001	12.6	95
Cl ⁻	0.01	0.33	5.5	95
SO ₄ ²⁻	0.016	0.22	2.7	95
SiO ₂	0.007	0.42	-2.9	95
DOC	0.23	< 0.001	76.6	75
Other properties				
Specific conductance	0.026	0.12	4.2	94
Acid-neutralizing capacity (ANC)	0.0089	0.37	26.2	94

(Pionke and others, 1996). Elevated baseflow at the MCW accounted for a smaller percentage of OP and TDP than at Town Brook, and a greater percentage of NO₃⁻ (Pionke and others, 1996). Stormflow at the MCW accounted for a greater percentage of OP and TDP and a smaller percentage of NO₃⁻ than at Town Brook. Total nutrient loads at Beerston (fig. 1) for 1991-96 (Longabucco and Rafferty, 1998) were averaged and divided by the drainage area above the site (91,000 ha) for comparison with Town Brook values. This comparison is limited to NO₃⁻, OP and TDP; TP and TN values are not comparable between the two studies because the filtering methods and analytical techniques differed. Ammonia was not included in the Beerston study. Nitrate export from Town Brook outlet was within the range of annual export reported for the Beerston site but was 0.4 (kg/ha)/yr greater than the 1991-96 mean. Orthophosphate and TDP exports from Town Brook were greater than at Beerston by 0.1 (kg/ha)/yr, for both nutrients. The

difference between the two sites could result from four possible mechanisms—(1) dilution by ground water and tributary inflow, (2) biological uptake and transformation of nutrients within the stream, or (3) transformation of inorganic to organic P and subsequent deposition within the West Branch Delaware channel (4) the export calculations for the sites were completed for different time periods.

The seasonal analysis of nutrients (fig. 5) indicates that the greatest export of NH₃, NO₃⁻, OP, and TDP occurred during winter, whereas the greatest export of TN and TP occurred during summer (mostly during the July 4 storm). Winter accounted for only 17 percent of TP export and 23 percent of TN export (fig. 5). The seasonal differences between NH₃ and NO₃⁻ export are attributed to differences in both concentration and flow volumes. The large winter export of NH₃, NO₃⁻, OP, and TDP was due to high concentrations and large flows, whereas the large summer export of TN and TP was due mainly to high concentrations because summer had the lowest total flow volume of any season. The differences in OP and TDP export with season (fig. 5) reflect the seasonal difference in flows; concentration exerted a secondary control. These results indicate that data covering the full range of flow conditions, as well as the full range of concentrations, are needed for interpretation of export patterns. Both variables are needed to calculate chemical export but are not necessarily closely correlated (table 4).

Nutrient-Transport Dynamics in Stormflow

Stormflow accounted for most of the nutrient export from Town Brook during 1999 (fig. 4). The two large storms of July 4 and September 16, accounted for the following percentages of the annual export: NH₃, 17 percent; NO₃⁻, 21 percent; TN, 45 percent; OP, 21 percent; TDP, 21 percent, and TP, 56 percent (fig. 4). The high percentages for TN and TP probably are due to the large particulate fraction of each constituent—high flows tend to carry increased amounts of sediment and particulate organic matter. A flood-frequency analysis of the July 4 storm, based on regional regression equations developed for unregulated streams in New York (Lumia, 1991), indicated a recurrence interval of more than 100 years. The large runoff from this storm was due to the wet antecedent moisture conditions from a previous storm

Table 5. Mean nutrient concentrations in Town Brook watershed, Delaware County, N.Y., 1999 by flow component and season.

[All values are flow-weighted means, standard deviations are shown in parentheses. All values are in milligrams per liter. TN is total organic nitrogen plus nitrite, nitrate, and ammonia. OP is orthophosphate, TDP is total dissolved phosphorus, TP is total phosphorus]

	NO ₃ ⁻	NH ₃	TN	OP	TDP	TP	n
Flow component							
Baseflow	0.53 (0.25)	0.02 (0.01)	0.79 (0.25)	0.02 (0.01)	0.03 (0.01)	0.03 (0.01)	21
Elevated baseflow	0.55 (0.17)	0.01 (0.01)	1.2 (0.55)	0.04 (0.02)	0.05 (0.02)	0.10 (0.04)	11
Stormflow	0.61 (0.32)	0.06 (0.05)	2.4 (1.8)	0.10 (0.05)	0.11 (0.06)	0.73 (0.57)	64
Season							
Winter	0.68 (0.14)	0.12 (0.08)	1.7 (0.63)	0.06 (0.05)	0.06 (0.05)	0.30 (0.21)	16
Spring	0.58 (0.22)	0.06 (0.03)	1.3 (0.55)	0.05 (0.03)	0.06 (0.03)	0.17 (0.17)	36
Summer	0.91 (0.41)	0.06 (0.04)	2.8 (2.5)	0.09 (0.05)	0.11 (0.06)	0.84 (0.73)	28
Fall	0.53 (0.19)	0.02 (0.01)	2.7 (1.2)	0.13 (0.06)	0.14 (0.07)	0.96 (0.50)	16
Annual Mean	0.60 (0.28)	0.05 (0.05)	2.2 (1.5)	0.09 (0.05)	0.10 (0.05)	0.64 (0.48)	96

on June 28, 1999 (the 7-day antecedent precipitation index was 37.4 mm) and the large amount of rainfall (124.5 mm).

The highest NO₃⁻ concentration during the July 4 storm coincided with the greatest runoff rate (fig. 6A). Nonetheless, more samples were collected during the rising limb of the hydrograph than during recession. Ammonia concentrations responded more quickly to the storm than NO₃⁻ or TN concentration, but the absolute change in NH₃ concentration was much smaller than that of NO₃⁻ or TN. Total nitrogen concentrations increased about threefold; one sample indicated a 15-fold increase. Nitrate concentrations doubled, and one sample showed a sevenfold increase. These results emphasize the need for frequent sampling during storms; NO₃⁻ and TN concentrations took less than 1 hour to increase sevenfold.

Absolute changes in phosphorus concentrations were large during both storms (fig. 6). Orthophosphate concentrations increased nearly tenfold—from 0.02 to 0.2 mg/L—in about 6 hours, and total dissolved phosphorus responded similarly (fig. 6). Total phosphorus concentration did not respond as quickly as TDP concentration, but the total response was much greater (0.1 to 3.5 mg/L). This delayed increase in TP concentrations was probably due to a delayed response in the particulate fraction of P that is closely linked to surface runoff. Surface runoff increases sharply as near-stream areas become saturated and allow saturation excess overland flow (Dunne and Black, 1970; Beven and Kirby, 1979; Bonell, 1993).

In contrast to the July 4 storm, peak nutrient concentrations during Hurricane Floyd (September 16, 1999) preceded the peak runoff rate (fig. 6). Hurricane Floyd was preceded by a drier period than the July 4 storm (7-day antecedent precipitation index 4.8 mm), and the peak runoff rate was less than half that measured for July 4. Nitrate concentrations initially were high and increased as the storm began, but became diluted rapidly, then reached a secondary peak. The NO₃⁻ concentrations at the end of the storm were lower than those measured before the storm began (fig. 6). Ammonia concentrations increased considerably (from 0.02 to 0.12 mg/L) during the storm but did not account for a large amount of total dissolved N export because the concentrations were low relative to NO₃⁻ concentration. Total nitrogen

Table 6. Volume-weighted mean nutrient concentrations during storms and baseflow at Town Brook (1999) and Cannonsville Reservoir inlet at Beerston (1991-96).

[Beerston gage concentrations from Longabucco and Rafferty, 1998. All values are in milligrams per liter. Locations are shown in fig. 1.]

	Storms		Baseflow	
	Beerston	Town Brook	Beerston	Town Brook
Total phosphorus	0.18	0.73	0.04	0.03
Total dissolved phosphorus	.04	.11	.03	.03
Orthophosphate*	.03	.10	.02	.02
Nitrate	.73	.61	.76	.53
Ammonia	.05	.06	.02	.02

* Longabucco and Rafferty (1998) report this constituent as soluble reactive phosphorus.

concentration peaked early in the storm before the peak runoff rate, declined, then reached a secondary peak similar to that of NO_3^- (fig. 6). Total nitrogen concentrations returned to prestorm levels by the end of the storm.

Phosphorus concentrations were less erratic than N concentrations. Orthophosphate, TDP, and TP concentrations all peaked before the peak runoff rate, then declined (fig. 6). Concentrations of all phosphorus species returned to near pre-storm levels by the end of the storm.

The differences between the nutrient-concentration patterns of the two storms are related, at least in part, to the magnitude of the two storms, but more information about the source and transport variables within the watershed would be needed to

describe the nutrient-release patterns in the watershed. Such information could be obtained through streamflow-tracer studies (geochemical, isotopic, or a combination of the two) combined with process-oriented, farm-scale research.

PESTICIDES AND THEIR METABOLITES

Nineteen pesticide samples were collected from January through July 1999 during baseflow and stormflow conditions. Special emphasis was placed on sampling during storms that closely followed late-spring and early-summer pesticide applications.

A greater number of pesticides and metabolites were measured during this study and we used much lower analytical detection limits, than is typical in

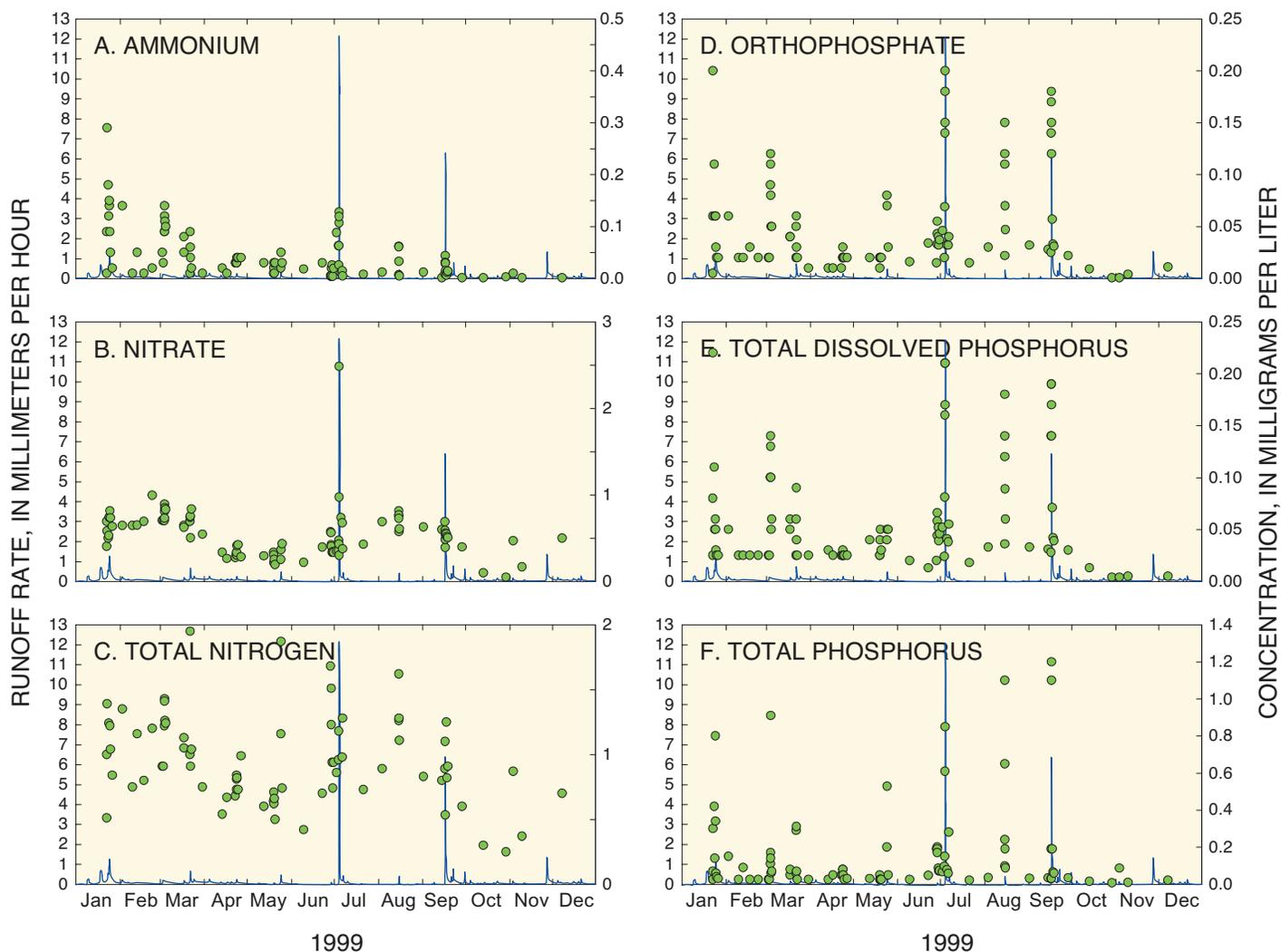


Figure 3. Runoff rate (blue lines) and concentrations (green dots) of ammonia, nitrate, total nitrogen, orthophosphate, total dissolved phosphorus, and total phosphorus in Town Brook, Delaware County, N.Y., 1999

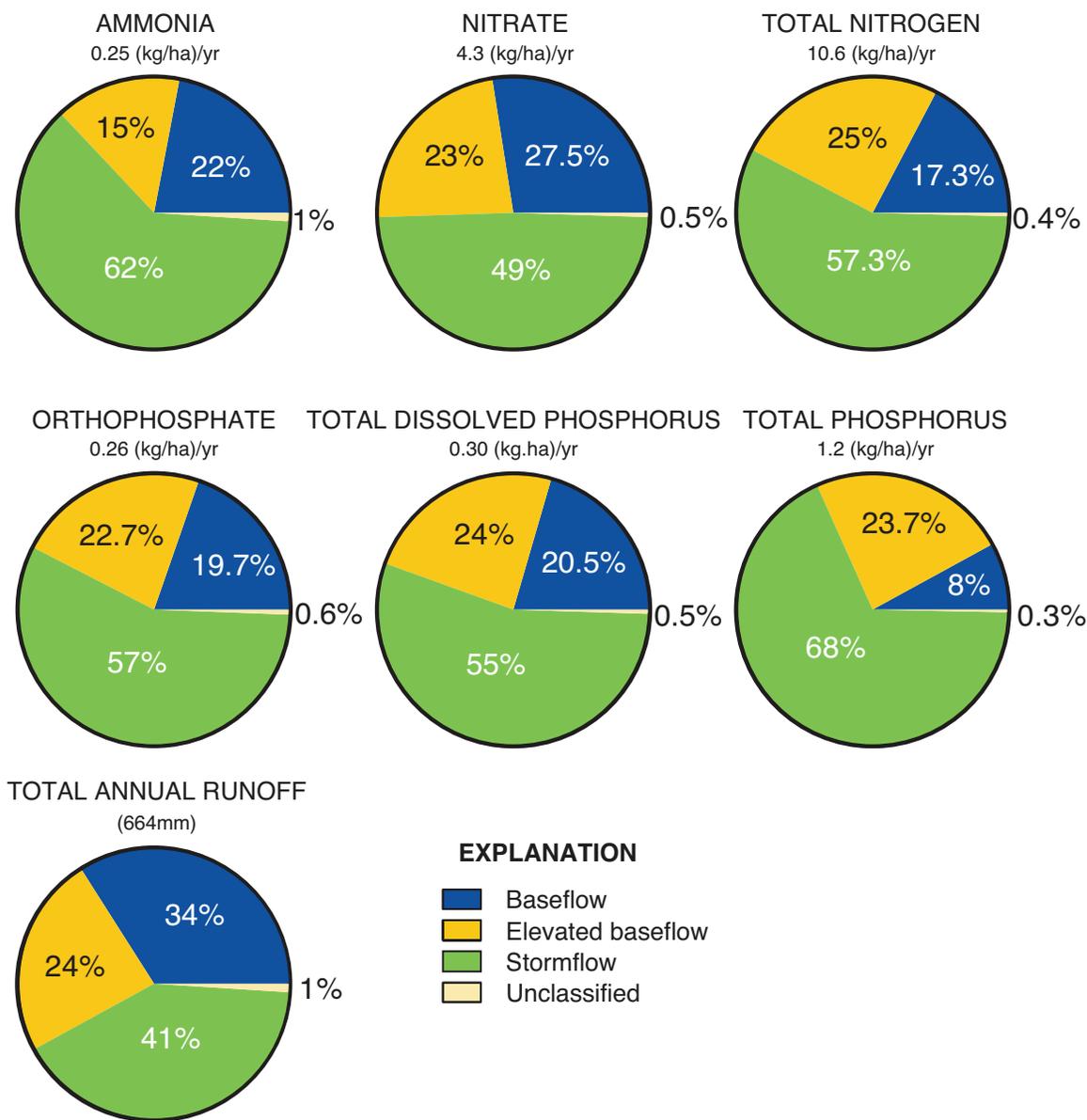


Figure 4. Total export of six nutrients, total annual runoff, and percentage of nutrient export and total runoff represented by flow component, Town Brook, Delaware County, N.Y., 1999. Total annual nutrient loads are given as kilograms per unit area (1 hectare) per year. Total annual loads are also given as the percentage exported during each flow condition in the pie charts. Total annual runoff is given as a depth over the entire watershed in millimeters.

routine pesticide monitoring of public water supplies. Special attention was given to two metabolites of the commonly used pesticide metolachlor, metolachlor ESA (ethanesulfonic acid) and metolachlor OA (oxanilic acid). These two metabolites frequently have been detected in streams that drain agricultural areas of New York and other States (Phillips and others, 1999; Eckhardt and others, 1999; Kahlkoff and others, 1998). Concentrations of these metabolites in

streamwater commonly are much higher than those of the parent compounds from which they are derived.

Concentrations in Town Brook

Of the 60 pesticides and pesticide metabolites for which samples were analyzed, four herbicides and four herbicide metabolites were detected (fig. 7).

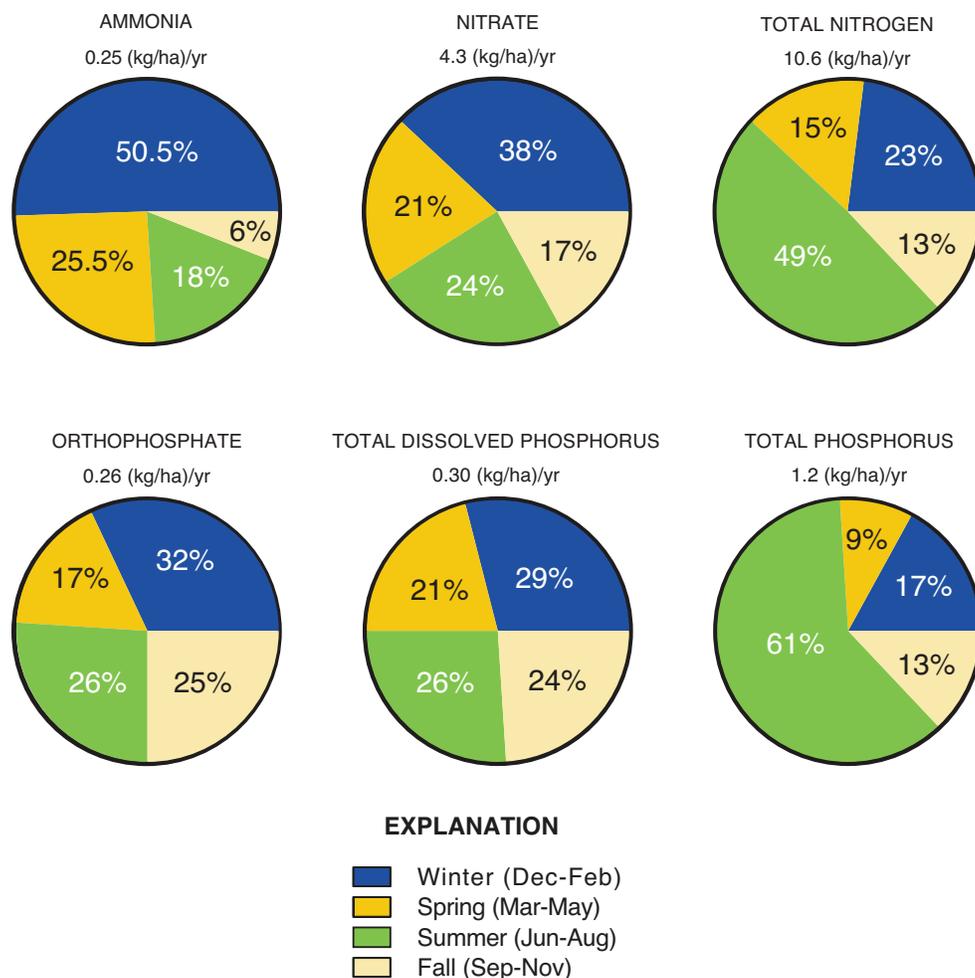


Figure 5. Percent total export of six nutrients from Town Brook, Delaware County, N.Y., in 1999, by season. Total annual nutrient loads are given as kilograms per unit area (1 hectare) per year. Total annual loads are also given as the percentage exported during each season in the pie charts.

Many of these compounds have been detected in other studies of pesticides in upstate New York waters (Phillips and others 1999). No insecticides or insecticide metabolites were detected in these samples.

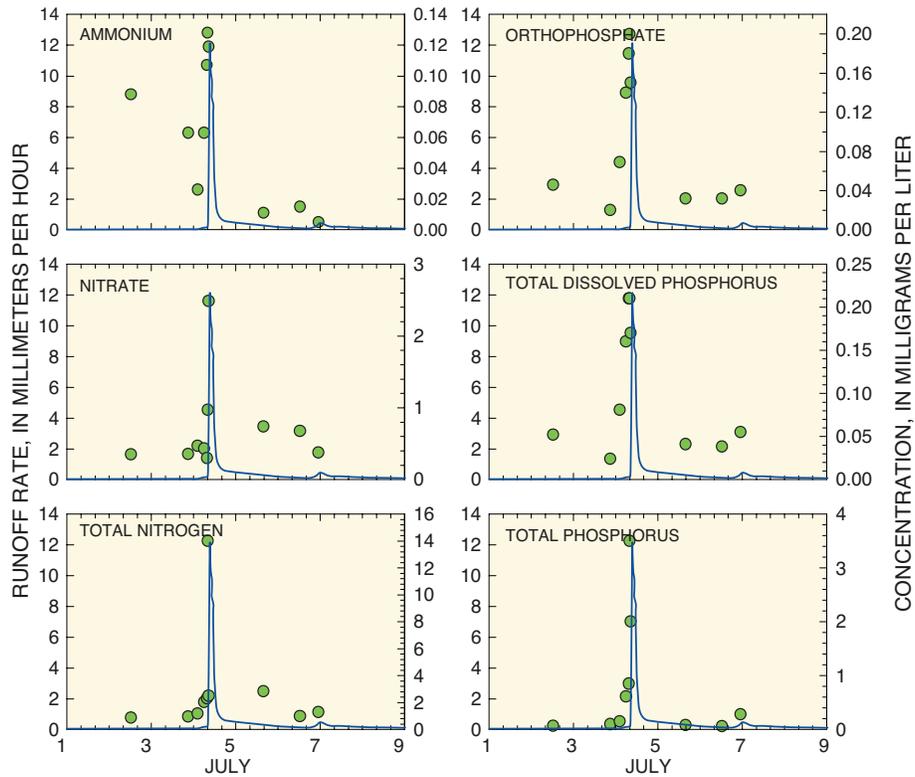
Concentrations of all but two of the compounds detected (deethylatrazine and pendimethalin) exceeded 0.2 µg/L in one or more samples, and the concentration of four compounds (metolachlor, atrazine, metolachlor ESA, and metolachlor OA) exceeded 1 µg/L in one or more samples. Metolachlor ESA and metolachlor OA generally were found at much higher concentrations than their parent compound.

Atrazine, deethylatrazine, and metolachlor

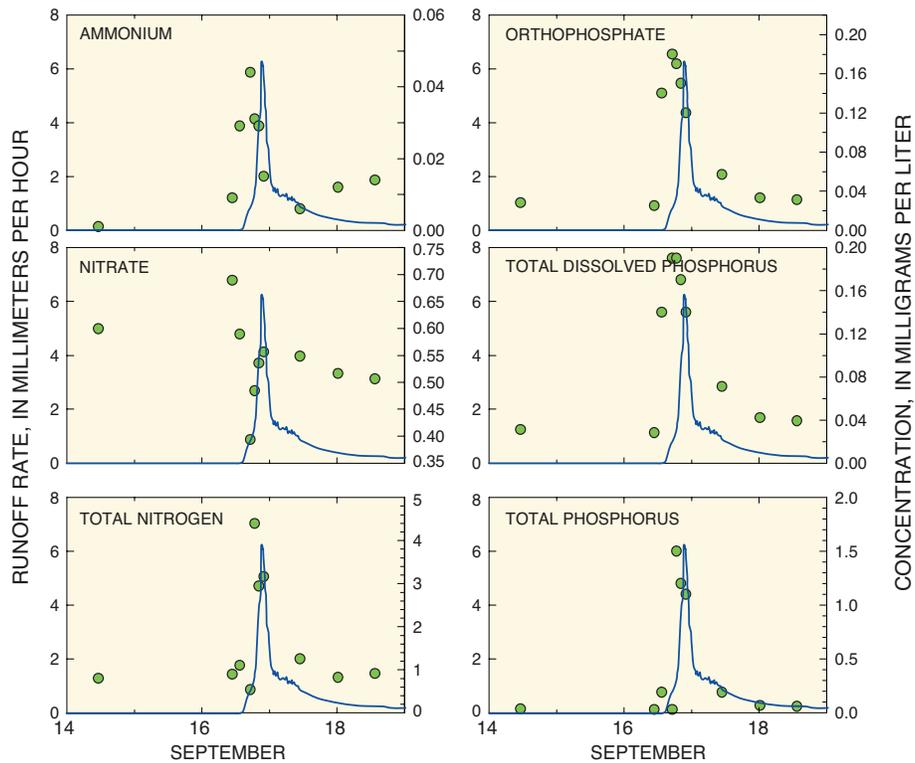
Atrazine and metolachlor are used on corn and other row crops. Atrazine, deethylatrazine (a metabolite of atrazine), and metolachlor were detected in every sample, but the concentrations of other compounds (including metolachlor ESA and metolachlor OA) frequently were higher. Concentrations of these three compounds ranged from less than 0.01 µg/L to 2.8 µg/L.

Metolachlor ESA, Metolachlor OA, and Simazine

Similar to metolachlor (the parent compound of metolachlor ESA and metolachlor OA), simazine is

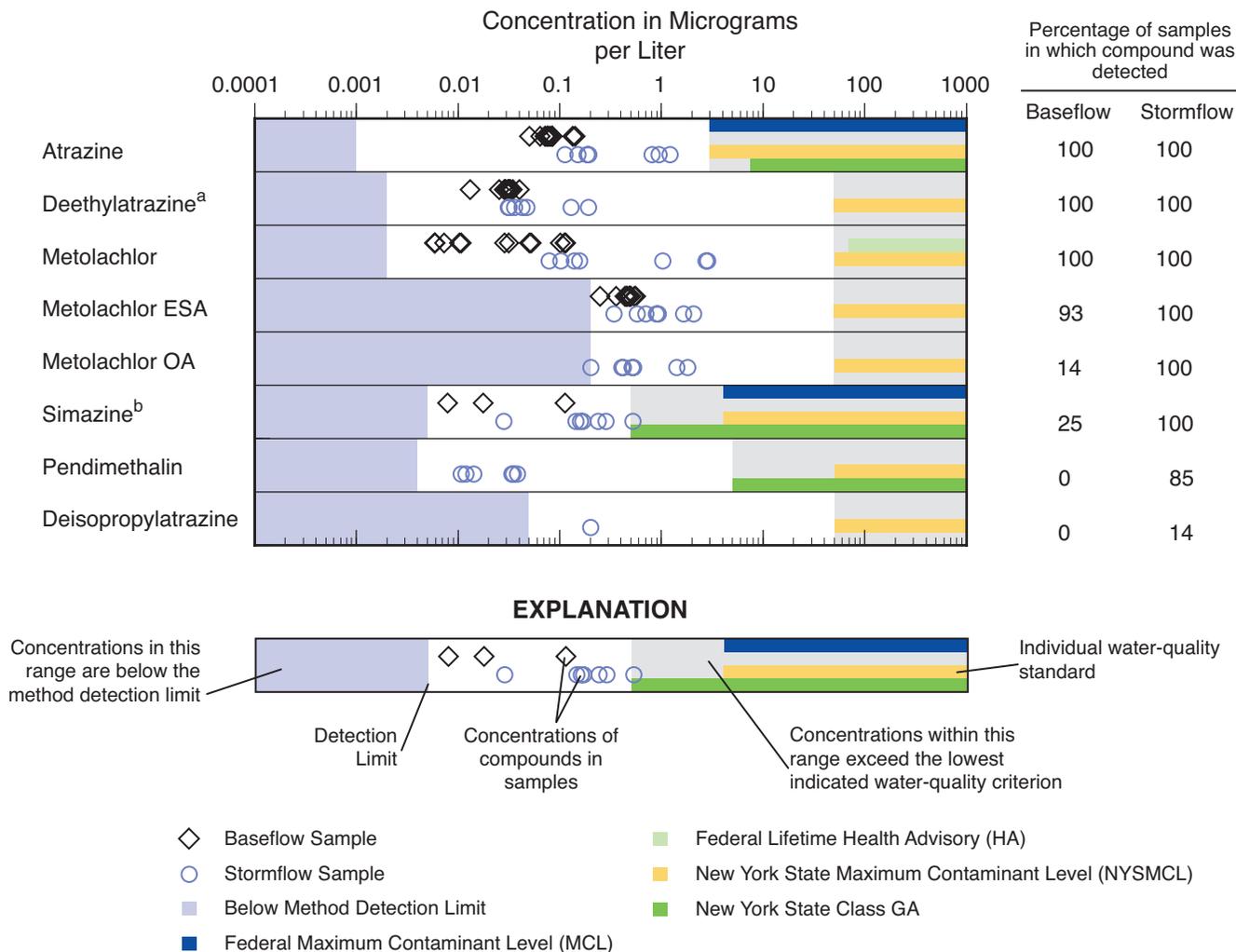


A. JULY 1-9, 1999



B. SEPTEMBER 14-19, 1999

Figure 6. Hydrographs of stormflows (blue lines) with corresponding nutrient concentrations (green dots) at Town Brook outlet, Delaware County, N.Y.: A. Storm of July 4, 1999. B. Storm of September 16, 1999. Nitrate is reported as NO_3^- -N, ammonia is reported as NH_3 -N, and orthophosphate is reported as PO_4^{3-} -P.



^a Estimated concentrations because of low and (or) inconsistent recovery.

^b New York State Surface Water Standard equals Class GA standard.

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.

State MCLs are similar to Federal MCLs but include general standards that apply to any organic chemical contaminant that does not have a specific MCL listed in regulation. These include (1) a standard of 5 µg/L for Principal Organic Contaminants (POCs), (2) a standard of 50 µg/L for any other organic contaminant (Unspecified Organic Contaminant UOC), and (3) a standard of 100 µg/L for the total of POCs and UOCs. New York State water-quality standards are based on 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.

Figure 7. Concentrations of pesticides and metabolites in baseflow and stormflow samples from Town Brook, Delaware County, N.Y., their relation to State and Federal standards, and the percentage of baseflow and stormflow samples in which each compound was detected.

used on corn and other row crops; it also is commonly used in orchards, vineyards, and rights-of-way. Simazine, metolachlor ESA, and metolachlor OA compounds were detected in all stormflow samples and in 14 to 93 percent of the baseflow samples. Concentrations of these compounds ranged from less than 0.01 µg/L to 2 µg/L.

Pendimethalin and Deisopropylatrazine

Pendimethalin, atrazine, and simazine (the parent compounds of deisopropylatrazine) are used on corn and other crops; pendimethalin also is used on lawns. Pendimethalin and deisopropylatrazine were detected only in stormflow samples. Pendimethalin was

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 in this report with the five State and Federal standards described below. 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.

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 no MCL officially has been set. <http://www.epa.gov/OST/Tools/dwstds.html>

New York State MCLs are established under the New York State Department of Health Public Water Systems Regulations (New York State Department of Health, 1998). State MCLs are similar to Federal MCLs but include (1) a standard of 50 µg/L for organic contaminants where the available health data are inadequate to set specific standards, and (2) a standard of 5 µg/L for Principal Organic Contaminants.

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) the 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 contamination that could diminish their esthetic quality or pose a threat to public health.

New York State Class GA standards are set by NYSDEC on the basis of esthetic quality or threat to public health according to procedures established by the State of New York (New York State Department of Health, 1998) to protect 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 typically are more stringent than drinking-water MCLs.

detected in most stormflow samples, whereas deisopropylatrazine was detected in only one stormflow sample. Concentrations of these compounds ranged from 0.01 to 0.2 $\mu\text{g/L}$.

Pesticide Concentrations in Relation to State and Federal Water-Quality Standards

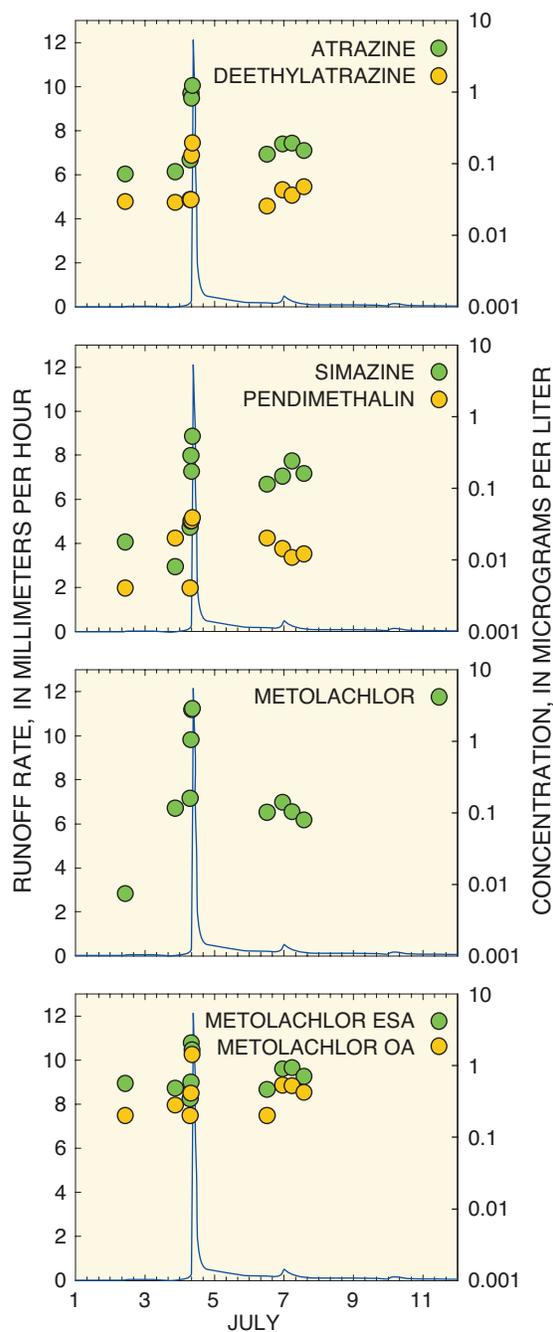
Only one of the pesticides detected was at a concentration that exceeded Federal or State water-quality standards (fig. 7). One stormflow sample from the July 4 storm had a simazine concentration above 0.5 $\mu\text{g/L}$, the New York State surface-water standard, but did not exceed Federal water-quality standards. Maximum concentrations of atrazine were 30 percent of the Federal Maximum Contaminant Level (MCL), maximum concentrations of simazine were 12 percent of the Federal MCL (excluding the one sample that exceeded the standards), and maximum concentrations of metolachlor were 5 percent of the Federal MCL.

Pesticide Concentrations in Relation to Hydrologic Conditions

A greater number of pesticides and pesticide metabolites were detected in stormflow samples than in baseflow samples. The stormflow samples contained all eight of the pesticides and pesticide metabolites detected in this study, whereas the baseflow samples contained only six (atrazine, deethylatrazine, metolachlor, metolachlor ESA, metolachlor OA, and simazine: fig. 7). Only one baseflow sample contained all six of the compounds detected in baseflow samples, but all stormflow samples contained all six compounds. Two other

Table 7. Percentage of baseflow and stormflow samples from Town Brook, Delaware County, N.Y., containing pesticides in concentrations exceeding 0.05 micrograms per liter, January through July 1999

Pesticide	Baseflow (n = 15)	Stormflow (n = 7)
Atrazine	100	100
Deethylatrazine	0	28
Metolachlor	22	100
Metolachlor ESA	92	100
Metolachlor OA	15	100
Simazine	7	80
Pendimethalin	0	0
Deisopropylatrazine	0	12



NOTE: Deisopropylatrazine was not included because it was detected in only one sample.

Figure 8. Runoff rate (blue lines) and concentrations (green dots) of the eight detected pesticides and pesticide metabolites during the July 4, 1999 storm at Town Brook, Delaware County, N.Y.

compounds (pendimethalin and deisopropylatrazine) were detected only in stormflow samples.

Concentrations of pesticides and pesticide metabolites were higher in samples collected during storms than during baseflow conditions—seven of the eight compounds were detected above concentrations of 0.05 µg/L in stormflow samples, whereas only three were detected at concentrations above 0.05 µg/L in baseflow samples. Four of the compounds (atrazine, metolachlor, metolachlor ESA, and metolachlor OA) were detected in every stormflow sample at concentrations greater than 0.05 µg/L (table 7), but only one (atrazine) was detected above 0.05 µg/L in every baseflow sample (table 7). Concentrations of all detected compounds were highest during the July 4 storm as a result of “flushing” after recent herbicide application. Concentrations of parent compounds increased by a factor of 10 or more during that storm (fig. 8); increases in the concentration of the metabolites were smaller. The increases in concentration were rapid during storms; for example, the concentration of atrazine increased 25-fold in 1.5 hours—from 0.113 µg/L at 07:15 a.m. to 2.83 µg/L by 08:50 a.m., about 1 hour before peak runoff.

Concentrations of pesticides and pesticide metabolites decreased after the July 4 storm as streamflow decreased, then briefly increased during a small storm on July 7 (fig. 8). Although concentrations during the July 7 storm were lower than on July 4, they were higher than those in samples collected before the July 4 storm.

The elevated concentrations of pesticides and metabolites in the July 4 samples are consistent with those commonly observed in streams during spring storms that directly follow pesticide applications to agricultural land in New York (Eckhardt and others, 1999; Wall and Phillips, 1998; Phillips and others, 1999). These studies generally have concluded that the maximum annual concentrations of many herbicides in streamflow occur during the first large storm after the application of pesticides in late June or early July. Thus, the elevated concentrations in the stormflow samples of July 4 probably are attributable to the recent application of pesticides in the Town Brook watershed and to the large amount of precipitation during that storm.

SUMMARY

A 1-year study was conducted in the Town Brook watershed in Delaware County, N.Y. to determine annual nutrient loads and characterize stream-water chemical and pesticide concentration dynamics. Town Brook drains a 37-km² watershed at the headwaters of the Cannonsville Reservoir watershed, which is part of the New York City drinking water supply. The Town Brook watershed was selected for study because it is about 54 percent agricultural land and 45 percent forest, and is the location of research to test the effectiveness of BMPs on farms within the watershed.

Annual nutrient loads for 1999 (in kilograms per hectare per year) were: ammonia, 0.25, nitrate, 4.3; total nitrogen, 10.6; orthophosphate, 0.26; total dissolved phosphorus, 0.30; and total phosphorus, 1.2. Although stormflow accounted for only 41 percent of annual runoff during 1999, it accounted for 49 to 68 percent of annual nutrient export. The combined nutrient export for two large storms, the first on July 4 the second on September 16 accounted for 17 to 56 percent of annual nutrient loads.

Eight pesticides and pesticide metabolites were detected in stream-water samples collected from January through July 1999. Metolachlor, atrazine, metolachlor ESA, and metolachlor OA were detected at concentrations greater than 1 µg/L in one or more samples. No pesticide or pesticide metabolite concentrations exceeded Federal water-quality standards during the study; but, one sample collected during the July 4 storm exceeded the New York State surface-water-quality standard for simazine (0.5 µg/L) with a concentration of 0.53 µg/L. Stormflow pesticide concentrations reflected the “flushing” that occurs during the first storms after spring pesticide applications. Pesticide and metabolite concentrations were as much as 25 times greater during storms than during baseflow and were detected in all stormflow samples.

These results emphasize the need for baseflow and stormflow sampling to characterize the dynamics of chemical and pesticide concentrations in streams and to accurately estimate annual nutrient export from agricultural watersheds. These results also illustrate the need for detailed research to define nutrient and pesticide sources and transport mechanisms.

REFERENCES CITED

- Beven, K.J. and Kirby, M.J., 1979, A physically based, variable contributing area model of basin hydrology: *Hydrological Sciences Bulletin*, v. 24, p. 43-69.
- Bonell, Michael, 1993, Progress in understanding of runoff generation dynamics in forests: *Journal of Hydrology*, v. 150, p. 217-275.
- Dunne, Thomas and Black, R.D., 1970, An experimental investigation of runoff production in permeable soils: *Water Resources Research*, v. 6, p.478-490.
- Eckhardt, D.A., Kappel, W.M., Coon, W. F., and Phillips, P.J., 1999, Herbicides and their metabolites in Cayuga Lake and its tributaries, New York, in Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2 of 3—Contamination of hydrologic systems and related ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, p. 395-403.
- Effler, S.W. and Bader, A.P., 1998, A limnological analysis of Cannonsville Reservoir, NY: *Journal of Lake and Reservoir Management*, v. 14, p. 125-139.
- Effler, S.W., Gelda, R.K., Perkins, MaryGail, Matthews, D.A., Owens, E.M, Stepczuk, Carol, and Bader, A.P., 1998, Characteristics and origins of metalimnetic dissolved oxygen minima in a eutrophic reservoir: *Journal of Lake and Reservoir Management*, v. 14, p. 332-343.
- U.S. Environmental Protection Agency, 1996, Drinking water regulations and health advisories: Washington, D.C., U.S. Environmental Protection Agency, Office of Water, EPA 822-B-96-002, Oct., 1996, 11 p.
- Ferrer, Imma, Thurman, E.M., Barcelo, Damia, 1997, Identification of ionic chloroacetanilide herbicide metabolites in surface and groundwater by HPLC/MS using negative ionspray: *Analytical Chemistry*, v. 69, p. 4547-4553.
- Gburek, W.J. and Sharpley, A.N., 1998, Hydrologic controls of phosphorus loss from upland agricultural Watersheds: *Journal of Environmental Quality*, v. 27, p. 267-277.
- Longabucco, Patricia and Rafferty, M.R., 1998, Analysis of material loading to Cannonsville Reservoir—advantages of event-based sampling: *Journal of Lake and Reservoir Management*, v. 14, p. 197-212.
- Lumia, Richard, 1991, Regionalization of flood discharges for rural, unregulated streams in New York, excluding Long Island: U.S. Geological Survey Water-Resources Investigations Report 90-4197, 119 p.
- Kalkhoff, S. J., Kolpin, D. W., Thurman, E. M., Ferrer, Imma, and Barcelo, Damia 1998, Degradation of chloroacetanilide herbicides—the prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwaters and surface waters: *Environmental Science and Technology*, v. 32 p. 1738-1740.
- New York City Watershed Memorandum of Agreement, January 21, 1997.
- New York State Department of Health, 1998, Water quality regulations for surface and groundwaters; Title 6 chapter X (Parts 703.5, Table 1), 10 NYCRR Subpart 5-1: Albany, N.Y., New York State Department of Health Public Water Systems Regulations, effective March 12, 1998.
- Phillips, P.J., Eckhardt, D.A., and Rosenmann, Larry, 1999, Pesticides and their metabolites in three small Public Water-supply reservoirs systems, Western New York, 1998-99: U.S. Geological Survey Water-Resources Investigations Report 99-4278, 20 p.
- Pionke, H.B., Gburek, W.J., Schnabel, R.R., Sharpley, A.N. and Elwinger, G.F., 1999, Seasonal nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed: *Journal of Hydrology*, v. 220, p. 62-73.
- Pionke, H.B., Gburek, W.J., Sharpley, A.N. and Schnabel, R.R., 1996, Seasonal nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed: *Water Resources Research*, v. 32, p. 1795-1804.
- Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National water-quality assessment program: U.S. Geological Survey Open-File Report 94-455, 42 p.
- Wall, G.R., and Phillips, P.J., 1998, Pesticides in the Hudson River Basin, 1994-96: *Northeastern Geology and Environmental Sciences*, v. 20, p. 299-307.
- Walter, M.T. and Walter, M.F., 1999, The New York City Watershed Agricultural Program (WAP): A model for comprehensive planning for water quality and agricultural economic viability: *Water Resources Impact*, v. 1, p. 5-8.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory -- Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography with selective-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.
- Zimmerman, L. R., and Thurman, E. M., 1999, Method of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of triazine and chloroacetanilide herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 98-634, 21 p.