In cooperation with
NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Hydrogeology and Water Quality of the Pepacton Reservoir Watershed in Southeastern New York

Part 1. Concentrations of Pesticides and their Degradates in Stream Baseflow, 2000-01.

Water-Resources Investigations Report - 03-4137

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

This page has been left blank intentionally.

Hydrogeology and Water Quality of the Pepacton Reservoir Watershed in Southeastern New York

Part 1. Concentrations of pesticides and their degradates in stream baseflow, 2000-2001

By Patrick J. Phillips and Paul Heisig

In cooperation with
New York State Department of Environmental Conservation

Water-Resources Investigations Report 03-4137

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

U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
Charles G. Groat, Director

U.S. Geological Survey, Reston, Virginia: 2004

For additional information about this report write to:
U.S. Geological Survey
425 Jordan Road
Troy, NY 12180
Email: askny@usgs.gov
World Wide Web: http://ny.usgs.gov/

For sale by U.S. Geological Survey, Information Services
Box 25286, Denver Federal Center
Denver, CO 80225

For more information about the USGS and its products:
Telephone: 1-888-ASK-USGS
World Wide Web: http://www.usgs.gov/

Contents

Figures

Tables

Hydrogeology and Water Quality of the Pepacton Reservoir Watershed in Southeastern New York
Part 1. Concentrations of pesticides and their degradates in stream baseflow, 2000-2001

by Patrick J. Phillips and Paul Heisig

Abstract

Baseflow samples were collected from 20 small streams in the Pepacton Reservoir watershed in Delaware County, N.Y., from December 2000 through November 2001 as part of an investigation to define the occurrence of pesticides in shallow ground water in watersheds containing either a recent (2001) corn crop, a previous (1993-94) corn crop , or no history of row-crop cultivation. Baseflow water quality was assumed to represent the chemical quality of shallow ground water within the drainage area above each sampling site.

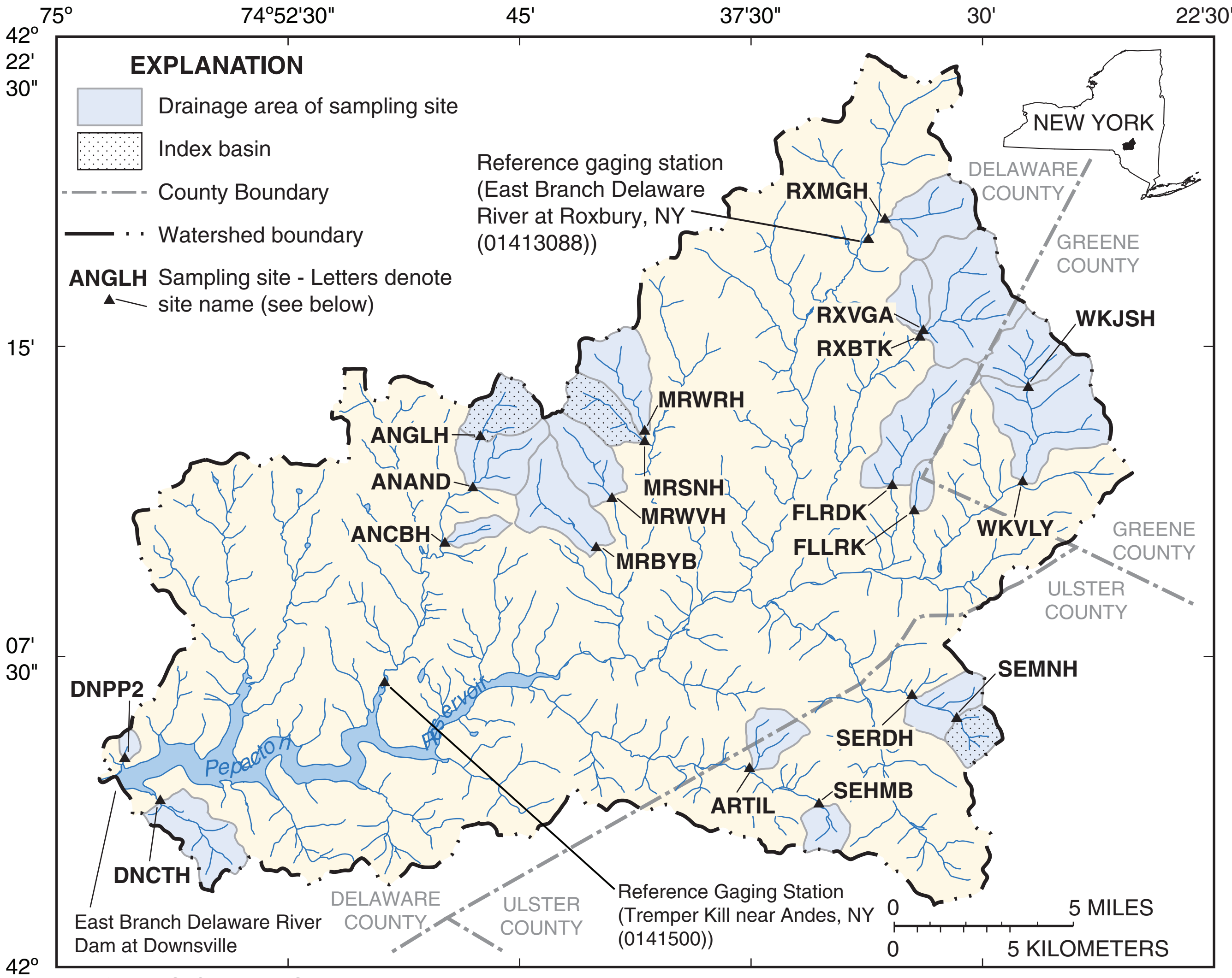
Baseflow samples were analyzed for 57 pesticides and pesticide degradates. Three herbicides (atrazine, metolachlor and simazine) and three herbicide degradates (alachlor ESA [ethanesulfonic acid], deethylatrazine, and metolachlor ESA) were detected, but no concentrations exceeded any Federal or State water-quality criteria, and the maximum concentrations of all compounds except metolachlor ESA were less than 0.10 microgram per liter. The most frequently detected compounds (atrazine, metolachlor, deethylatrazine and metolachlor ESA) are either those typically used on corn crops, or those whose parent compounds are commonly used on corn crops and have been detected in streams that drain row-crop settings elsewhere in New York State. The pesticide and pesticide-degradate concentrations in baseflow samples collected in December 2000 and July 2001 samples generally corresponded to the amount of cornfield acreage in each watershed in 2001.

The types of pesticides detected, and their median concentrations, were similar to those noted in two previous ground-water studies in row-crop areas elsewhere in upstate New York. Also the SAM ratios (ratio of metolachlor ESA concentration to metolachlor concentration) for the Pepacton samples were similar to those for ground-water samples from other agricultural settings in upstate New York, but were significantly higher than that for stormflow and baseflow samples collected in 1997-98 from Canajoharie Creek, an upstate stream that drains row-crop farmland. These comparisons confirm that the baseflow samples were derived from, and were representative of, ground water in their respective watersheds. Late-summer decreases in atrazine and deethylatrazine concentrations at a site where corn was grown in 2001 may have resulted from the seasonally dry conditions and the accompanying decrease in ground-water discharge from the upper-most part of the surficial aquifer system to streams. The lack of a similar decrease in metolachlor ESA concentrations during this period may reflect the transport of metolachlor ESA to deeper parts of the surficial aquifer that continued to discharge to streams during the dry period.

Introduction

The Pepacton Reservoir watershed (372 mi^2 [mile] fig. 1) is in the western part of the Catskill Mountains of central New York and is part of the Delaware Reservoir system, which supplies about 50 percent of New York City's drinking water. The watershed, which is located in Delaware County, is 69 percent forested, but some areas contain substantial amounts of agricultural land (dairy farming and row crops). The recent detection of agricultural herbicides and their degradates in the Pepacton Reservoir (Phillips and others, 2000) has caused concern as to whether pesticides used in agricultural parts of the watershed are affecting the water quality of the reservoir. In 2000, the U.S. Geological Survey (USGS), in cooperation with the New York State Department of Environmental Conservation, began a 2-year study to evaluate shallow ground-water quality throughout the Pepacton watershed in an effort to identify the effects of agriculture on the quality of water entering the Pepacton Reservoir (fig. 1).

Past research on pesticides in ground waters in agricultural areas in New York State (Eckhardt and others, 2001; Phillips and others, 2000) has indicated that herbicides that are commonly used on corn are present in shallow ground water, although usually at concentrations well below Federal and State water-quality criteria. Two such herbicides that are commonly used on corn—atrazine and metolachlor—and their



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

ANAND	Gladstone Hollow Brook near Andes	MRWRH	Winter Hollow Brook
ANCBH	Campbell Hollow Brook	MRWVH	Weaver Hollow Brook
ANGLH	Gladstone Hollow Brook north of Andes	RXBTK	Batavia Kill
ARTIL	Mill Brook Tributary	RXMGH	Montgomery Hollow
DNCTH	Cat Hollow Brook	RXVGA	Tributary to Batavia Kill
DNPP2	Pepacton Reservoir West End Tributary	SEHMB	Mill Brook
FLLRK	Little Red Kill	SEMNH	Rider Hollow Brook east of Mapledale
FLRDK	Red Kill	SERDH	Rider Hollow Brook near Mapledale
MRBYB	Bryants Brook	WKJSH	Vly Creek above Halcott Center
MRSNH	Sanford Hollow Brook	WKVLY	Vly Creek near Halcott Center

Figure 1. Baseflow-sampling sites in the Pepacton Reservoir watershed, December 2000 through November 2001. (Additional data on these sites are given in table 1.)

degradates deethylatrazine and metolachlor ethanesulfonic acid (ESA), respectively, which form by the breakdown of the parent compound, are frequently detected in ground water beneath fields or corn and other row crops.

Purpose and Scope

This report (1) describes the sampling approach, and the methods of chemical and statistical analysis, (2) compares concentrations of selected pesticides in Pepacton baseflow samples with those in ground-water samples from other row-crop areas in upstate New York, (3) use the ratios of the concentration of metolachlor ESA to that of metolachlor (its parent compound) to confirm that the Pepacton baseflow samples reflect ground-water quality, (4) relates the occurrence and concentrations of pesticides and degradates in baseflow samples to the history of corn cultivation (2001, 1993-94, or neither) within the respective watersheds, and (5) evaluates the seasonal changes in pesticide concentrations and relates them to the effects of drought conditions.

Baseflow was used as a surrogate indicator of shallow ground-water quality because ground water sustains stream discharge during dry periods—either from springs or from seepage directly into stream channels. Baseflow accounts for most of the water that enters the New York City reservoirs during periods of little or no rain and represents 60 to 70 percent of total annual stream discharge.

Baseflow samples were collected at 20 sites (table 1) representing small watersheds of less than 2 mi^2 within the Pepacton watershed for chemical analysis to relate land use to pesticide presence in shallow ground water. Samples were collected in December 2000 and July 2001. Three types of watersheds (defined based on the extent of agricultural use) were selected for comparison—those in which corn was grown during 1993-94 and in 2001, those in which corn was grown during 1993-94 but not in 2001, and those with no history of corn grown in either 1993-94 or 2001. From five to seven additional samples were collected at each of three sites (one from each watershed type) between December 2000 and November 2001.

Table 1. Sites sampled for pesticide analysis in the Pepacton Reservoir watersheds, Delaware County, N.Y., December 2000 through November 2001.

[All sites were sampled once except as indicated; additional sampling (in parentheses) at three sites occurred from June through November 2001. mi 2 , square miles. Locations are shown in fig. 1; no,number; USGS, U. S. Geological Survey.]

Site abbreviation	USGS Station no.	Site name	Drainage area (mi^2)	Housing density (per mi^2)[a]	Percentage of watershed used for corn crop[a]		Corn-crop classification[b]
					1993-94	2001	
Sites Sampled in December 2000 and July 2001							
ANAND	01414840	Gladstone Hollow Brook near Andes	5.8	13.3	2.8	1.2	Active
ANCBH	01414860	Campbell Hollow Brook	.9	2.2	.54	0	Inactive
ANGLH (9 times)	01414835	Gladstone Hollow Brook north of Andes	2.6	6.6	3.5	.89	Active
ARTIL	01414290	Mill Brook Tributary	2.0	1.5	0	0	No Corn
FLRDK	01413346	Red Kill	5.5	11.6	.23	0	Inactive
MRBYB	01413990	Bryants Brook	4.4	9.1	1.1	0	Inactive
MRSNH (9 times)	01413930	Sanford Hollow Brook	2.5	23.2	.16	0	Inactive
MRWRH	01413920	Winter Hollow Brook	3.5	22.5	1.8	1.5	Active
MRWVH	01413950	Weaver Hollow Brook	3.1	10.2	.03	0	Inactive
RXBTK	0141309740	Batavia Kill	9.0	13.2	.2	.17	Active
RXVGA	0141309730	Tributary To Batavia Kill	1. 7	20.4	.88	0	Inactive
SEHMB	01414280	Mill Brook	1.4	0	0	0	No Corn
SERDH	01413276	Rider Hollow Brook near Mapledale	4.1	5.7	0	0	No Corn
WKJSH	01413303	Vly Creek above Halcott Center	3.3	4.0	.86	.36	Active
WKVLY	01413306	Vly Creek near Halcott Center	10.2	8.8	.47	.12	Active
Sites Sampled July 2001 but not December 2000							
DNCTH	01416870	Cat Hollow Brook	3.7	9.3	0	0	No Corn
DNPP2	01416895	Unnamed tributary to Pepacton Reservoir	.38	5.3	0	0	No Corn
FLLRK	01413343	Little Red Kill	.79	29.1	0	0	No Corn
RXMGH	01413085	Montgomery Hollow	3. 7	10.1	.01	0	Inactive
SEMNH (7 times)	01413274	Rider Hollow Brook East of Mapledale	1.7	0	0	0	No Corn

[a] Corn-crop estimates for 1993-94 and housing density are based on New York City Department of Environmental Protection (1999). Corn-crop estimates for 2001 based on photointerpretation and field checking.

[b] "Active" denotes sites with a corn crop in 2001; "inactive" denotes sites with corn crop observed in 1993-94 but not in 2001, and "No Corn" denotes sites with no evidence of corn crop in 1993-94 or 2001

Geologic Setting

The Pepacton watershed is underlain by sandstone, siltstone, shale, and conglomerate of Devonian age and is blanketed by glacial-drift deposits of variable thickness. Bedrock dips gently to the southwest with low, broad folds that trend northeast-southwest (Woodward, 1957; Soren, 1963). Ground-water flow in bedrock is primarily through fractures. The most common unconsolidated deposit in the uplands is till, an unsorted mixture deposited by glaciers and primarily derived from local bedrock. Till thickness within the watershed ranges from zero to more than 200 ft (feet) (Fluhr, 1953). The thickest deposits generally are near the base of south-facing hills that were in the lee of regional ice advance during glaciation (Coates, 1966). The predominant soil textures developed on till are silty and sandy loam (Ozsvath, 1985). All but the shallowest upland soils that developed on till are underlain by a compact hardpan subsoil of low permeability (Lounsbury and others, 1930). The floors of small tributary valleys typically are covered by uncompacted, poorly sorted sediment (with some minor sorted zones) that melted out of stagnant ice (Ozsvath, 1985). Till in the valley-bottom areas gradually transitions to stratified sediments in the down-valley direction, and stratification and sorting of valley-bottom deposits tend to be proportional to valley size (Ozsvath, 1985).

Methods

Baseflow conditions were defined as those preceded by at least 3 days without substantial rain. Samples were not collected during the winter snowpack period nor during spring periods with above-freezing daily high temperatures to avoid potential meltwater contributions to baseflows. None of the 20 sites had a continuous stream discharge gage; therefore, the smallest gaged watershed (13.5 mi^2) within the Pepacton Reservoir watershed—the East Branch Delaware River at Roxbury (fig. 1)—was used to represent baseflow conditions and seasonal changes in baseflow discharge. The Roxbury station, although useful for representing discharge conditions for the 2-year study period, was not useful for comparisons with long-term average flow conditions because its short period of record beginning in 2000; therefore, discharge records for the Tremper Kill near Andes station (fig. 1) were used to relate flow conditions during the study period to long-term flow conditions. The Tremper Kill site represents a 33.2-mi^2 drainage area, and its period of record is from 1937 through 2001.

Baseflow samples were collected at 15 of the 20 sites during December 2000 and July 2001 (fig. 1). July was selected because it represents the 1- or 2-month period that closely follows the spring pesticide application, and December was chosen as representative of baseflow conditions several months after the spring application. The other five sites (table 1) were added in July 2001 to increase the representation of watersheds with little or no history of pesticide application. Additional baseflow samples were collected from December 2000 through November 2001 to investigate the seasonal variability in pesticide concentrations; these samples were collected nine times at the ANGLH and MRSNH sites and seven times at the SEMNH site (table 1) . The ANGLH site was considered to represent the drainage area with the greatest pesticide use; the SEMNH represented the drainage area with no pesticide use, and the MRSNH site represented the drainage area with an intermediate amount.

Estimates of corn-crop history in the watershed above each site were available for two periods— 1993-94 and 2001; estimates of corn crop are not available for the period 1995-2000 . Values for 1993-94 were estimated by the New York City Department of Environmental Protection (New York City Department of Environmental Protection, 1996, 1999) from Landsat Thematic Mapper scenes acquired in 1992 and 1993; these estimates were ground truthed through field visits in 1993 and 1994 and interpretation of aerial photography. Values for 2001 were based on aerial photos and field visits by the USGS in the late summer of that year. The aerial photographs were used to delineate fields, and each field was visited in August or September to verify that corn was grown. After field checks, the amount of watershed represented by corn crop was calculated for each watershed (table 1); the small watershed size and the small amount of cornfield acreage in the study area allowed accurate estimation of corn-crop acreage from the aerial photographs and field verification. Sites with corn grown in 2001 are referred to here as "active"; those with a corn crop reported for 1993-94 but not observed in 20001 are referred to as "inactive," and those with no corn grown either in 1993-94 or 2001 are designated as "no corn." All of the sites at which corn was grown in 2001 were found to have had corn growth in 1993-94.

Sample Collection

Samples were collected in accordance with methods described in Shelton (1994). The small width (generally less than 20 ft wide) and shallow depth of the streams (generally less than 1 ft deep) required collection from midchannel with an open bottle. Equal-width-increment samples were collected at the two largest watersheds (sites WKVLY, RXBTK; table 1) during December 2000. Stream discharge at sampling sites was measured only during December 2000 and July 2001.

Analytical Methods and Quality Control

Samples were analyzed through two USGS analytical procedures: (1) a gas-chromatography/mass-spectrometry method (referred to as schedule 2010), which was used for 47 pesticides and degradates at the USGS National Water Quality Laboratory in Denver, Colo. (Zaugg and others, 1995; table 2a), and (2) a liquid-chromatography/mass-spectrometry method (referred to as the Chloroacetanilide Herbicide Degradate [CHD] method), which was used for 10 degradates of chloroacetanilide herbicides at the USGS Organic Research Laboratory in Lawrence, Kans. (Lee and others, 2001) (table 2b). The detection limits of the schedule 2010 and CHD methods ranged from 0.001 µg/L to 0.1 µg/L (table 2a, 2b). This range is much lower than that obtained by analytical methods typically used in public-water-supply-monitoring programs and provides much higher rates of detection than would be possible with the less sensitive analytical methods. Both methods used here require a filtered sample extracted on a solid-phase cartridge; thus, these concentrations represent the dissolved phase of pesticides and pesticide degradates.

Blank and replicate samples were collected as quality-control samples. Three blanks were collected for each analytical method; no target analytes were detected. Twelve replicates were collected for each analytical method; these were found to contain the 16 compounds that were also detected in field samples. Differences between the field and replicate concentrations in these 16 comparisons ranged from 0 to 20 percent; the difference for most compounds was less than 10 percent. Two compounds were detected in one replicate sample, but not in the corresponding field sample; the concentration of both compounds were at the detection limit.

Statistical and Computational Methods of Analysis

Median concentrations were compared among sites and seasons through Kruskal-Wallace and Tukey nonparametric analyses of variance tests. Nonparametric statistical techniques were used because they are more appropriate than parametric techniques for censored data (values below detection limits) and for data that are not normally distributed (Helsel and Hirsch, 1992).

SAM ratios (concentration of metolachlor ESA divided by concentration of metolachlor) were calculated for all sites. Previous investigations in New York have shown that ground water has higher SAM ratios (higher concentrations of metolachlor ESA than of metolachlor) than surface water because metolachlor ESA is transported from land surface to ground water more readily than metolachlor, and because metolachlor is washed into streams by storm runoff more readily than metolachlor ESA (Phillips and others, 1999a, b). SAM ratios obtained in these studies indicate that the baseflow samples reflect ground-water quality and did not contain surface runoff. SAM ratios were calculated through methods described by Phillips and others (1999a, 1999b). Calculation of the SAM ratio for samples in which metolachlor ESA

Table 2. Method detection and laboratory reporting limits for pesticides and pesticide degradates for which base-flow samples were measured from Pepacton Reservoir watershed, Delaware County, N.Y., 2000-01.
[Detection- and reporting-limit concentrations are in micrograms per liter. Asterisk denotes degradation product.]

Pesticide	Detection Limit	Pesticide	Detection Limit	Pesticide	Detection Limit	Pesticide	Detection Limit
A. Method detection limits for Schedule 2010 GCMS [a] method of U.S. Geological Survey National Water Quality Laboratory, Denver, Colo							
Acetochlor	0.0041	Deethylatrazine *	0.006	Metolachlor	0.013	Propyzamide	0.0041)
Alachlor	0.0024	Diazinon	0.005	Metribuzin	0.006	Propachlor	0.010)
alpha-HCH	0.0046	Dieldrin	0.0048	Molinate	0.0016	Propanil	0.011)
Atrazine	0.007	Disulfoton	0.021	Napropamide	0.007	Propargite	0.023)
Benfluralin	0.010	EPTC	0.002	p,p'-DDE *	0.0025	Simazine	0.011)
Butylate	0.002	Ethalfluralin	0.009	Parathion	0.007	Tebuthiuron	0.016
Carbaryl	0.041	Ethopropos	0.005	Parathion-methyl	0.006	Terbacil	0.034
Carbofuran	0.020	Fonofos	0.0027	Pebulate	0.0016	Terbufos	0.017
Chlorpyrifos	0.005	Lindane	0.004	Pendimethalin	0.010	Terbuthylazine	0.1
Cyanazine	0.018	Linuron	0.0035	*cis*-Permethrin	0.006	Thiobencarb	0.0048
Dacthal	0.003	Malathion	0.027	Phorate	0.011	Tri-allate	0.0023
2,6-Diethylaniline*	0.0017	Methyl azinphos	0.05	Prometon	0.015	Trifluarlin	0.009
B. Laboratory reporting limits for chloroacetanilide herbicide degradate method by the LCMS[1] method of U.S. Geological Survey Organic Research Laboratory, Lawrence, Kansas							
Acetachlor ESA*	0.05	Dimethenamid ESA*	0.05	Metolachlor OA*	0.05		
Acetachlor OA*	0.05	Dimethenamid OA*	0.05	Metolachlor ESA*	0.05		
Alachlor ESA*	0.05	Flufenacet ESA*	0.05				
Alachlor OA*	0.05	Flufenacet OA*	0.05				

[a] GCMS, gas chromatography and mass spectrometry
LCMS, liquid chromatography and mass spectrometry
ESA , ethanasulfonic acid
OA, oxanilic acid

and metolachlor concentrations were measurable was straightforward, and all samples in which metolachlor was detected also contained metolachlor ESA. SAM ratios for the 11 samples in which metolachlor ESA was measurable, but metolachlor concentrations were below the detection limit, were calculated as the metolachlor ESA concentration divided by 0.001 µg/L, which is lower than the lowest reported metolachlor concentration (0.0013 µg/L). This method was used in similar studies by Phillips and others (1999a, b).

Concentrations of Pesticides and Selected Degradates

Of the 57 pesticides and pesticide degradates for which samples were analyzed, 6 were detected – 3 herbicides (atrazine, metolachlor and simazine) and 3 herbicide degradates (alachlor ESA, deethylatrazine, and metolachlor ESA). No insecticide or insecticide degradates were detected.

Maximum concentrations of detected compounds ranged from 0.006 µg/L (simazine) to 0.42 µg/L (metolachlor ESA). Maximum concentrations of all compounds except metolachlor ESA were less than 0.10 µg/L (table 3). Maximum concentrations of alachlor ESA, atrazine, and deethylatrazine were between 0.01 µg/L and 0.1 µg/L, and maximum concentrations of metolachlor and simazine were below 0.007 µg/L. The two most frequently detected herbicides were atrazine and metolachlor, which are applied on corn; the two most frequently detected herbicide degradates were deethylatrazine (a degradate of atrazine) and metolachlor ESA (a degradate of metolachlor). No concentrations exceeded any Federal or State water-quality criteria.

All compounds (or their parent compounds) detected in this study except simazine are used primarily on corn crops and, thus, are derived from agricultural applications (simazine is used in row-crop and nonagricultural settings; see Hoffman and others, 2000). The restriction of sampling to baseflow conditions presumably yielded concentrations that were much lower than the annual maximum concentrations, which tend to occur during stormflows after the late-spring or early-summer pesticide application.

Pepacton Baseflow Data in Relation to Ground-Water Data from Similar Row-Crop Areas

A comparison of the pesticide concentrations in the Pepacton baseflow samples with those in samples from (1) 16 monitoring wells in row-crop settings elsewhere in upstate New York (Phillips and others, 2000), and (2) 32 public-water-supply wells in agricultural settings in upstate New York (Eckhardt and others, 2000) indicates strong similarity. All monitoring wells and all but one of the public-supply were finished in highly permeable sand and gravel aquifers.

The most commonly detected pesticides in all three studies were atrazine, metolachlor, and deethylatrazine; these compounds were detected in more than 25 percent of the samples from the public-supply wells and in more than half of the samples from the monitoring wells. Metolachlor ESA was not measured in the monitoring-well study, but was detected in more than 25 percent of the samples from the public-supply wells. Comparison of atrazine, metolachlor, deethylatrazine, and metolachlor ESA concentrations in the Pepacton baseflow samples (separated into December 2000 and July 2001 groups) with those measured in the monitoring- and public-supply wells in row-crop areas indicate no significant differences (fig. 2).

The similarity between the assemblages of herbicides and herbicide degradates detected in the Pepacton study and those in the public-supply and monitoring-well studies indicates that the quality of baseflow in the Pepacton watershed is typical of that in ground water underlying row-crop farmland in upstate New York.

SAM Ratios

The lack of significant difference between the SAM ratios for the Pepacton baseflow samples (79) and those of the ground-water samples from upstate public-supply wells (350) (fig. 3) confirms that the baseflow samples reflect the local shallow-ground-water quality. In contrast, median SAM ratios for the Pepacton baseflow and public-supply-well samples were significantly greater than those for samples collected from Canajoharie Creek (in a crop-growing area of east-central New York) in June and July 1997-98 (9.1) and from August and September of 1997 and 1998 (4.9; fig 3).

Surface-water samples from Canajoharie Creek had higher concentrations of metolachlor than of metolachlor ESA and, thus, lower SAM ratios than ground-water samples from similar upstate row-crop settings, because metolachlor is readily transported by surface runoff to streams, where its high concentrations can result in low SAM ratios, particularly during stormflows. (The Canajoharie Creek data represent stormflow as well as baseflow). The higher SAM ratios in ground water result from the formation of metolachlor ESA within the soil as a metolachlor degradate, and its rapid migration to the water table because it is less easily bound to soils than metolachlor (Phillips and others, 1999a, 199b). Most SAM ratios for the Pepacton baseflow samples and the public-supply well samples were greater than 40, whereas most SAM ratios for Canajoharie Creek samples were below 40.

Further evidence that the Pepacton baseflow samples reflect shallow-ground-water quality is given by the time-series data from the ANGLH site (fig. 4). SAM ratios for ANGLH samples ranged from 70 to 150, and those for the June and July samples were similar to those for samples collected in other months. In contrast, median SAM ratios for Canajoharie Creek samples collected in June and July were significantly lower than those for samples collected during other months (fig. 3). The low SAM ratios for the June and July samples from Canajoharie Creek are attributed to elevated concentrations of metolachlor at the time of sampling – just after pesticide application in June, when the washoff of metolachlor during storms causes the highest concentrations of metolachlor (and the lowest SAM ratios) (Phillips and others, 1999b). The lack of substantially lower SAM ratios for ANGLH baseflow samples in June and July confirms that these samples consisted of ground water and were not affected by surface runoff.

Relation of Pesticide Concentrations to Corn-Crop History

Comparison of atrazine, metolachlor, deethylatrazine, and metolachlor ESA concentrations among sampling sites with corn-crop acreage and history indicates that the highest

Table 3 . Summary of pesticide analyses of base-flow samples from Pepacton Reservoir watershed, Delaware County, N.Y., 2000-01
[µg/L, micrograms per liter. A dash (--) indicates no water-quality criteria available. Site locations are shown in fig. 1.]

Sampling location and common pesticide name	Method detection limit (µg/L)	Percentage of samples with a detection[a]	Percentage of samples with concentration exceeding indicated value		Water-quality criterion (µg/L)	Maximum concentration (µg/L)	Site or month with highest concentration
			0.01 µg/L	0.05 µg/L			
A. All 15 sites in Pepacton Reservoir watershed (one sample per site)							
December 2000							
Herbicides							
Atrazine [b]	0.007	53	0	0	1.8 [f]	0.0065	MRWRH
Metolachlor [b]	.013	33	0	0	7.5 [d]	.0051	MRWRH
Herbicide degradates							
Alachlor ESA [c]	.05	13	13	13	50 [e]	0.07	ANAND
Deethylatrazine [b]	.006	53	0	0	--	.009	MRWRH
Metolachlor ESA [c]	.05	40	40	40	50 [e]	.20	WKJSH
July 2001 - samples collected from the five additional sites at this time (DNCTH, DNPP2, FLLRK, RXMGH, and SEMNH) contained no targeted compounds and were not used in statistical summaries**.**							
Herbicides							
Atrazine [b]	0.007	47	6.7	6.7	1.8 [f]	0.0586	MRWRH
Metolachlor [b]	.013	13	0	0	7.5 [d]	.0059	WKJSH
Herbicide degradates							
Deethylatrazine [b]	.006	47	6.7	0	--	.011	WKJSH
Metolachlor ESA [c]	.05	40	40	40	50 [e]	.42	WKJSH
B. Sites that were sampled nine times from December 2000 through November 20001							
MRSNH (Sanford Hollow Brook)							
Herbicide							
Simazine[b]	0.011	11	0	0	.5 [d]	0.006	October 2001
Herbicide degradate							
Deethylatrazine[b]	.006	11	0	0	--	.0009	December 2000
ANGLH (Gladstone Hollow Brook north of Andes)							
Herbicide							
Atrazine[b]	0.007	67	11	0	1.8 [e]	0.011	June 2001
Herbicide degradates							
Alachlor ESA [c]	.05	56	56	56	50 [d]	.09	June 2001
Deethylatrazine[b]	.006	67	0	0	--	.0052	June 2001
Metolachlor ESA [c]	.05	89	89	89	50 [d]	.15	August 2001

[a] Includes reported concentrations below method detection limit.

[b] Analytical method described by Zaugg and others, 1995

[c] Analytical method described by Lee and others, 2001

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

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

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

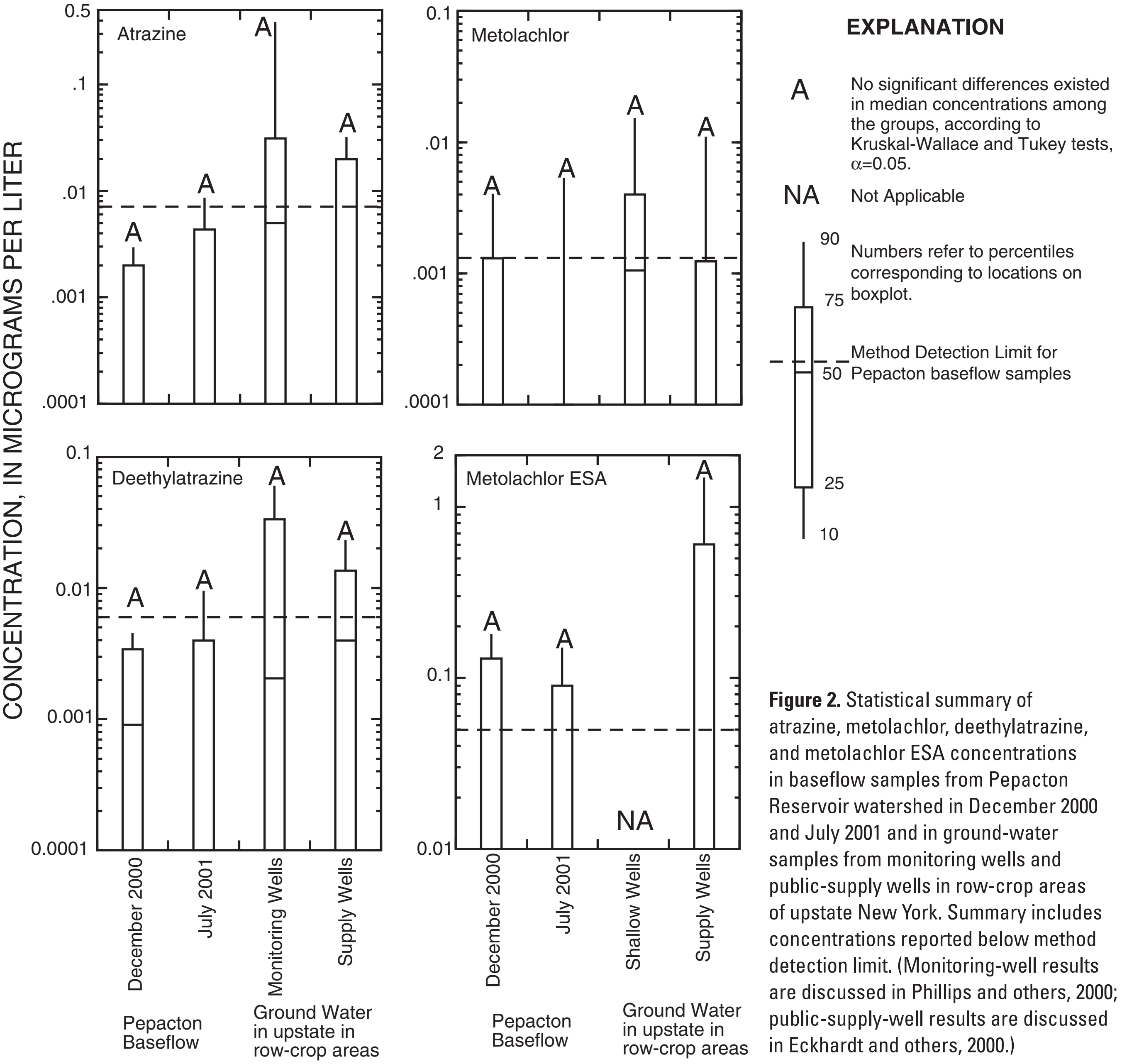


Figure 2. Statistical summary of atrazine, metolachlor, deethylatrazine, and metolachlor ESA concentrations in baseflow samples from Pepacton Reservoir watershed in December 2000 and July 2001 and in ground-water samples from monitoring wells and public-supply wells in row-crop areas of upstate New York. Summary includes concentrations reported below method detection limit. (Monitoring-well results are discussed in Phillips and others, 2000; public-supply-well results are discussed in Eckhardt and others, 2000.)

concentrations of pesticides and pesticide degradates were at “active” sites – those within watersheds with recently grown corn (2001). Few pesticides or pesticide degradates were detected in samples from “inactive sites” (corn grown in 1993-94 but not in 2001), and no pesticides or degradates were detected in samples from “no-corn” sites (no history of corn crop during 1993-94 or 2001). Median concentrations of atrazine, deethylatrazine, and metolachlor ESA were higher among samples from active sites than inactive sites or no-corn sites (fig. 5) and did not differ significantly between inactive and no-corn sites. More than two-thirds of the samples from the six active sites contained measurable amounts of these three compounds, whereas only a third (or fewer) of the inactive sites contained these three compounds. No pesticide or pesticide degradate was detected in any of the samples from the no-corn sites.

Median concentrations of metolachlor did not differ significantly among samples from the three types of sites, probably because the active-site samples showed relatively few metolachlor detections – four detections among the six active-site samples collected in December 2000 and two among the six active-site samples collected in July 2001 (fig 5). The active-site samples showed more frequent detections of the other three commonly detected pesticide or pesticide degradate compounds –five or six detections in the six samples collected during each period. Metolachlor was infrequently detected in samples from inactive sites – only one detection among the December 2000 samples, and none in the July 2001 samples.

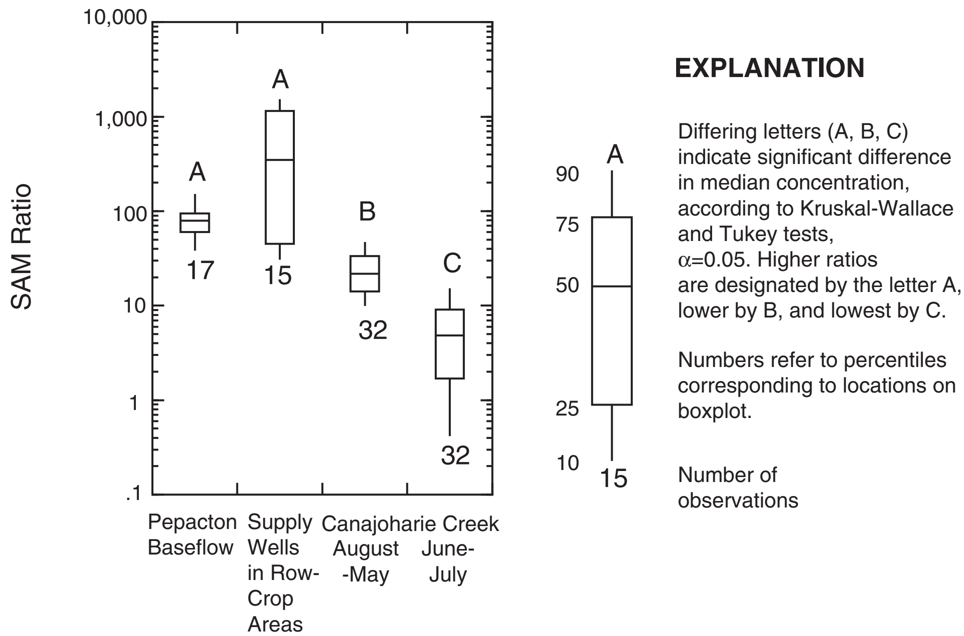


Figure 3. SAM ratios for Pepacton baseflow samples, shallow ground water from public-supply wells in upstate row-crop areas, and Canajoharie Creek samples, 1997-98. (Public-supply-well data from Eckhardt and others, 2001, Canajoharie Creek data from Phillips and others, 1999a,b)

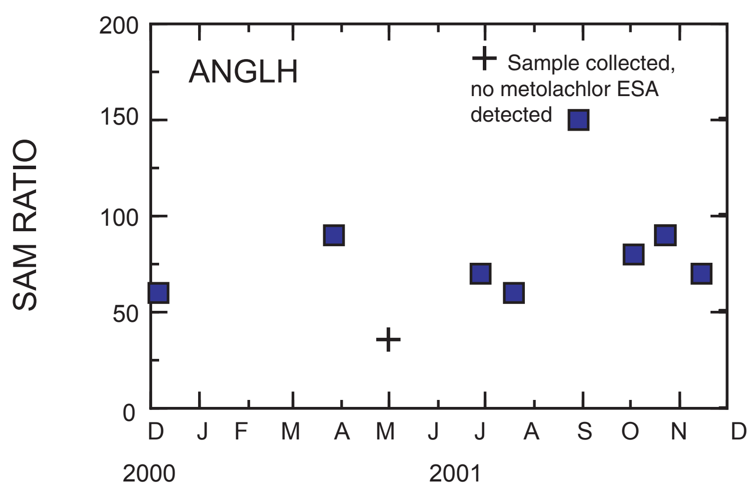


Figure 4. SAM ratios (ratio of metolachlor ESA concentration to metolachlor concentration) for samples from ANGLH site, December 2000 through November 2002. (Site location is shown in fig. 1; SAM ratio not computed for May 2001 sample because metolachlor ESA was not detected.)

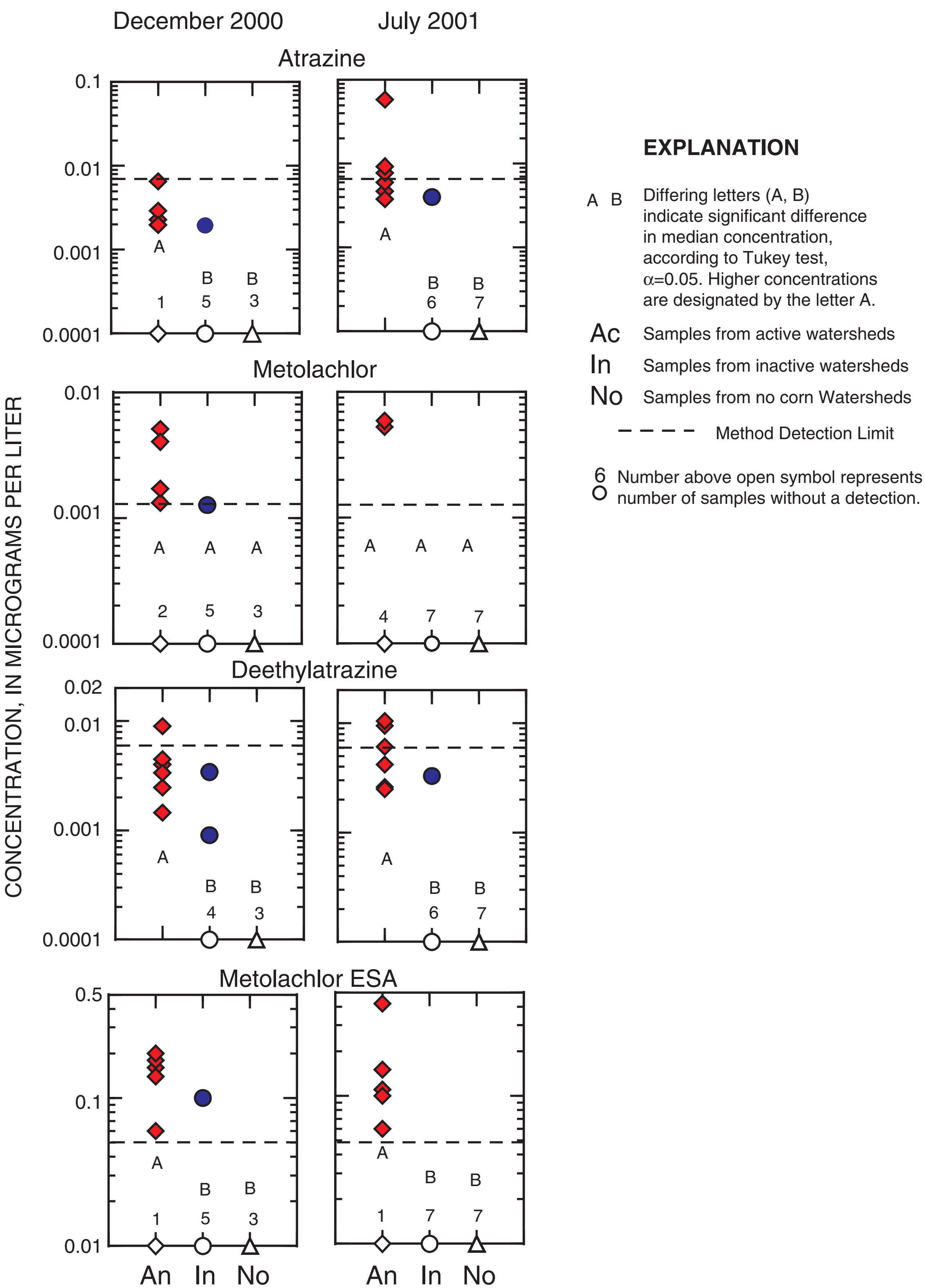


Figure 5. Concentrations of atrazine, metolachlor, deethylatrazine, and metolachlor ESA in December 2000 and July 2001 baseflow samples from streams in Pepacton Reservoir watershed, by watershed corn-crop history (active, inactive, or none). Summary includes concentrations reported below method detection limit.

Seasonal Variability in Pesticide and Pesticide Degradate Concentrations

Seven or more samples were collected at three sites (ANGLH, MRSNH, and SEMNH) from December 2000 through November 2001. No pesticides were detected in samples from SEMNH, which represents a watershed that is nearly 100 percent forested and contained no corn crop in either 1993-94 or 2001. The samples from the inactive MRSNH site contained two pesticides (table 3B), with maximum concentrations less than 0.01 µg/L. The samples from the active ANGLH site (table 3B) contained four compounds, with three of these compounds (atrazine, deethylatrazine, and metolachlor ESA) were detected in more than 60 percent of the samples from this site, and three compounds (atrazine, alachlor ESA, and metolachlor ESA) exceeding 0.01 µg/L.

The decrease in the concentrations of atrazine and deethylatrazine during the Summer at the ANGLH site may reflect the dry conditions of that season. The concentrations of those compounds peaked in July at ANGLH, probably in response to the atrazine application earlier that spring, but from July through October, the concentrations decreased, and no atrazine was detected after September (fig. 6). The dry conditions of that period are indicated by discharge records from neighboring streams and precipitation data from Arkville (fig. 1). Baseflow discharge at the East Branch Delaware River site for sampling days between December 2000 through May 2001 ranged from 10 to 17 ft^3/s (cubic feet per second), and were highest in early May, after a period of snowmelt, whereas discharge on the sampling dates from August through November was less than 3.5 ft3/s (fig. 6). Precipitation from April through November 2001 was 18 percent lower than normal (National Climatic Data Center, 2002). A comparison of monthly discharge (expressed as percentage of the mean monthly flow) for Tremper Kill near Andes (the smallest gaged watershed in the Pepacton watershed with a long-term discharge record) from July through December 2001 (fig. 6) indicates that monthly mean discharges after June 2001 were less than 50 percent of the long-term mean monthly discharge. Conditions were especially dry from August through December 2001, when discharges did not exceed 30 percent of the long-term mean monthly discharge (fig 6).

The decrease in atrazine and deethylatrazine concentrations in ANGLH samples from the summer through the fall of 2001 reflects the gradual decrease in ground-water discharge from shallow-most part of the surficial aquifer system as the drought continued into the fall. The lack of a similar decrease in metolachlor ESA concentrations during this period is consistent with the tendency of metolachlor ESA to migrate more readily than metolachlor to the water table and therefore to be discharged from deeper parts of the aquifer to streams. The short study duration makes this explanation of the difference between the late-summer concentration changes

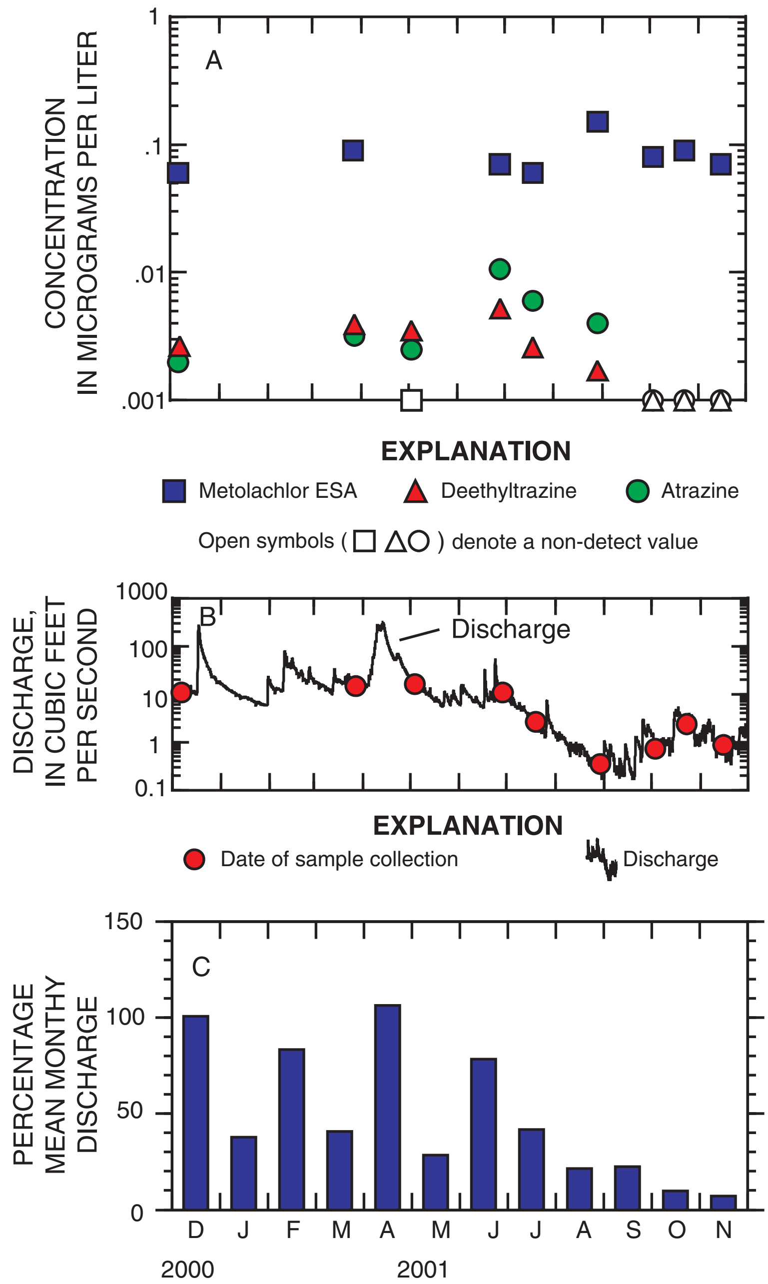


Figure 6. A. Concentration of atrazine, deethylatrazine, and metolachlor ESA in samples collected from ANGLH site, December 2000-November 2001, B. discharge of East Branch of the Delaware River at Roxbury, and date when samples collected at ANGLH, C. monthly mean discharge at Tremper Kill near Andes expressed as percentage of mean monthly discharge for 1937-2001. (Locations are shown in fig. 1).

of atrazine and those of metolachlor ESA difficult to confirm, but if the shallow-most aquifer zone is the major source of atrazine and deethylatrazine, the decrease in discharge from this zone could account for the autumn decline in their concentrations. The continued discharge of metolachlor ESA-bearing water from deeper parts of the aquifer during this period (fig. 6) would maintain fairly constant concentrations in baseflow. In other words, the atrazine and deethylatrazine contributions from shallow ground water decrease during periods of low flow, while the metolachlor ESA contributions from deeper ground water continue.

Summary

Small streams in the Pepacton Reservoir watershed were sampled between December 2000 and November 2001 as part of a cooperative project between the USGS and New York State Department of Environmental Conservation to assess the occurrence of pesticides in shallow ground water with differing amounts of corn cultivation. Baseflow samples from 20 sites in the Pepacton watershed, a part of the Delaware Reservoir system that supplies about 50 percent of New York City's water drinking water, were analyzed for pesticides. Of the 57 pesticides and pesticide degradates for which samples were analyzed, only 6 were detected – 3 herbicides (atrazine, metolachlor and simazine) and 3 herbicide degradates (alachlor ESA, deethylatrazine, and metolachlor ESA). No insecticide or insecticide degradates were detected. Maximum concentrations of all compounds except metolachlor ESA were less than 0.10 µg/L, and no concentrations exceeded any Federal or State water-quality criteria. The pesticides detected in this study are generally used on corn and, thus, represent the effect of agricultural applications.

A comparison of the pesticide concentrations in the Pepacton baseflow samples with those of the most frequently detected pesticides in ground-water samples from monitoring wells and public-supply wells in row-crop areas of upstate New York indicated that the most commonly detected pesticides in all three studies were atrazine, metolachlor, and deethylatrazine. A fourth compound (metolachlor ESA) was detected in many of the Pepacton baseflow samples and in the public-supply samples. The similarity of concentrations among the three studies indicates that the concentrations in the Pepacton samples are typical of those in ground water in other agricultural areas of upstate New York.

SAM ratios (ratio of metolachlor ESA concentration to metolachlor concentrations) for the Pepacton baseflow samples were similar to SAM ratios for the supply-well samples, but were significantly higher than the median SAM ratio for a stream in upstate New York that drains a row-crop area; this confirms that the Pepacton baseflow samples were derived from ground water and did not contain surface runoff. Metolachlor is transported in surface runoff more readily than to ground water, in part because it is sorbed to soil. Thus, surface waters have lower SAM ratios than ground water.

Concentrations of three of the most frequently detected pesticides and pesticide degradates were related to current distribution of cornfields. The highest median concentrations of atrazine, deethylatrazine, and metolachlor ESA in baseflow samples collected at 15 sites in December 2000 and 20 sites in July 2001 were from watersheds in which corn was grown in 2001; the median concentration of these compounds for samples from watersheds with corn grown in 1993-94 but not in 2001 was statistically similar to that for watersheds with no history of corn crop during or after 1993-94.

More than 60 percent of the nine samples collected at the active ANGLH site (corn crop gown in 1993-94 and 2001) contained atrazine, deethylatrazine, and metolachlor ESA. Decreases in the baseflow concentration of atrazine and deethylatrazine at this site during the summer of 2001 may reflect the decline of ground-water discharge from the shallow-most part of the surficial aquifer in response to a drought. The lack of a similar decrease in metolachlor ESA concentrations during this period may reflect the transport of metolachlor ESA into deeper parts of the surficial aquifer that continued to discharge to streams throughout the fall.

References Cited

Coates, D. R., 1966, Glaciated Appalachian Plateau - till shadows on the hills: Science, v. 152, p. 1617-1619.

Canadian Council of Resource and Environment Ministers, 1997, Canadian water quality guidelines (rev. ed.): Ottawa, Ontario, Task Force on Water Quality Guidelines, Canadian Council of Resource and Environment Ministers, loose-leaf (originally published 1987), 23 appendixes.

Eckhardt, D.A., Hetcher, K.K., Phillips, P.J., and Miller, T.S., 2001, Pesticides and their metabolites in community water-supply wells of central and western New York, August 1999: U. S. Geological Survey Water Resources Investigations Report 00-4128, 12 p.

Environment Canada, 1999, Canadian water quality guidelines for the protection of aquatic life, Summary tables, (http://www.ec.gc.ca/ceqg-rcqe), accessed on 6/23/99.

Fluhr, T.W., 1953, Geology of New York City's water supply system - a progress report: The Municipal Engineer's Journal, v. 39, 4th quart. issue, p. 125-145.

Hoffman, R.S., Capel, P. D., and Larson, S. J., 2000, Comparison of pesticides in eight U.S. urban streams: Environmental Toxicology and Chemistry, v. 19, p. 2249-2258.

Helsel, D. R., and Hirsch, R. M., 1992, Statistical methods in water resources: New York, Elsevier, 552 p.

International Joint Commission Canada and United States, 1977, New and revised Great Lakes water quality objectives, volume II, an IJC report to the governments of the United States and Canada: Windsor, Ontario, Canada, International Joint Commission (http://www.ijc.org/agree/quality.html#art5).

Kolpin, D.W., Thurman, E.M., and Linhart, S.M., 1998, The Environmental occurrence of herbicides - The importance of degradates in ground water: Archives of Environmental Contamination and Toxicology, v. 35, p. 385-390.

Lee, E.A., Kish, J.L., Zimmerman, L.R., and Thurman, E.M., 2001, Methods of Analysis by the U.S Geological Survey Organic Geochemistry Research Group- Update and Additions to the Determination of Chloroacetanilide Herbicide Degradation Compounds in Water Using High-Performance Liquid Chromatography/Mass Spectrometry: U.S. Geological Survey Open File Report 01-10, 17 p.

Lounsbury, Clarence, Beers, P. D., Howe, F. P., Waite, E. E., Pearson, C. S., and Diebold, C.H., 1930, Soil Survey of Delaware County, New York: U. S. Department of Agriculture, Series 1930, no. 7, 31 p.

National Climatic Data Center, 2002, Climatological Data Annual Summary New York 2001: Asheville, North Carolina, National Atmospheric and Oceanic Administration, v. 113, no. 13, ISSN –0364-5606, 30 p.

New York City Department of Environmental Protection, 1996, Land Cover for the Pepacton Reservoir Basin, GIS coverage created 3/25/1996, 25 meter grid cell size, 1:40,000, (coverage name lu1992pepg, version 1).

New York City Department of Environmental Protection, 1999, Land Cover/Land Use for the Pepacton Reservoir Basin, created 1/25/1999, GIS coverage created 25 meter grid cell size, 1:40,000, (coverage name lu1992pepg, version 2).

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, New York State Department of Health Public Water Systems Regulations, effective March 12, 1998.

Ozsvath, D. L., 1985, Glacial geomorphology and Late Wisconsin deglaciation of the western Catskill Mountains, New York: State University of New York at Binghamton, Ph.D. dissertation, 181p.

Phillips, P.J., Eckhardt, D.A., Thurman, E.M., and Terracciano, S.A.,1999a, Ratios of metolachlor to its metabolites in ground water, tile-drain discharge, and surface water in selected areas of New York State, 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 Investigation Report 99-4018B, p. 383-394.

Phillips, P.J., Wall, G.R., Thurman, E.M., Eckhardt, D.A., and VanHoesen, J., 1999b, Metolachlor and its metabolites in tile drain and stream runoff in the Canajoharie Creek Watershed: Environmental Science and Technology, v. 33, p. 3531-3537.

Phillips, P. J., Eckhardt, D. A., Smith, M. A., and Rosenmann, Larry, 2000, Pesticides and their metabolites in selected surface-water public supplies in New York State, 1999: U.S. Geological Survey Water-Resources Investigations Report 00-4119, 16 p.

Phillips, P.J., Wall, G.R., and Ryan, C.M., 2000, Pesticides in wells in agricultural and urban areas of the Hudson River Basin: Northeastern Geology, v. 22, p. 1-9.

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.

Soren, Julian, 1963, The ground-water resources of Delaware County, New York: State of New York Water Resources Commission Bulletin GW-50, 59 p.

Woodward, H. P., 1957, Structural elements of northeastern Appalachians: Am. Assoc. of Petroleum Geologists Bulletin, v. 41, no. 7, p. 1429-1440.

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 ¾ 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.