

In cooperation with New York State Department of Environmental Conservation

Chemical Quality of Base Flow in 18 Selected Streams in the Upper Susquehanna River Basin, New York

Water-Resources Investigations Report 03-4100



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Chemical Quality of Base Flow in 18 Selected Streams in the Upper Susquehanna River Basin, New York

By Kari K. Hetcher, Todd S. Miller, and Steven C. Komor

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CONVERSION FACTORS AND VERTICAL DATUM

| Multiply | By | To Obtain |
|--|------------------|------------------------|
| Length | | |
| inch (in.) | 2.54 | centimeter |
| foot (ft) | 0.3048 | meter |
| mile (mi) | 1.609 | kilometer |
| Area | | |
| square mile (mi ²) | 2.59 | square kilometer |
| Flow | | |
| cubic foot per second (ft ³ /s) | 0.02832 | cubic meter per second |
| inch per year (in/yr) | 25.4 | millimeter per year |
| Mass | | |
| pound, avoirdupois (lb) | 0.4536 | kilogram (kg) |
| Temperature | | |
| degrees Fahrenheit (°F) | °C = 5/9 (°F-32) | degrees Celsius |
| Specific Conductance | | |
| microsiemens per centimeter at 25° Celsius (µS/cm) | | |
| Equivalent Concentration Terms | | |
| milligrams per liter (mg/L) = parts per million | | |
| micrograms per liter (µg/L) = parts per billion | | |

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Chemical Quality of Base Flow in 18 Selected Streams in the Upper Susquehanna River Basin, New York

By Kari K. Hetcher, Todd S. Miller, and Steven C. Komor

ABSTRACT

The base-flow and runoff components of total streamflow at four selected sites in the upper Susquehanna River Basin in New York were calculated through hydrograph-separation techniques from long-term (1941-93) discharge records. Base flow was found to constitute more than 60 percent of the total annual flow of each stream. Base-flow samples were then collected at 18 stream sites several times during 2001 to define the chemical quality of base flow. The concentrations of selected common ions, nutrients, and pesticides were plotted in relation to the amount of agricultural land and carbonate bedrock in the drainage basin upstream of each site. Sites were selected at locations distant from and unaffected by development and urban areas. Twelve of the sites were again sampled in November 2001 for pesticide analysis.

The predominant cations detected in the samples were calcium, magnesium, and sodium; the major anions were chloride, sulfate, and bicarbonate. The predominant nutrient was nitrate. Higher nitrate concentrations in the winter samples than in the summer samples are attributed to the seasonal decrease in plant growth and microbial activity in the streams during the winter, which allows nitrate to persist in the stream water. Lower nitrate concentrations in the summer samples probably result from nitrogen uptake by vegetation and microbial activity in the streams.

Base-flow samples from the agricultural, carbonate-rich northern part of the study area had higher concentrations of most inorganic chemical

constituents than those from the forested, noncarbonate (shale, siltstone, and sandstone) central and southern parts. The highest nitrate concentrations were in samples from subbasins dominated by agricultural land, and the lowest were in subbasins dominated by forest. The concentrations in samples from subbasins with forested as well as agricultural land were intermediate.

Six pesticides were detected in samples from 10 of the 12 sites. All were herbicides. The highest concentrations of pesticides, and the most frequent pesticide detections, were in samples from agricultural subbasins and large main-stem subbasins with mixed land use and mixed bedrock geology. A correlation was indicated between land use and concentrations of atrazine and deethylatrazine. The concentrations of all six compounds were at least an order of magnitude lower than New York State and Federal water-quality standards.

Ground water from four production wells in the villages of Afton, Sidney, Unadilla, and Otego was analyzed for chlorofluorocarbons (CFCs) to indicate the approximate age of the water in these wells and the potential for induced infiltration of river water. The water at two of these wells is probably between 26 and 50 years old; the ages of water at the other two wells could not be reliably estimated because of CFC contamination from a nonatmospheric source. The two wells for which CFC analysis gave reliable results (Afton and Otego) probably do not induce infiltration of river water into the aquifer.

I. INTRODUCTION

A. Base-flow concerns and study objectives

Concentrations of nutrients, sediment, and other constituents in the Susquehanna River and Chesapeake Bay have been increasing for several decades. At least 60 percent of the annual discharge at four stream sites in the upper Susquehanna River Basin consists of base flow.

The chemical quality of base flow in streams in the northernmost part of the Susquehanna River Basin has not been extensively documented. This study was designed to calculate the base-flow contribution to total annual flow and document the chemical quality of base flow at selected sites.

The Susquehanna River Basin drains most of south-central New York and half of Pennsylvania and eventually flows into Chesapeake Bay, the nation's largest estuary (fig. 1). Concentrations of nutrients, sediment, and other constituents in Chesapeake Bay have increased over the past 50 years as a result of deforestation, growth of urban areas, poor land management, and water-treatment plant effluent within its basin (Sprague, 2001; U.S. Environmental Protection Agency, 1988; Bell and others, 1996; Belval and others, 1995; Belval and Sprague, 1999).

Concerns about water quality of Chesapeake Bay and its principal tributary, the Susquehanna River, have led to hydrologic investigations by several Federal, State, and local organizations, including the New York State Department of Environmental Conservation (NYSDEC), the Upper Susquehanna Coalition, the Susquehanna River Basin Commission, and the U.S. Geological Survey (USGS). Most of the assessments that were done in New York, which contains the uppermost part of the basin, addressed surface-water quality (Ku and others, 1975), surface-water and ground-water quantity, or the interaction between surface water and ground water (MacNish and Randall, 1982; Randall, 1986; Randall and others, 1988; Yager, 1986; Yager, 1993), but none investigated the chemical quality of base flow (the ground-water component of streamflow). Base flow is defined as the component of streamflow that remains when little or no precipitation or snowmelt has occurred for at least 5 days and a hydrograph of the stream is steady or slowly declining. Most of the flow in the stream during base-flow conditions is derived from ground water; therefore, a base-flow sample is an approximation of the chemical quality of the ground water discharging to that stream.

In 2001, the USGS, in cooperation with the NYSDEC, began a 1-year study to (1) calculate the contribution of base flow to annual flow at four sites in the upper Susquehanna River Basin, (2) measure the

concentrations of common ions and nutrients in base flow at 18 selected stream sites within the upper Susquehanna River Basin during the winter and summer of 2001, and (3) document whether the drainage basin above each site was mostly agricultural, mostly forested, or a mixture, and whether it was underlain by carbonate (limestone) bedrock, noncarbonate bedrock, or a mixture, for comparison with the analytical results. Sampling was done at 12 of the sites in November 2001 to document the concentrations of pesticides in base flow and their relation to the presence or absence of agricultural land within their drainage areas.

This report (1) explains the base-flow separation analysis, (2) briefly summarizes the hydrogeologic conditions within the study area, (3) presents and interprets the results of the common-ion and nutrient analyses in relation to agricultural land use and bedrock geology, and the results of the pesticide analyses and their relation to agricultural land, and (4) estimates the age of ground water at 4 production wells on the Susquehanna River and the potential for induced infiltration of river water at these sites. This data can be used by water managers throughout the upper Susquehanna River Basin to compare the concentrations of chemical constituents in base flow to those in production wells, or in future studies to compare base-flow water quality to the water quality of stormflow.

Acknowledgments

The authors thank the landowners for permitting access to streams along their property, for allowing the installation of monitoring equipment, and for information on the history of their land. Thanks also are extended to the USGS colleagues who helped collect samples, interpret results, and prepare the graphics for this report.

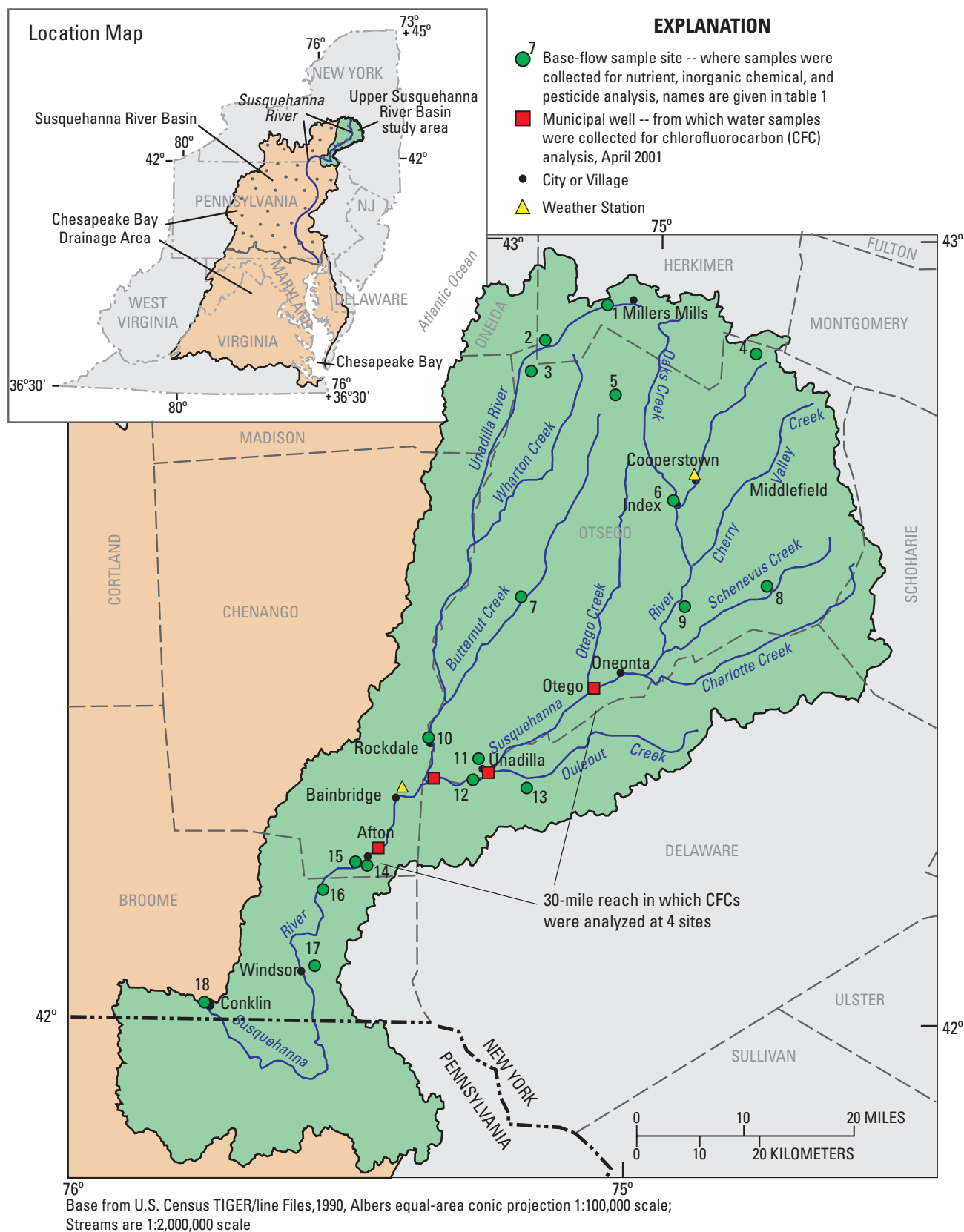


Figure 1. Location of 18 surface-water sampling sites and 4 production wells, and principal geographic features of the upper Susquehanna River Basin between Millers Mills and Conklin, New York. (Site names are given in table 1.)

I. INTRODUCTION (CONTINUED)

B. Study-area characteristics and quality-control procedures

Base-flow samples were collected at 18 sites representing three land-use categories and three bedrock categories.

The sampling sites represent drainage areas dominated by forested, agricultural, or mixed land use underlain by carbonate bedrock, noncarbonate bedrock, or both. Base-flow samples were analyzed for common inorganic constituents, nutrients, and pesticides. Standard analytical and quality-control procedures were followed.

The upper Susquehanna River Basin encompasses 2,235-mi² in the northernmost part of the Susquehanna River Basin (fig. 1). The northern part of the study area is characterized by low relief and contains mostly agricultural land and wetlands, whereas the central and southern parts are characterized by moderate to high relief and a mixture of forested and agricultural land. The study area is predominantly rural; it contains one major city (Oneonta) and many scattered villages in the valleys. It consists mostly of undeveloped, forested land (71 percent) and agricultural land (26 percent); 2 percent of the area consists of water, commercial, transportation, or other land uses, and the few urban or residential areas represent only about 1 percent of the area. Most of the developed areas are within the Susquehanna and Unadilla River valleys. Total population of the study area in 2000 was about 112,000 (U.S. Bureau of Census, 2000). Community-water-supply systems provide water to more than 53,000 people in the study area (New York State Department of Health, 1982). Most of the water-supply systems primarily use ground water; the rest use surface water from reservoirs and lakes.

The concentrations of certain chemical constituents in base flow can be related to land use, bedrock geology, and carbonate content of the surficial material. Base-flow samples were collected at 18 sites in January and June 2001; 9 sites also were sampled during August or September 2001. Twelve of the sites were resampled in November 2001 for pesticide analysis. Sampling sites were selected according to the predominant land use within their drainage basins—some represent mostly agricultural land, some mainly forested land, and others a mixture of both. Locations directly affected by contamination from urban runoff and point sources such as sewage outfalls were excluded. A description of all sites is given in table 1; their locations are shown in figure 1.

Water samples were collected and processed by methods described in Wilde and others (1998) and were analyzed for selected nutrients and inorganic constituents by the USGS at the National Water Quality Laboratory (NWQL) in Denver, Colo. Samples collected for pesticide analyses were collected and processed by the methods of Shelton (1994) and Sandstrom and others (2001) and were analyzed at the NWQL and the Kansas Organic Geochemistry Research Laboratory (OGRL) for 113 pesticides and pesticide degradates through methods described by Zaugg and others (1995), Meyer and others (1993), and Ferrer and others (1997). The analytical method devised by Zaugg and others (1995), developed in cooperation with the U.S. Environmental Protection Agency, detects some of the most commonly used pesticides in the United States.

Quality-assurance samples were collected to assess the accuracy and reproducibility of the analytical data. Blank and replicate samples were collected for at least 10 percent of the samples. Blank samples used either inorganic-grade blank water or pesticide-grade blank water provided by the USGS Water-Quality Services Unit in Ocala, Fla; no blank samples contained any constituents in concentrations above the detection limits of the analytical methods used. The replicate samples showed no statistically significant differences in concentrations of any of the constituents detected.

A pilot study was conducted within a 30-mile reach of the Susquehanna River valley (fig. 1) in February 2001 to calculate the age of ground water at four production wells that tap sand and gravel aquifers beneath the flood plain and to assess the likelihood that these wells are inducing infiltration of river water into the aquifer. Concentrations of chlorofluorocarbons (CFCs) in the samples were measured to estimate the age of the well water and to assess the likelihood of induced infiltration.

Table 1. Site information, land use, and stream discharge at 18 surface-water sampling sites within the upper Susquehanna River Basin study area, N.Y., January and June 2001.
[mi², square miles; agr, agricultural; Vt, valley tributary; Ut, upland headwater tributary; Vm, main-stem valley stream; carb, carbonate; noncarb, noncarbonate. Site locations are shown in fig. 1.]

| Site no. | Station name | USGS station number ¹ | Lat./long. | Drainage area (mi ²) ² | Cate-gory ³ | Land use | | Type of stream ⁴ | Bed-rock ⁴ | Stream discharge ⁵ | |
|----------|---|----------------------------------|----------------|---|------------------------|------------------|------|-----------------------------|-----------------------|-------------------------------|------|
| | | | | | | Percent of basin | | | | Jan. | June |
| | | | | | | Forest | Agr | | | | |
| 1 | Unadilla River at Millers Mills | 01500832 | 425527/0750508 | 2.2 | agr | 37.7 | 60.4 | Vt | carb | 0.58 | 0.63 |
| 2 | North Winfield Creek at West Winfield | 01500850 | 425303/0751120 | 16.0 | agr | 37.3 | 58.8 | Vt | carb | 11.5 | 25.9 |
| 3 | Cambell Brook at Lloydsville | 01500859 | 424955/0751317 | 3.5 | forest | 73.6 | 26.3 | Ut | carb | 2.55 | 6.64 |
| 4 | Shadow Brook at East Springfield | 01496330 | 424952/0744906 | 7.0 | agr | 31.1 | 65.9 | Vt | carb | 1.80 | 1.74 |
| 5 | Dundee Brook tributary at Brainard Corners | 01501092 | 424728/0750652 | 0.47 | agr | 46.4 | 53.6 | Ut | carb | 0.40 | 0.19 |
| 6 | Oaks Creek at Index | 01496500 | 423956/0745736 | 102.0 | mixed | 49.8 | 40.9 | Vm | carb | 108 | 92.4 |
| 7 | Butternut Creek at Morris | 01502000 | 423243/0751422 | 60.0 | mixed | 69.6 | 28.6 | Vm | noncarb | 40.1 | 27.7 |
| 8 | Schenevus Creek tributary southwest of Chaseville | 01497818 | 423153/0745139 | 0.75 | forest | 96.8 | 0.2 | Ut | noncarb | 0.34 | 0.37 |
| 9 | Upland tributary east of Portlandville | 01497309 | 423147/0745708 | 0.22 | forest | 99.8 | 0.2 | Ut | noncarb | 0.11 | 0.08 |
| 10 | Unadilla River at Rockdale | 01502500 | 422240/0752423 | 520.0 | mixed | 63.7 | 34.1 | Vm | noncarb | 357 | 566 |
| 11 | Unadilla Springs at Unadilla | 0150050210 | 421957/0751903 | 0.32 | forest | 77.6 | 22.1 | Ut | noncarb | 0.02 | 0.02 |
| 12 | Susquehanna River at Unadilla | 01500500 | 421917/0751901 | 982.0 | mixed | 69.6 | 26.1 | Vm | noncarb | 518 | 557 |
| 13 | Smokey Kill west of Sidney Center | 01500628 | 421806/0751644 | 0.30 | mixed | 50.2 | 49.8 | Ut | noncarb | 0.14 | 0.07 |
| 14 | Route 41 stream south of Afton | 01502702 | 421256/0753132 | 1.1 | agr | 74.0 | 23.7 | Vt | noncarb | 0.38 | 0.04 |
| 15 | Route 7 stream south of Afton | 01502703 | 421253/0753200 | 0.66 | forest | 91.0 | 9.0 | Ut | noncarb | 0.23 | 0.06 |
| 16 | Unnamed stream at Plains Road east of Nineveh | 01502707 | 421153/0753534 | 0.51 | forest | 86.1 | 7.6 | Vt | noncarb | 0.29 | 0.48 |
| 17 | Hotchkiss Creek near Windsor | 0150273301 | 420452/0753654 | 0.72 | forest | 99.5 | 0.4 | Ut | noncarb | 0.18 | 0.05 |
| 18 | Susquehanna River at Conklin | 01503000 | 420207/0754812 | 2,232.0 | mixed | 70.6 | 26.0 | Vm | noncarb | 1190 | 1550 |

¹ Station identifier is downstream-order station number assigned by U.S. Geological Survey.

² Drainage area upstream from sampling point. Data from U.S. Geological Survey (1997).

³ Land-use classification based on land-use percentages and field reconnaissance (site 14). Four of the six mixed-land-use sites (6, 10, 12, and 18) have drainage areas greater than 100 mi². They contain more forested land than agricultural land but also contain urban land, transportation corridors, and commercial land. These sites are on large streams that receive drainage from forested and agricultural subbasins and therefore are classified as mixed-land-use sites.

⁴ Sites 14 and 16 originate on the valley floor, not the upland, and most of their drainage areas are underlain by stratified glacial drift. The actual drainage area in such terrane is a function of the water-table configuration (not delineated in this study) and may not coincide with the topographic drainage divide on which the drainage-area value here is based.

⁵ Discharge, in cubic feet per second (cfs), was measured at the time of sampling during base-flow conditions.

II. BASE-FLOW-SEPARATION ANALYSIS

The base-flow component of streamflow was calculated as a percentage of total annual streamflow through hydrograph-separation techniques.

Base flow at four stream sites in the study area that had continuous long-term discharge records (1941-93) was found to constitute more than 60 percent of total annual flow of each stream.

Streamflow consists of a mixture of base flow (ground water that has discharged to the stream) and stormflow except under base-flow conditions, when most stormflow is absent. A stream is considered to be under base-flow conditions when little or no precipitation or snowmelt has occurred in the drainage area for at least 5 days or if the streamflow hydrograph shows that discharge is steady or slowly declining. Most flow in a stream during base-flow conditions consists of ground water that has discharged to the stream; therefore, a water sample collected during base flow is an approximation of the chemical quality of the ground water discharging to that stream.

Base-flow (and ground-water) chemistry differs from stormflow chemistry in that base flow has been in contact with the subsurface material long enough to leach soluble minerals from it; thus, the concentrations of most inorganic chemical constituents in base flow tend to be higher than those in stormflow (Ku and others, 1975). The chemistry of base flow is also important because base flow in a stream is an aggregate of the ground-water quality over the whole basin above the sampling point, in contrast to a water sample from a single well, which may receive water from a smaller area.

The HYSEP hydrograph-separation program (Sloto and Crouse, 1996) quantifies the base-flow and stormflow components of total streamflow and was

used to calculate base flow as a percentage of mean total annual flow at four sites in the study area that had continuous discharge data for 1941-93 (fig. 2A). These sites were selected because they met the conditions recommended for use of HYSEP: (1) the stream is not regulated by a dam or flood-control reservoir, which would cause an apparent decrease in stormflow and an apparent increase in base flow after a storm, and (2) streamflow records span a period sufficient (at least 30 years) to represent long-term average conditions and thereby increase the accuracy of the estimates. All data were retrieved from the USGS National Water Information System (NWIS).

Results of the analysis indicate that base flow constitutes more than 60 percent of total annual discharge of each of the four streams (fig. 2B). The stream with the highest percentage of base flow (82 percent) was Oaks Creek at Index, possibly because (1) the carbonate bedrock in the northern part of this subbasin may allow more precipitation to infiltrate into the aquifer than in areas to the south, providing less stormflow in the stream and more ground-water discharge to the stream as base flow, and (2) the low relief in the northern part of the study area could allow more precipitation to infiltrate, and less to enter the stream as stormflow, than in the high-relief areas to the south.

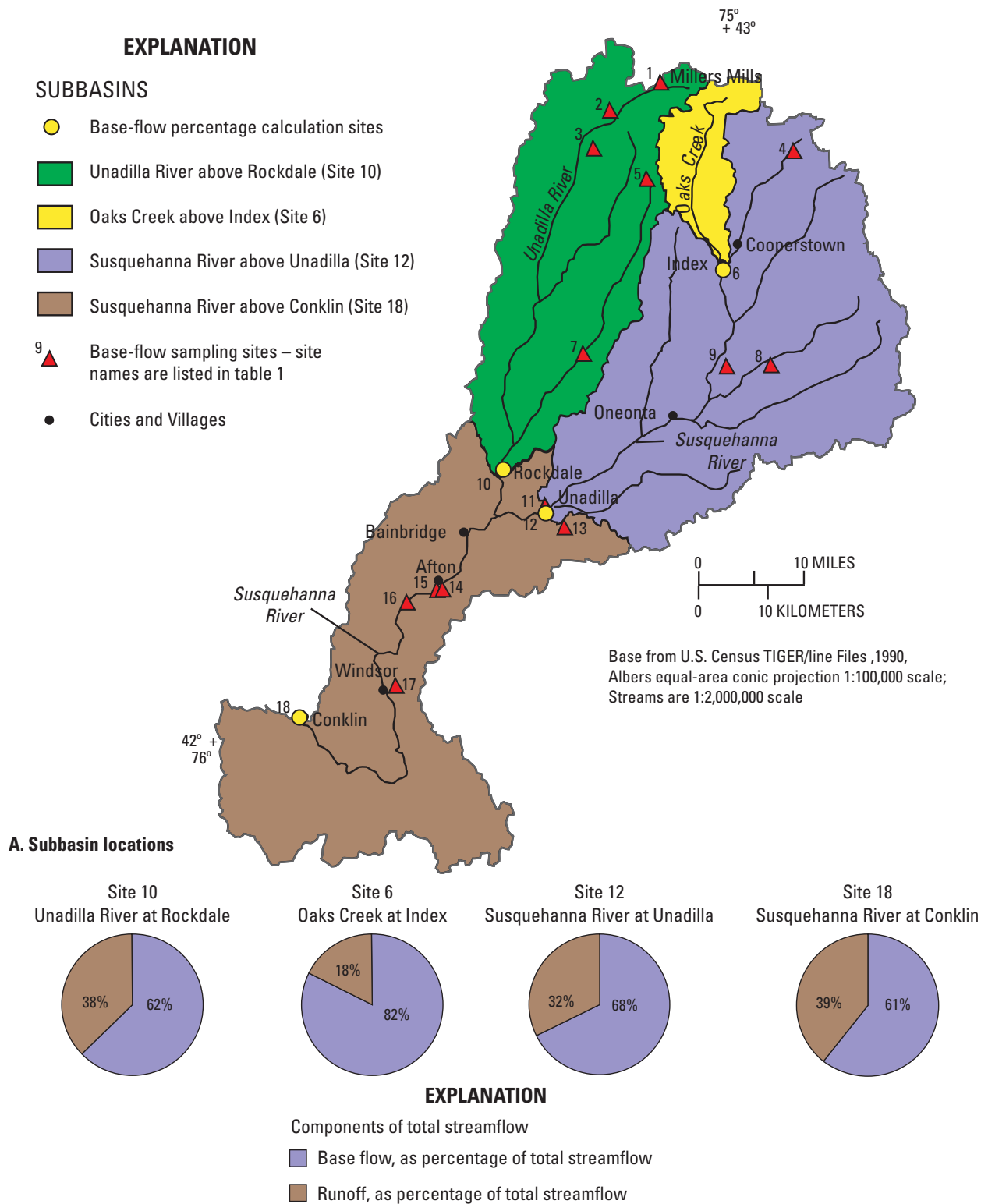


Figure 2. Annual mean base flow as percentage of total annual streamflow for the period 1941-93 at four streamflow-gaging stations in study area. (Locations are shown in map above.)

III. HYDROGEOLOGY

A. Air-temperature and precipitation data

Air temperature and precipitation patterns are similar throughout most of the study area.

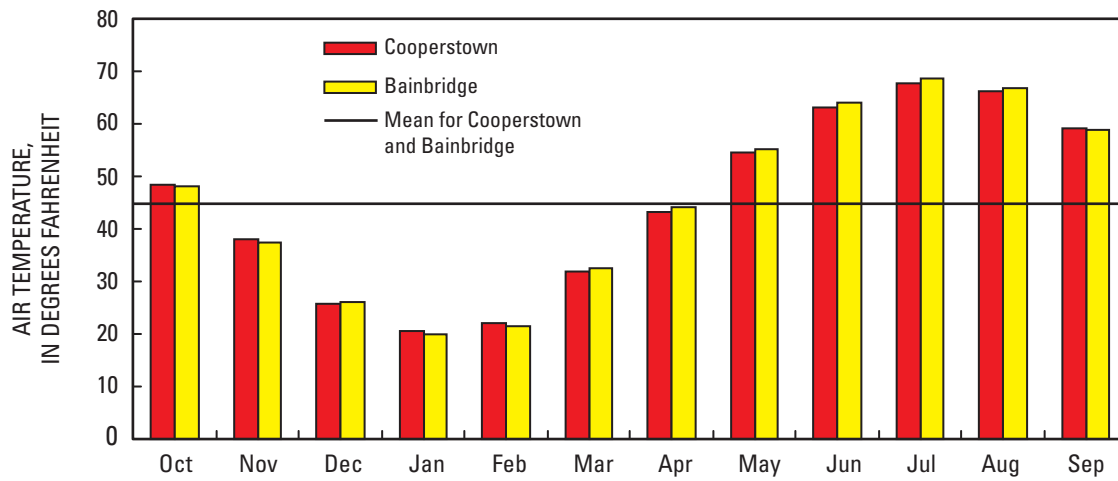
Precipitation and air-temperature records from two monitoring sites indicate that mean air temperatures and precipitation volumes are similar throughout the study area. Mean monthly temperatures range from about 20° F to 70° F. Precipitation typically ranges from 2.4 in. in January and February to 4.1 in. in June, and averages 3.3 in. per month.

Air-temperature and precipitation data from two weather stations in the study area (Cooperstown and Bainbridge, fig. 1) were obtained from the Northeast Regional Climate Center CLIMOD system (http://met-www.cit.cornell.edu/nrcc_web_climod.html); [accessed April 2001]. The long-term (1961-90) mean air temperature for Cooperstown was 45.0 °F and for Bainbridge was 45.3 °F (fig. 3A). Air Temperatures during the growing season (May through September) averaged 62.1 °F at Cooperstown and 62.8 °F at Bainbridge; air temperatures for October through April averaged 32.8 °F at both locations. Mean monthly temperatures ranged from about 20° F to 70° F.

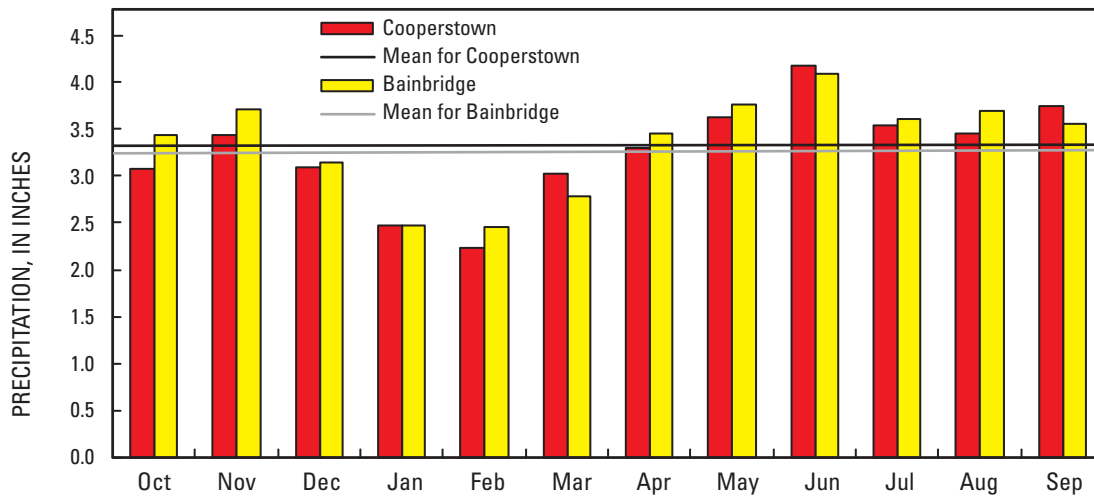
Mean annual precipitation at Cooperstown during 1961-90 was 39.1 in., and at Bainbridge was

40.1 in. (fig. 3A). Monthly mean precipitation at Cooperstown was 3.26 in. and at Bainbridge was 3.34 in.; Monthly means are slightly lower during the winter and early spring (December through March) than at other times. Nearly half of the precipitation during 1961-90 occurred during the growing season (May-September). Precipitation typically ranges from 2.4 in. in January and February to 4.1 in. in June, and averages 3.3 in. per month.

Parts of the study area that are distant from Cooperstown and Bainbridge may have slightly different temperature and precipitation rates, depending on elevation, topography, and average cloud cover.



Mean monthly air temperatures (1961-90)



Mean monthly precipitation (1961-90)

Figure 3A. Mean monthly air temperature and precipitation at Cooperstown and Bainbridge weather stations in upper Susquehanna River Basin, N.Y., 1960-90. (Data from Northeast Regional Climate Center CLIMOD system, 2001.) (Locations are shown in fig. 1.)

III. HYDROGEOLOGY (CONTINUED)

B. Precipitation, runoff, evapotranspiration, and recharge

Recharge depends on precipitation and on the rates of evapotranspiration and infiltration.

Some of the runoff that infiltrates into the soil is returned to the atmosphere through evapotranspiration (ET); the rest infiltrates to the water table. Published mean precipitation, runoff, and ET values are as follows: precipitation, 38-46 in/yr; runoff, 19-27 in/yr; and evapotranspiration, 19 in/yr.

Once precipitation has saturated the thin soils and till in the uplands of the study area, it flows quickly overland into streams. Some surface runoff seeps into openings in the soil such as frost cracks, desiccation cracks, root tubes, burrows, etc., then makes its way to streams and rivers in the drainage area. Some shallow ground water is lost to the atmosphere through evaporation or through uptake by plant roots and transpiration of the moisture from plant leaves before it reaches a stream or river. This process (evapotranspiration) increases during summer months when temperatures increase and more plants and crops are growing, and decreases the amount of shallow ground water that recharges streams.

The amount and distribution of precipitation, runoff, and evapotranspiration (ET) in the Susquehanna River Basin in New York were calculated in a previous study by Randall (1996), who estimated precipitation to range from 38 to 46 in/yr (fig. 3B) from an analysis of 1951-80 precipitation records from stations managed by the U.S. National Oceanic and Atmospheric Association and summarized by Lyford and Cohen (1988). Randall (1996) also partitioned precipitation at each station into runoff and ET so that the ET values would vary smoothly across the region and would decrease with increasing altitude and latitude. Runoff in the study area (fig. 3B) was considered to represent all precipitation that did not return to the atmosphere as ET and was estimated from streamflow records for 1951-80 to range from 19 to 27 in/yr (Randall, 1996). Runoff increases with increasing precipitation and, in this case, includes the component of precipitation that recharges the ground water.

The valley-fill aquifers that supply water to the local residents are recharged by (1) precipitation that falls directly on the coarse-grained, permeable surficial material, (2) infiltration of streamflow in reaches that cross the aquifer (losing reaches), (3) unchanneled runoff from upland hillsides that seeps into the coarse valley-fill deposits along the edges of the main-stem

river valleys, and (4) induced infiltration of river water in response to pumping (Randall and others, 1988; MacNish and Randall, 1982). Main-stem river channels within the study area are commonly floored by sand and gravel deposits that provide direct hydraulic connection to underlying unconfined aquifers (fig. 3D; MacNish and Randall, 1982). Aquifers in the study area discharge water to streams and rivers, springs, and pumping wells.

Whether a stream or river reach gains or loses water through the streambed depends on whether the water level is higher or lower than the surrounding water table. Water seeps from a streambed or riverbed into the underlying aquifer where the stream water is higher than the water table, and moves from the aquifer into the streambed or riverbed where the water table is higher than the stream surface. Most main-stem rivers gain ground water throughout their course, whereas upland tributaries typically gain water in the uplands but lose some or all their flow where they cross alluvial fans as they enter main-stem river valleys (Ku and others, 1975; Morrissey and others, 1988).

Some valley reaches do not entirely consist of permeable material but also contain thick deposits of lacustrine fine sand, silt, or clay. These materials do not readily transmit water to underlying aquifers but, rather, confine them (Randall, 2001). These confined aquifers can receive recharge along the edges of the valleys where coarse-grained permeable glacial deposits are in contact with the confined units (MacNish and Randall, 1982). Water discharged to a stream from a deep, confined aquifer may be older than water from shallow, unconfined sand and gravel aquifers and, therefore, may have higher concentrations of inorganic chemical constituents. The complexity of the ground-water flow paths in the upper Susquehanna River Basin was not investigated in this study.

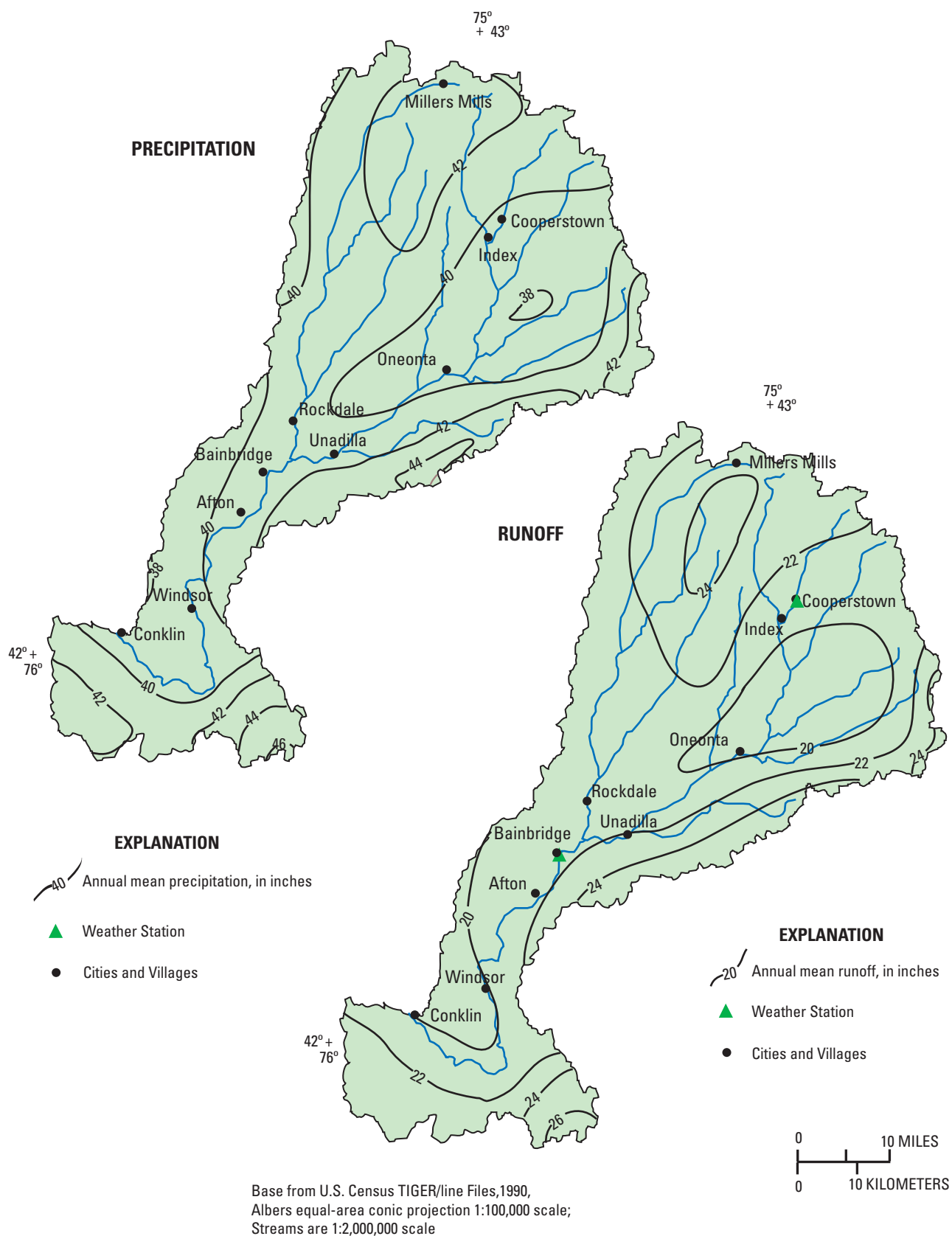


Figure 3B. Annual mean precipitation and runoff in the upper Susquehanna River Basin, N.Y., 1951-80. (Modified from Randall, 1996, plates 1 and 2).

III. HYDROGEOLOGY (CONTINUED)

C. Bedrock

The northern part of the study area is underlain by carbonate bedrock; the central and southern parts are underlain by younger noncarbonate sandstone, siltstone, and noncalcareous shale.

The bedrock in the northernmost part of the study area consists of Upper Silurian and Lower Devonian carbonates (limestone, dolostone), and calcareous shales, whereas bedrock in the central and southern parts consists of later (Middle and Upper Devonian) sandstone, siltstone, and noncalcareous shale.

The eastern part of North America during the late Ordovician period (460 to 435 million years ago) and Devonian period (409-363 million years ago) was undergoing mountain-building events (orogenies) that occurred when part of the North American plate, including the area that is now southeastern Canada and New England, collided with an island arc (Taconic Orogeny) and a microcontinent called the Avalon terrane (Acadian Orogeny) (Isachsen and others, 1991; Dott and Prothero, 1994). These collisions caused uplift of mountains to the east of New York and downwarping of much of the region west of the mountains. This downwarping resulted in the formation of a hinterland basin (Hancock, 1994) in the area that is now central and western New York. A wide, shallow inland sea occupied the basin during the Upper Silurian and Lower Devonian periods, and thick layers of carbonate minerals (the precursors of limestone and dolostone) were deposited upon the sea floor through the precipitation of calcium and magnesium. Later, erosion of the mountains to the east resulted in the deposition of sediment along the edges

of this sea. Later uplift to the east resulted in renewed deposition of mud and sand above the carbonate layers; these deposits subsequently became consolidated by the weight of still later sediments to form the Upper Devonian sandstones, shales, and siltstones that are now exposed in the central and southern parts of the study area.

Later stresses from subsequent tectonic events caused the bedrock units to dip gently southward and southwestward; thus, the older (deep) carbonate layers are exposed in the northern part of the study area, and the overlying younger (noncarbonate) layers become exposed progressively southward.

The northern part of the study area is characterized by low relief, with gently rolling hills, numerous bedrock outcrops, and localized karst topography (fig. 3C). The central and southern parts are characterized by steep-sided valleys, uplands incised by many small headwater streams, and several broad valleys whose floors range from 600 to 800 feet below the upland summits.

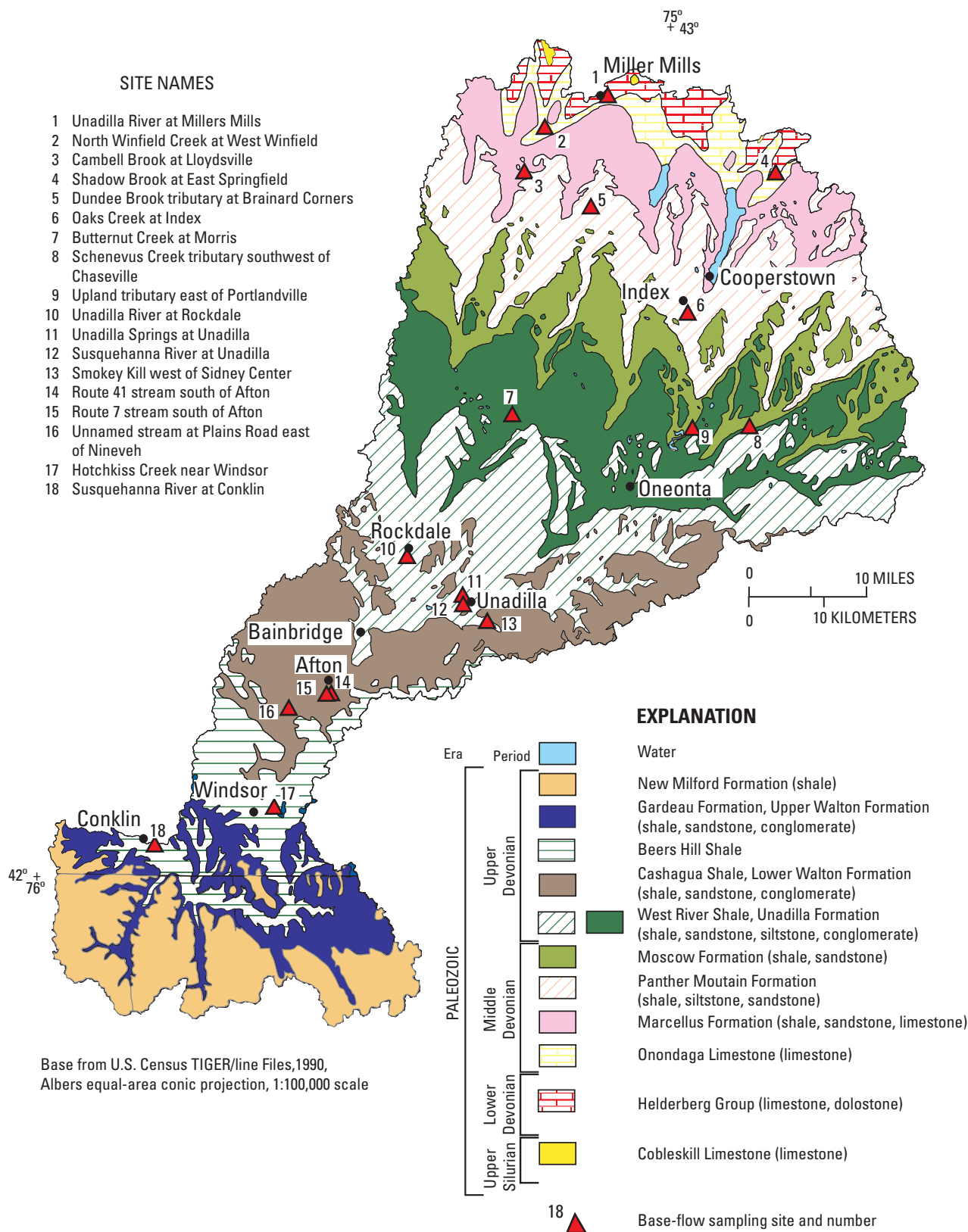


Figure 3C. Bedrock geology of the upper Susquehanna River Basin, N.Y. (Modified from New York State Geological Survey, Map and Chart Series No. 15, Fisher and others, 1970.)

III. HYDROGEOLOGY (CONTINUED)

D. Surficial material

Glaciers modified the topography and deposited glacial sediments throughout the study area.

Glaciers eroded the bedrock surface of the entire study area and deposited till in the uplands and glaciofluvial and glaciolacustrine sediments in the major valleys. Thick layers of till mantle south-facing upland hillsides in the central and southern parts of the study area.

Continental glaciers covered most of New York at least twice during the Pleistocene Epoch (between 1 million and 13,000 years ago) as they advanced and retreated in response to changes in climate. The glaciers deeply incised and widened the major valleys; then, during deglaciation, left large amounts of glaciofluvial material (sand and gravel deposited beneath, in front of, or alongside a glacier by meltwater streams) and glaciolacustrine deposits (clay, silt, and fine sand that settled within proglacial lakes) within the valleys (fig. 3D).

Glacially derived landforms within the valleys throughout the study area include kames, eskers, outwash valley terraces, kettles, and morainal valley plugs and ridges. Recent alluvium covers most of the flood plains of the larger streams and rivers. The glaciofluvial deposits form the most productive aquifers within the study area; the fine-grained glaciolacustrine deposits are relatively impermeable and form confining units that yield little water to wells but may confine deeper aquifers locally.

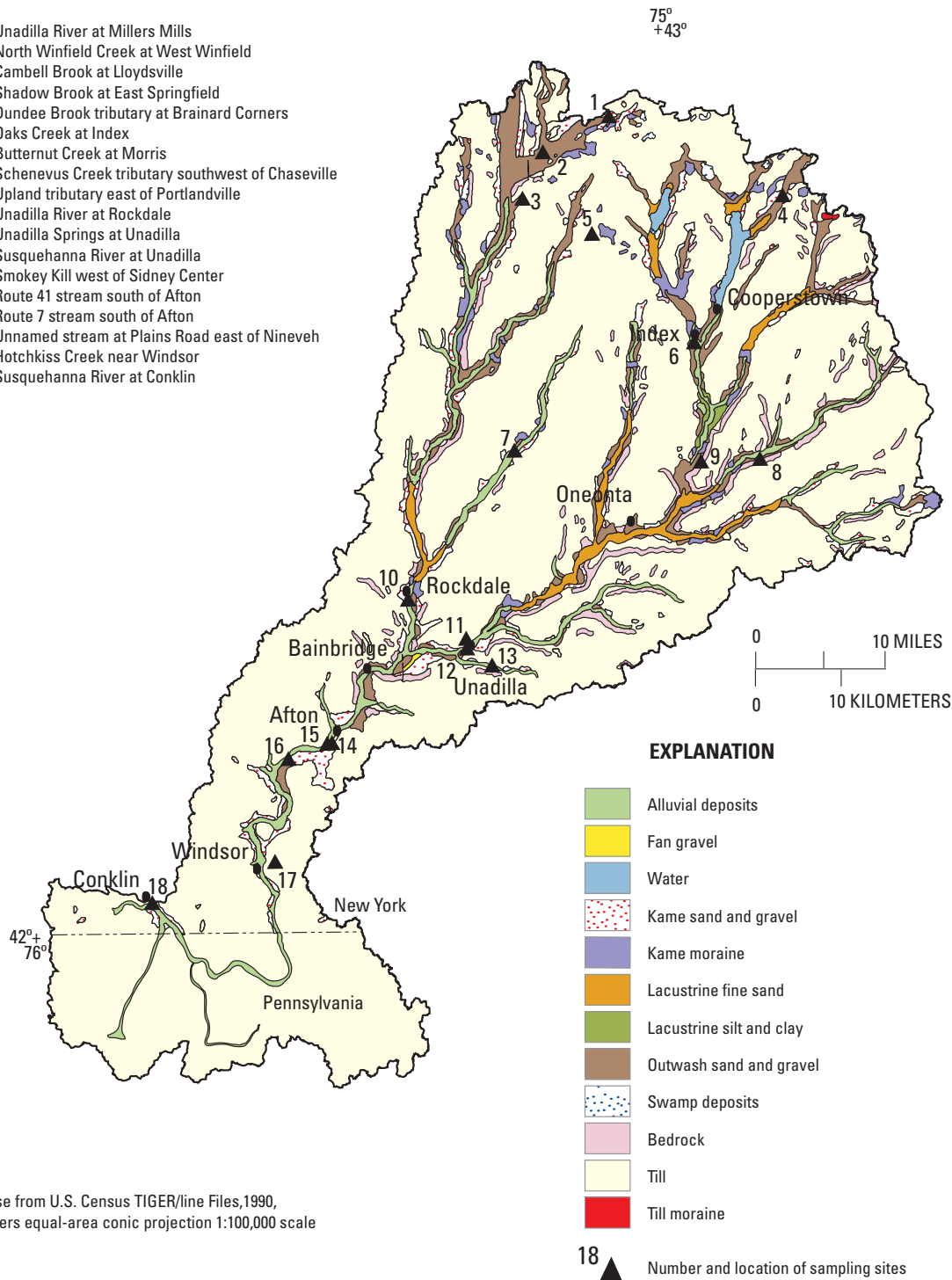
The most recent glacier scraped the tops and northern sides of most hills down to bedrock. As it

flowed over the bedrock hilltops, generally southward, it deposited a mantle of till (a poorly sorted mixture of clay, silt, sand, and cobbles that can be more than 100 ft thick locally) along the southern sides of the hills (Coates, 1966). Subtle differences in the glacier's direction of flow probably resulted in the deposition of some till on the west and east-facing slopes as well. The glacial processes and glacial deposits within the study area are described in detail by Randall (2001), Fleisher (1977, 1986a, 1986b), and MacNish and Randall (1982).

Upland streams within the study area commonly begin on thick till or on bedrock slopes, then flow through small upland valleys to a main-stem river valley, where they lose velocity and deposit alluvial material as fans at the valley edge. The main-stem river valley floors are characterized by a few hummocky moraines, many gently sloping terraces capped by gravel, and flood plains of modern streams. Silt and clay deposits are widespread at depth beneath the valley floors.

SITE NAMES

- 1 Unadilla River at Millers Mills
- 2 North Winfield Creek at West Winfield
- 3 Cambell Brook at Lloydsville
- 4 Shadow Brook at East Springfield
- 5 Dundee Brook tributary at Brainard Corners
- 6 Oaks Creek at Index
- 7 Butternut Creek at Morris
- 8 Schenevus Creek tributary southwest of Chaseville
- 9 Upland tributary east of Portlandville
- 10 Unadilla River at Rockdale
- 11 Unadilla Springs at Unadilla
- 12 Susquehanna River at Unadilla
- 13 Smokey Kill west of Sidney Center
- 14 Route 41 stream south of Afton
- 15 Route 7 stream south of Afton
- 16 Unnamed stream at Plains Road east of Nineveh
- 17 Hotchkiss Creek near Windsor
- 18 Susquehanna River at Conklin



Base from U.S. Census TIGER/line Files, 1990,
Albers equal-area conic projection 1:100,000 scale

Figure 3D. Surficial geology of the upper Susquehanna River Basin, N.Y. (Pennsylvania portion was formatted differently than New York portion; alluvial and stratified drift deposits are shown undifferentiated). (Modified from New York State Geological Survey, Map and Chart Series No. 40, Cadwell and others, 1991.)

IV. WATER QUALITY

A. Sampling-site locations

Base-flow samples were collected at least twice from each of 18 stream sites in 2001 for nutrients and inorganic-constituent analysis; 12 of these sites were resampled in November for pesticide analysis.

Sampling sites represented three land-use categories (agricultural, forested, or mixed) and were established in areas unaffected by local wastewater discharge and urban runoff; they also were classified in terms of their geographic location within the upper Susquehanna River Basin.

Base-flow samples were collected at each of 18 stream sites during January and again in June 2001 for analysis for nutrients, and common inorganic constituents (cations and anions) to characterize the chemistry of base flow representing each type of land use. Additional samples were collected at 12 of these sites during November 2001 for pesticide analysis. Results are presented in the sections that follow.

Base flow is an approximation of the chemical quality of ground water, but the concentrations of some constituents can be altered in the stream through contact with air and stream biota. For example, increased temperatures in the spring and summer cause an increase in microbial activity and algal growth in the streams, which can decrease dissolved oxygen concentrations, utilize the nitrogen in the water, and might decrease nitrate concentrations through denitrification if denitrifying bacteria are present. Therefore, base-flow quality under non-snowmelt conditions in winter, when temperatures, microbial activity, and algal growth are minimal, provides a good approximation of the average chemical quality of shallow ground water within the drainage area.

Of the 18 sites sampled, five represented subbasins dominated by agriculture, seven represented subbasins dominated by forests, and six represented subbasins with a mixture of forest and agricultural land. Six were in the northern part of the study area that is mostly underlain by carbonate bedrock (limestone, dolostone, and calcareous shale), and 12 were in the central and southern parts that are underlain by noncarbonate bedrock (sandstone, siltstone, and shale). Site data are summarized in table 1; land use within each subbasin is depicted in figure 4A.

Site selection was facilitated through a GIS (Geographic Information System) analysis of spatial

data sets of topography. The subbasins were classified according to predominant land use (at least 50 percent of subbasin area) and bedrock type, as listed below:

- mostly agricultural land underlain by carbonate bedrock,
- mostly agricultural land underlain by noncarbonate shale, siltstone, and sandstone,
- mostly forested land underlain by carbonate bedrock,
- mostly forested land underlain by noncarbonate shale, siltstone, and sandstone, and
- mixed land use (nearly equal amounts of forested and agricultural land use), underlain by carbonate bedrock and noncarbonate shale, siltstone, and sandstone.

The “mixed” subbasins tend to be along the main stem of the Susquehanna and Unadilla Rivers, and those that encompass more than 100 mi² contain tributaries that drain two or more of the above land-use and bedrock categories. The drainage areas above the sampling sites ranged from 0.22 mi² (site 9) to 2,232 mi² (site 18, table 1.)

Most of the sampling locations were upstream from the nearest village and sewage outfalls to minimize the local effects of wastewater and urban runoff. The sampling sites also were designated as one of three types according to relative location (See table 1), as listed below:

- upland headwater tributaries (streams that originate in the uplands),
- valley tributaries (streams that originate within the valley instead of in the uplands), or
- main-stem valley streams.

These three types were designated to determine if small streams that originate in the main valley have water quality similar to those that originate in the uplands or to the large, main-stem valley streams.

SITE NAMES

- 1 Unadilla River at Millers Mills (2.2 mi²)
- 2 North Winfield Creek at West Winfield (16.0 mi²)
- 3 Cambell Brook at Lloydsville (3.5 mi²)
- 4 Shadow Brook at East Springfield (7.0 mi²)
- 5 Dundee Brook tributary at Brainard Corners (0.47 mi²)
- 6 Oaks Creek at Index (102.0 mi²)
- 7 Butternut Creek at Morris (60.0 mi²)
- 8 Schenevus Creek tributary southwest of Chaseville (0.75 mi²)
- 9 Upland tributary east of Portlandville (0.22 mi²)
- 10 Unadilla River at Rockdale (520.0 mi²)
- 11 Unadilla Springs at Unadilla (0.32 mi²)
- 12 Susquehanna River at Unadilla (982.0 mi²)
- 13 Smokey Kill west of Sidney Center (0.30 mi²)
- 14 Route 41 stream south of Afton (1.1 mi²)
- 15 Route 7 stream south of Afton (0.66 mi²)
- 16 Unnamed stream at Plains Road east of Nineveh (0.51 mi²)
- 17 Hotchkiss Creek near Windsor (0.72 mi²)
- 18 Susquehanna River at Conklin (2,232.0 mi²)

EXPLANATION

- Forest or wetlands
- Agricultural land
- Urban land
- Water

- 18 ▲ Location and number of sampling sites.

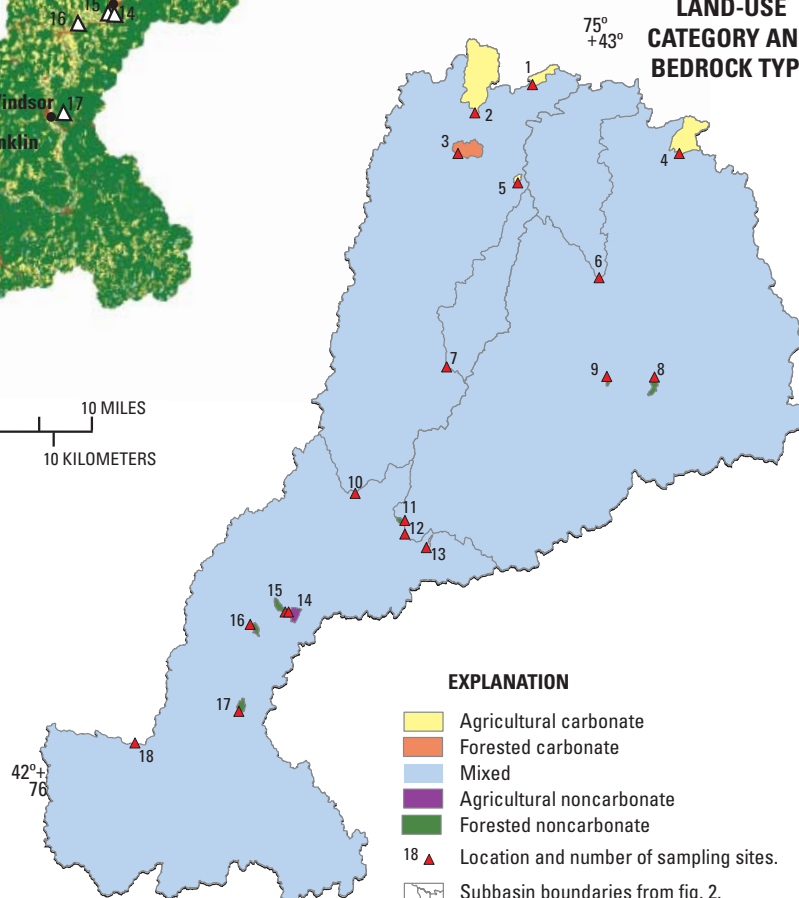


LAND-USE CATEGORY AND BEDROCK TYPE

EXPLANATION

- Agricultural carbonate
- Forested carbonate
- Mixed
- Agricultural noncarbonate
- Forested noncarbonate

- 18 ▲ Location and number of sampling sites.
- Subbasin boundaries from fig. 2.



Base from U.S. Census TIGER/line Files, 1990,
Albers equal area conic projection 1:100,000 scale

Figure 4A. Land use in the upper Susquehanna River basin, N.Y. (Modified from U.S. Geological Survey, 1997) and land-use categories in the 18 subbasins sampled in 2001.

IV. WATER QUALITY (CONTINUED)

B. Inorganic constituents

Concentrations of common inorganic constituents in base flow reflect upstream land use and showed little change from winter to summer.

The predominant cations in base flow were calcium, sodium, and magnesium, and the predominant anions were chloride, sulfate, and bicarbonate. Concentrations in the January samples were similar to those in the June samples. The highest concentrations of most inorganic constituents were in samples from agricultural subbasins underlain by carbonate bedrock, and the lowest were in samples from forested subbasins underlain by noncarbonate bedrock. Concentrations in samples from subbasins with mixed land use were intermediate.

Base-flow samples were analyzed for pH, alkalinity, specific conductance, dissolved solids, and common inorganic chemical constituents (cations and anions). The predominant cations in the samples were calcium, magnesium, and sodium; the predominant anions were chloride, sulfate, and bicarbonate (table 2). Concentrations of most constituents in the January 2001 samples were similar to those in the June 2001 samples (table 2).

The highest concentrations of most inorganic constituents were in samples from agricultural subbasins underlain by carbonate bedrock, and the

lowest were in samples from the forested subbasins with noncarbonate bedrock (fig. 4B). The concentrations in samples from the largest subbasins, which contain agricultural and forested land as well as a mixture of carbonate and noncarbonate bedrock, had intermediate concentrations of most constituents. An exception was the samples from two small streams that receive runoff from a major highway (sites 14 and 16); these samples contained anomalously high concentrations of sodium, chloride, and other constituents, as discussed in section IV-I.

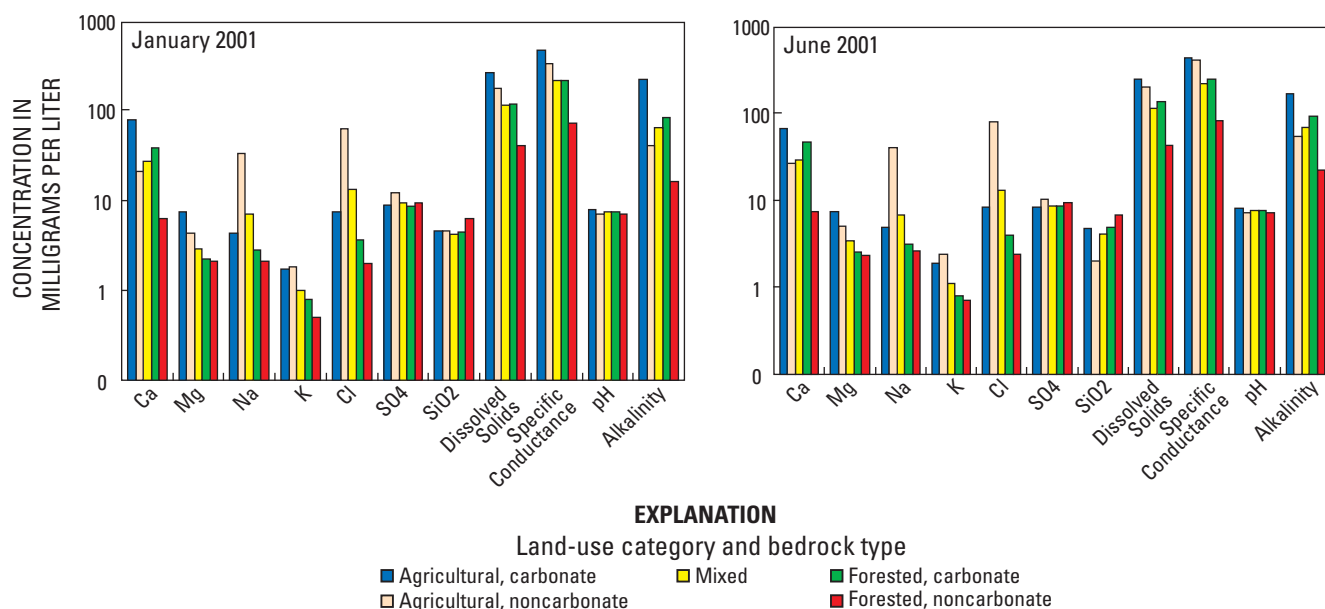


Figure 4B. Concentrations of inorganic constituents in base-flow samples collected in January and June 2001 in the upper Susquehanna River Basin, N.Y. (Land-use category and bedrock type shown in fig. 4A and table 1.)

Table 2. Mean, median, maximum, and minimum values for solutes, pH, and specific conductance of base-flow samples from upper Susquehanna River Basin study area, N.Y., January and June 2001.
[Concentrations are in milligrams per liter; pH in units, specific conductance in microsiemens per centimeter. n = number of samples.]

| Constituent or physical property | Agricultural, carbonate (n = 4) | | Agricultural, noncarbonate (n = 1) | | Mixed land use and bedrock (n = 6) | | Forested, carbonate (n = 1) | | Forested, noncarbonate (n = 6) | |
|--|---------------------------------------|-------|--|-------|--|-------|-----------------------------------|-------|--------------------------------------|-------|
| | January | June | January | June | January | June | January | June | January | June |
| Calcium (Ca) | | | | | | | | | | |
| mean | 74.6 | 64.5 | 15.2 | 26.1 | 27.8 | 30.1 | 29.9 | 45.8 | 6.0 | 10.9 |
| median | 87.2 | 65.8 | | | 25.3 | 28.8 | | | 4.3 | 7.3 |
| maximum | 95.5 | 94.1 | | | 51.1 | 53.1 | | | 13.7 | 30.0 |
| minimum | 28.3 | 32.1 | | | 9.2 | 8.2 | | | 2.9 | 5.0 |
| Magnesium (Mg) | | | | | | | | | | |
| mean | 7.5 | 7.9 | 3.5 | 5.0 | 2.9 | 6.8 | 1.9 | 2.5 | 1.8 | 2.8 |
| median | 7.5 | 7.4 | | | 2.8 | 3.4 | | | 1.7 | 2.3 |
| maximum | 12.7 | 14.7 | | | 3.9 | 24.5 | | | 3.2 | 5.9 |
| minimum | 2.2 | 2.4 | | | 2.2 | 2.7 | | | 0.9 | 1.4 |
| Sodium (Na) | | | | | | | | | | |
| mean | 3.9 | 4.7 | 26.0 | 39.1 | 7.3 | 6.4 | 2.4 | 3.1 | 5.3 | 7.1 |
| median | 3.8 | 4.9 | | | 7.5 | 6.7 | | | 1.7 | 2.6 |
| maximum | 6.0 | 6.1 | | | 8.4 | 8.9 | | | 23.7 | 28.1 |
| minimum | 2.2 | 2.9 | | | 5.5 | 2.4 | | | 1.3 | 1.9 |
| Potassium (K) | | | | | | | | | | |
| mean | 1.5 | 1.7 | 1.2 | 2.4 | 1.0 | 1.1 | 0.7 | 0.8 | 0.5 | 1.2 |
| median | 1.7 | 1.9 | | | 1.0 | 1.1 | | | 0.5 | 0.7 |
| maximum | 1.7 | 2.6 | | | 1.3 | 1.4 | | | 1.0 | 4.2 |
| minimum | 0.9 | 0.4 | | | 0.7 | 0.5 | | | 0.2 | 0.3 |
| Chloride (Cl) | | | | | | | | | | |
| mean | 7.2 | 7.9 | 48.1 | 77.2 | 12.9 | 11.5 | 3.3 | 3.9 | 8.7 | 12.7 |
| median | 7.0 | 8.2 | | | 13.0 | 12.9 | | | 1.4 | 2.4 |
| maximum | 9.9 | 10.9 | | | 15.1 | 16.4 | | | 45.2 | 59.5 |
| minimum | 4.8 | 4.5 | | | 10.6 | 1.6 | | | 0.9 | 1.0 |
| Sulfate (SO₄²⁻) | | | | | | | | | | |
| mean | 15.6 | 19.7 | 13.7 | 10.1 | 10.1 | 8.9 | 8.7 | 8.5 | 9.1 | 8.3 |
| median | 10.0 | 8.2 | | | 9.8 | 8.6 | | | 9.4 | 9.2 |
| maximum | 37.3 | 58.4 | | | 12.9 | 10.3 | | | 12.1 | 9.9 |
| minimum | 5.0 | 3.9 | | | 8.5 | 8.1 | | | 5.7 | 4.7 |
| Silica (SiO₂) | | | | | | | | | | |
| mean | 4.1 | 4.0 | 7.1 | 2.0 | 4.2 | 3.9 | 4.0 | 4.8 | 5.9 | 6.4 |
| median | 4.2 | 4.7 | | | 4.4 | 4.1 | | | 5.8 | 6.7 |
| maximum | 4.5 | 5.6 | | | 4.9 | 4.9 | | | 7.0 | 7.5 |
| minimum | 3.5 | 1.1 | | | 3.1 | 2.8 | | | 4.5 | 4.0 |
| Dissolved solids | | | | | | | | | | |
| mean | 249.8 | 222.0 | 149.0 | 198.0 | 116.5 | 108.8 | 102.0 | 133.0 | 50.2 | 65.5 |
| median | 278.0 | 240.5 | | | 114.0 | 112.0 | | | 35.0 | 42.0 |
| maximum | 329.0 | 298.0 | | | 183.0 | 158.0 | | | 130.0 | 181.0 |
| minimum | 114.0 | 109.0 | | | 54.0 | 43.0 | | | 28.0 | 39.0 |
| pH | | | | | | | | | | |
| mean | 7.7 | 8.0 | 6.5 | 7.2 | 7.0 | 7.6 | 7.2 | 7.6 | 6.5 | 7.2 |
| median | 7.7 | 8.0 | | | 7.0 | 7.6 | | | 6.5 | 7.2 |
| maximum | 8.1 | 8.1 | | | 7.7 | 8.2 | | | 6.8 | 7.5 |
| minimum | 7.3 | 7.8 | | | 6.2 | 6.8 | | | 6.0 | 7.1 |
| Specific conductance | | | | | | | | | | |
| mean | 400.3 | 392.3 | 266.0 | 396.0 | 215.5 | 210.5 | 185.0 | 239.0 | 83.8 | 126.0 |
| median | 495.0 | 424.5 | | | 208.5 | 212.0 | | | 56.0 | 80.0 |
| maximum | 576.0 | 519.0 | | | 332.0 | 335.0 | | | 247.0 | 368.0 |
| minimum | 35.0 | 201.0 | | | 115.0 | 79.8 | | | 34.0 | 67.3 |
| Alkalinity (as CaCO₃) | | | | | | | | | | |
| mean | 216.3 | 162.5 | 26.0 | 54.0 | 67.5 | 70.7 | 73.0 | 90.0 | 10.8 | 28.9 |
| median | 237.0 | 164.5 | | | 61.0 | 68.0 | | | 8.5 | 21.9 |
| maximum | 246.0 | 240.0 | | | 132.0 | 136.0 | | | 20.0 | 73.0 |
| minimum | 145.0 | 81.0 | | | 19.0 | 23.0 | | | 5.0 | 11.0 |

IV. WATER QUALITY (CONTINUED)

C. Effect of carbonate bedrock on base-flow quality

Carbonate minerals in bedrock and unconsolidated deposits affect base-flow quality.

The study area was divided into two water-quality domains on the basis of bedrock type—the northern part, underlain by carbonate rocks and blanketed by carbonate-rich surficial deposits, and the central and southern parts, underlain by noncarbonate bedrock and mainly noncarbonate surficial deposits.

The presence of carbonate material in a subbasin increases the concentration of calcium (Ca) and the alkalinity and, therefore, the specific conductance and dissolved-solids concentrations of base flow. Carbonate minerals (calcium and magnesium carbonates) are more soluble than the silicate minerals that make up the remainder of the bedrock and glacial deposits; thus, the dissolved mineral content of water where carbonate minerals are abundant is typically much higher (and the water much “harder”). The northern part of the study area is underlain mostly by carbonate-rich bedrock of the Onondaga Formation (limestone), the Helderberg Group (limestones and dolostones), and the Marcellus Formation (calcareous shales, sandstone, and limestone) (fig. 3C); the central and southern parts are underlain by sandstone, siltstone, and shales that contain little carbonate.

Glaciers eroded the carbonate rocks in the northern part of the study area and deposited them as carbonate-rich till throughout the uplands and for many miles southward into the noncarbonate-bedrock area. Meltwater during deglaciation transported carbonate-rich fluvial sediments several tens of miles down major valleys. For example, sand and gravel terraces whose composition is at least 40 percent limestone clasts are found in the Unadilla River valley north of South Edmeston, the Susquehanna River valley north of Index, and Cherry Valley north of Middlefield (Ku and others, 1975).

The study area was divided into two water-quality domains that reflect the presence or absence of carbonate material. The northern domain (Area A in

fig. 4C) is underlain by carbonate bedrock, its uplands contain carbonate-rich till, or the glacial deposits in the major valleys are at least 10 percent carbonate pebbles. Area B to the south is underlain by noncarbonate shale, siltstone, and sandstone, the till in the uplands contains little carbonate material, and the glacial deposits in the major valleys are less than 10 percent carbonate pebbles (percentages from Ku and others, 1975). The median concentration of calcium, and the median alkalinity and specific conductance values of base flow in the major valleys of Area A were markedly higher than those in Area B. Upland sites in both areas had much lower concentrations of calcium and alkalinity, and lower specific conductance values than the valley sites, and the upland sites in Area A had higher concentrations of calcium and alkalinity, and higher specific conductance values, than upland sites in Area B (table 3).

Streams throughout Area B were similar in water quality and had fairly low concentrations of major cations and anions (table 2). Three sampling sites in Area B [sites 10, 12, and 18] have their headwaters in Area A and were along the main-stem of the Unadilla or Susquehanna Rivers, receive water from subbasins representing more than one land-use and bedrock category, and had drainage areas larger than 100 mi² (fig. 4C). Median calcium and alkalinity concentrations and specific conductance values for these “mixed” sites are intermediate between those of the agricultural carbonate-bedrock sites and the forested noncarbonate-bedrock sites (fig. 4C).

Table 3. Median concentrations of calcium and alkalinity and specific conductance values in base-flow samples from Area A (underlain by carbonate bedrock) and Area B (underlain by noncarbonate bedrock), January and June 2001.

[Locations of Areas A and B are shown in fig. 4C. mg/L, milligrams per liter; μ S/cm, microsiemens per centimeter.]

| Area | Site description | No. of samples | Calcium (mg/L) | Alkalinity as CaCO ₃ (mg/L) | Specific conductance (μ S/cm) |
|---------------------|------------------|----------------|----------------|--|------------------------------------|
| A (carbonate) | Upland sites | 2 | 31 | 91 | 193 |
| | Valley sites | 4 | 87 | 234 | 495 |
| B (noncarbonate) | Upland sites | 6 | 5 | 14 | 66 |
| | Valley sites | 6 | 26 | 61 | 233 |

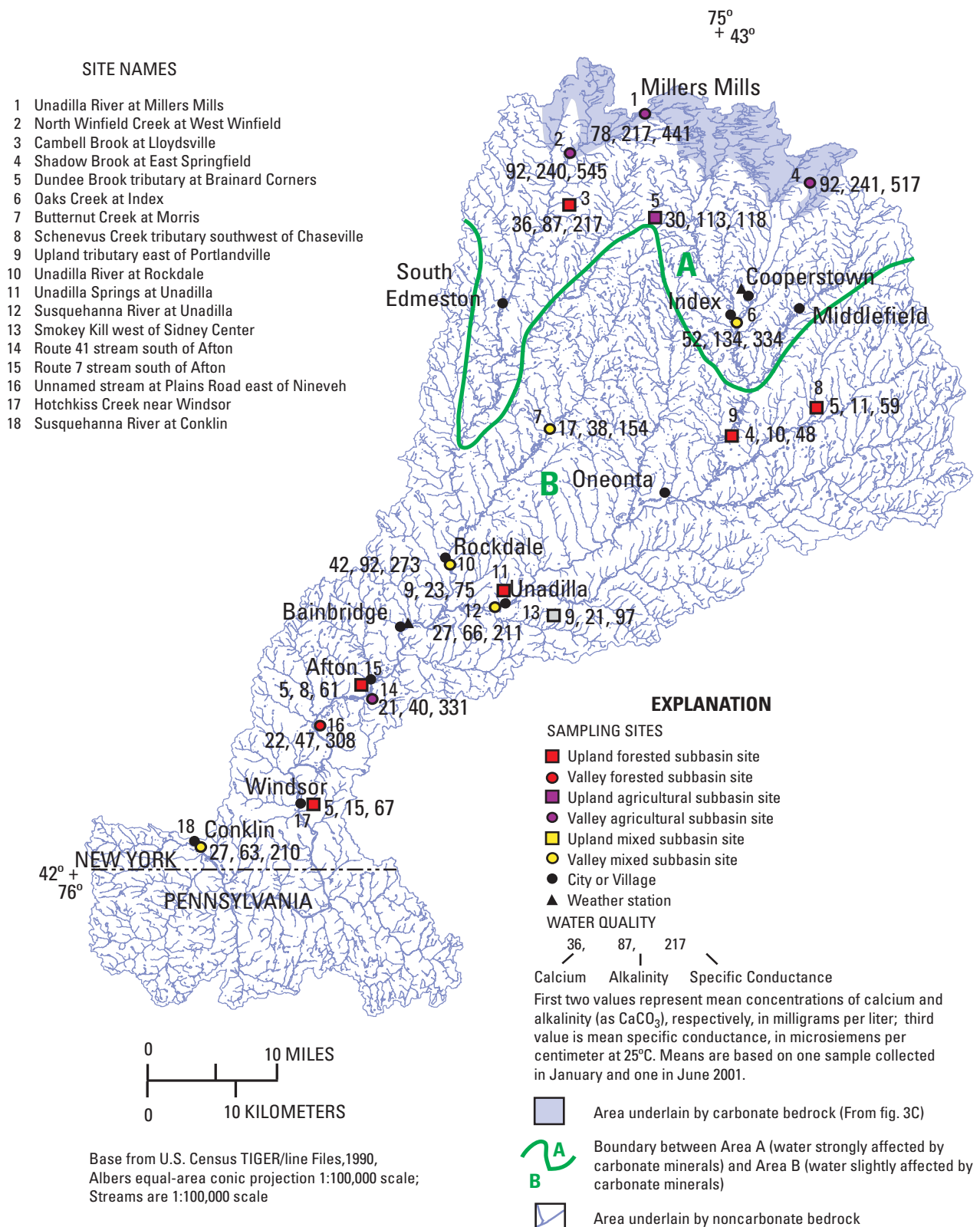


Figure 4C. Mean concentrations of calcium and alkalinity, and mean specific conductance, for water samples collected during base-flow conditions in Areas A and B of the upper Susquehanna River Basin, N.Y., January and June 2001.

IV. WATER QUALITY (CONTINUED)

D. Nitrogen

Nitrogen concentration in water can be an indicator of water quality.

Nitrogen is vital to the growth of vegetation, but too much nitrogen in streams, derived mainly from fertilizers and sewage, can cause excessive plant and algal growth that can clog waterways and deplete oxygen needed by other aquatic life.

Nitrogen sustains the growth of plants. It is derived from precipitation, biological fixation of nitrogen, and the decomposition of organic matter, but rarely in amounts sufficient to replenish the nitrogen lost from the soils through the harvesting of crops and denitrification (conversion of nitrogen to unusable N_2 gas by soil bacteria). Therefore, most crops require fertilizer.

Excessive amounts of nitrogen within a water body stimulate the growth of algae and aquatic plants that can clog waterways and deplete oxygen needed by other aquatic life (fig. 4D). The chemical fertilizers and manure that are applied to agricultural land, and fertilizers used by homeowners and commercial lawn-care companies, can be washed into rivers and streams; effluent from point sources such as sewer-overflow pipes also add substantial amounts of nitrogen to rivers. Excessive nitrate in drinking water is also a human health concern; as a result, the U.S. Environmental Protection Agency (USEPA) has established 10 mg/L (as N) as the maximum contaminant level of nitrate in drinking water (USEPA, 2000). Recent initiatives by Federal, State, and local governments to provide water-treatment-facility upgrades have led to decreased nitrogen loadings to waterways, and measures such as crop rotation and erosion control have decreased the erosion of soil. Nevertheless, runoff from agricultural areas throughout the Susquehanna River Basin has been a major cause of eutrophication in Chesapeake Bay.

Nitrogen occurs in terrestrial and aquatic systems in several forms that are interconverted through what is known as the nitrogen cycle (table 4)

(Maidment, 1993). The predominant form of nitrogen in stream water is nitrate. The principal source of nitrate that enters terrestrial and aquatic systems is nitrification of ammonia, which entails two steps that are brought about primarily by aerobic bacteria. The first step oxidizes ammonia (NH_4^+) to nitrite (NO_2^-), and the second step oxidizes NO_2^- to nitrate (NO_3^-). Nitrite generally does not accumulate during nitrification; rather, it is oxidized to NO_3^- as quickly as it forms. The conversion of ammonia to nitrite requires oxygen; therefore, waters receiving large loadings of ammonia have a considerable demand for oxygen.

The principal nitrate sinks are denitrification to gaseous forms, and assimilation by plants. Denitrification is carried out by anaerobic bacteria that reduce nitrate to the gaseous forms (N_2 and N_2O) in oxygen-poor conditions, which are common in many aquatic systems. Assimilation entails the consumption of inorganic nitrogen by plants and algae to form organic nitrogen. Nitrogen fixation is the reduction of nitrogen gas (N_2) to ammonia and organic nitrogen; plants that “fix” nitrogen are the source of virtually all nitrogen used by living organisms. Ammonification (mineralization) is the conversion of organic nitrogen to ammonia. Heterotrophic conversion is the conversion of organic nitrogen from one organic compound to another when organisms consume organic matter.

The base-flow samples collected in January and June 2001 were analyzed for several nitrogen species; the predominant species in all samples was nitrate. (See sections IV-E, IV-F.)



Figure 4D. Agricultural field in the upper Susquehanna River Basin, N.Y.

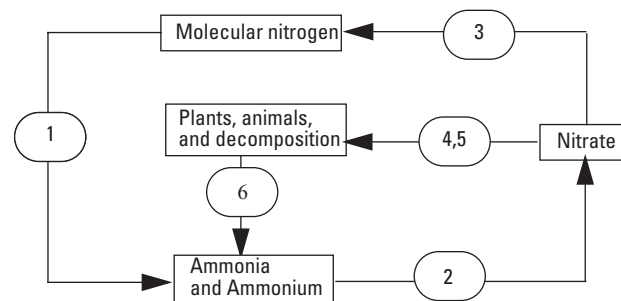


Table 4. Six biological transformation processes of the nitrogen cycle.
[Modified from Atlas, 1998.]

| Process | Description |
|-----------------------------|--|
| 1. Nitrogen fixation | biological and industrial reduction of molecular nitrogen gas (N_2) to ammonia (NH_3) and organic nitrogen (ammonium; NH_4^+) |
| 2. Nitrification | aerobic bacterial oxidation of ammonia (NH_3) to nitrite (NO_2^-), then from nitrite to nitrate (NO_3^-) |
| 3. Denitrification | anaerobic bacterial reduction of nitrate to gaseous forms—nitric oxide (NO), nitrous oxide (N_2O) and molecular nitrogen (N_2)—under anoxic conditions |
| 4. Assimilation | inorganic forms of nitrogen (NO_3^-) are absorbed and incorporated (as food) by autotrophic algae and higher plants to form organic nitrogen |
| 5. Heterotrophic conversion | conversion of organic nitrogen from one organic compound to another when organisms consume organic matter |
| 6. Ammonification | decomposition of organic nitrogen to ammonia |

IV. WATER QUALITY (CONTINUED)

E. Nitrate - seasonal patterns

Nitrate concentrations in base flow fluctuated seasonally in all subbasins.

Nitrate concentrations in streamflow are lowest in summer when the growth of aquatic plants results in consumption of nitrogen, and increased denitrification and minimal recharge inhibit the migration of nitrate to the stream. Nitrate concentrations are highest during winter, when nitrate moves into streams through increased recharge, and aquatic plant growth is minimal.

Nitrate concentration in base flow fluctuates seasonally and is highest in winter (Bauters and Eckhardt, 1999; Lindsey and others, 1997). The summer decrease can be attributed to a combination of factors, including (1) microbial processes in anaerobic sediments along streambanks increase in summer, thereby decreasing the nitrate concentrations in base flow through denitrification (Lindsey and others, 1997), (2) summer recharge of shallow ground water is lower than in the winter because most rainfall is lost to ET, which thereby inhibits the movement of nitrogen from the soil into the stream, and (3) nitrogen in the soil is taken up by plant roots and soil biota during the growing season. However, the strongest influence on nitrate concentrations in summer base flow can be attributed to algae and other aquatic plants that consume much of the nitrate that enters the stream, resulting in apparent decreases in nitrate concentrations.

During the fall and winter, (1) temperatures and biologic activity (plant and algae growth) in streams decrease, allowing more nitrate from ground-water recharge to persist in base flow, (2) decreasing temperatures inhibit the denitrification process along the stream, (3) less rainfall is lost to ET, resulting in more shallow ground-water recharge to the stream, and (4) plants within the subbasin consume less nitrogen. Therefore, cold-weather, non-growing-season base-flow samples are better indicators of nutrient concentrations in ground-water discharge than are samples collected during the summer.

An exception was noted in the June 2000 samples from two streams in agricultural subbasins (sites 2 and 14 in fig. 4E and table 1). These streams were sampled during base-flow conditions in January, June, and September of 2001; the stream at site 2 was also sampled in August 2001. The nitrate concentrations in the January and June samples from site 2 had the highest nitrate concentrations of any site sampled during this study (2.27 mg/L and 2.40 mg/L, respectively). The relative proportions of nitrate in the January, August, and September base-flow samples at

site 2 show the effects of increased biologic activity (and lower nitrate concentrations) in the streams that would be expected during warmer months and decreased biologic activity (and higher nitrate concentrations) in the streams during the colder months. However, the elevated June concentrations at both sites may be influenced by fertilizer and manure applications to agricultural fields near these streams before the samples were collected.

Two sites in large, mixed land use subbasins (sites 10 and 18 in fig. 4E and table 1) had their greatest nitrate concentrations in the January samples, concentrations decreased in the June samples, and were lowest in the September samples. These sites did not show the early-summer nitrate peak seen at the agricultural sites in figure 4E, possibly because these sites represent mixed subbasins that are much larger than the agricultural subbasins and contain a smaller percentage of agricultural land, and (or) because much of their base flow is from thick glacial deposits that provide relatively long ground-water travel times that would obscure seasonal changes in base-flow chemistry.

Nitrate concentrations at site 9, a small upland stream that drains a forested basin (fig. 4E) differ markedly from those at the agricultural and main-stem sites—the nitrate concentrations in the January and June samples from this site were the lowest of all January and June samples in the study and also were lower than the August and September nitrate concentrations at this site. The most likely reason is that this forested subbasin receives no applications of manure or other fertilizers, and its soils are thin and could become quickly saturated by any late-summer and fall storms. This would allow any nitrate to be flushed through the hydrologic system quickly and would result in relatively low nitrate concentrations in base flow during winter.

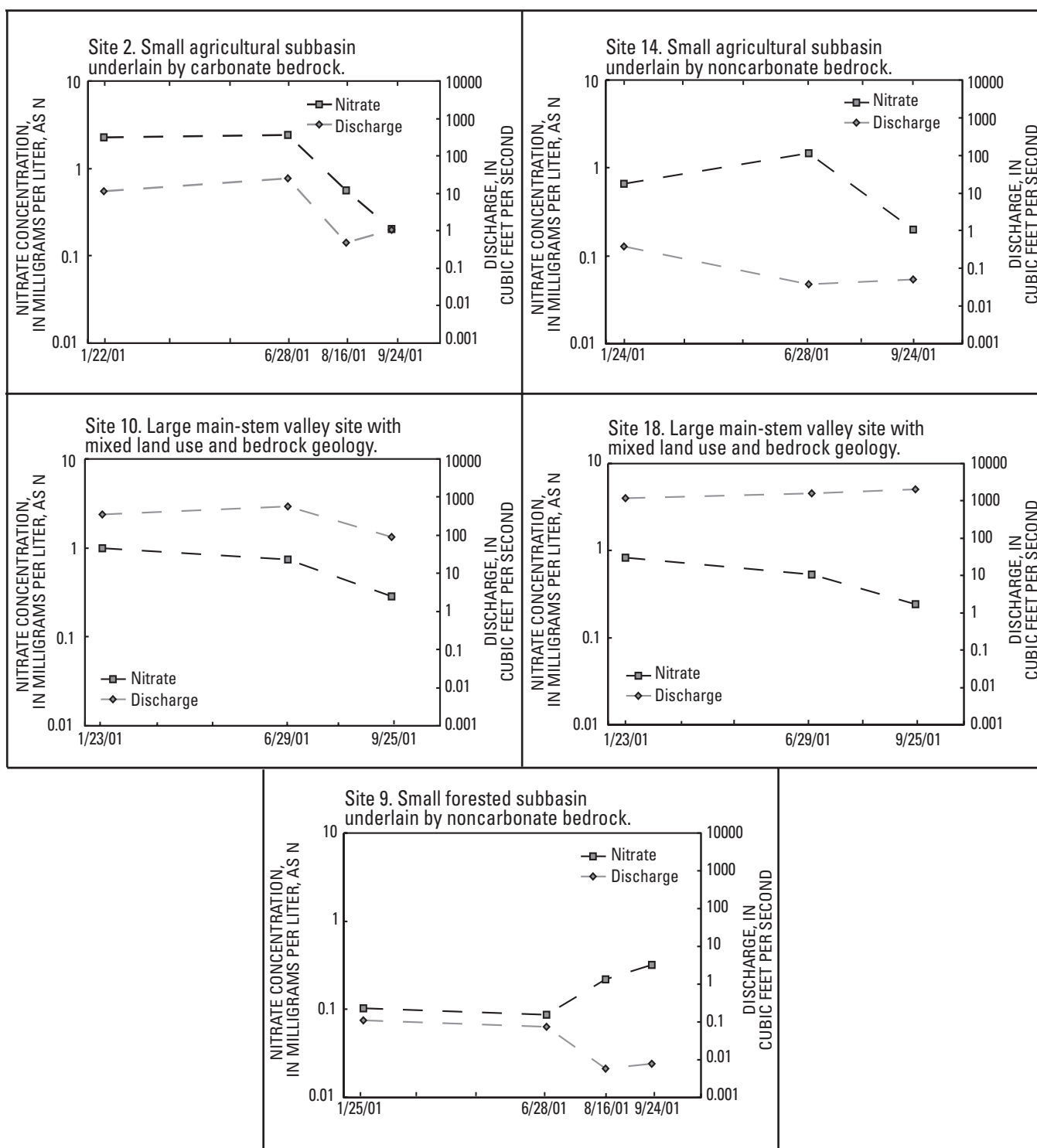


Figure 4E. Nitrate concentration and discharge of five streams within the upper Susquehanna River Basin, N.Y., on selected base-flow sampling dates, 2001, by land-use and bedrock category. (Site locations are shown in fig. 1.)

IV. WATER QUALITY (CONTINUED)

F. Nitrate - spatial patterns

Spatial patterns of nitrate concentrations in base flow reflect land use.

Median base-flow nitrate concentrations were highest in samples from subbasins dominated by agriculture and lowest in samples from forested subbasins; mixed land-use watersheds had intermediate nitrate concentrations.

The nitrate concentrations in the January and June 2001 samples from all sites reflect the effects of the dominant land use within the subbasins on nitrate concentrations. In general, the highest median nitrate

concentrations were in agricultural subbasins, the lowest were in forested subbasins, and those in mixed (agricultural and forested) subbasins were intermediate (fig. 4f, table 5).

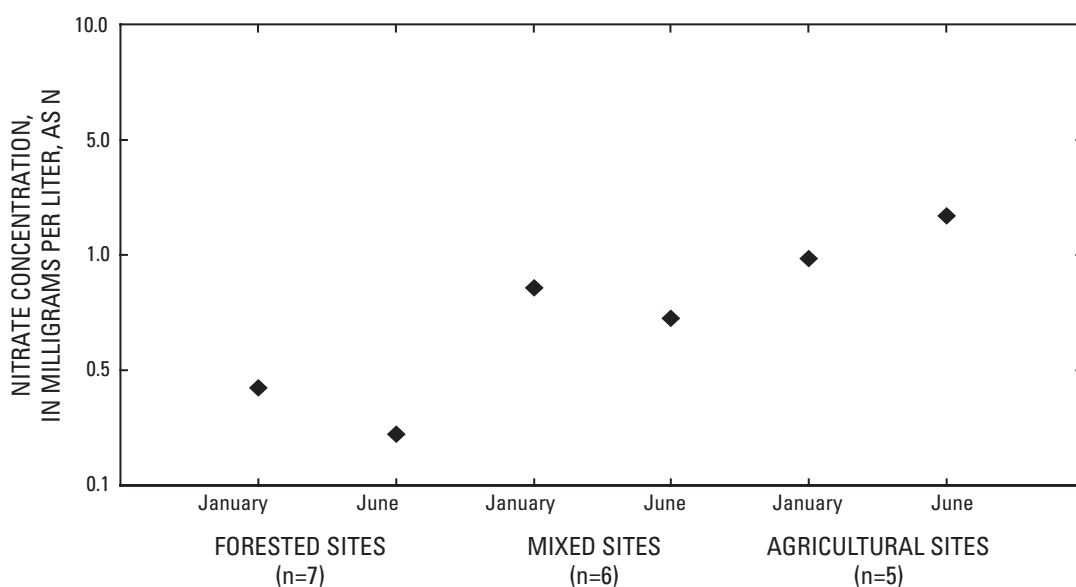


Figure 4F. Median nitrate concentrations in base-flow samples from the 18 stream sites in the upper Susquehanna River Basin, N.Y., January and June 2001, by land-use category. (Site locations with land-use category shown in fig. 4A and table 1.)

Table 5. Mean, median, maximum, and minimum concentrations of nitrate in base-flow samples from upper Susquehanna River Basin study area, N.Y., by land-use and bedrock category, January and June 2001.

| Statistic | Agricultural, carbonate (n = 4) | | Agricultural, noncarbonate (n = 1) | | Mixed land use and bedrock (n = 6) | | Forested, carbonate (n = 1) | | Forested, noncarbonate (n = 6) | |
|-----------|---------------------------------------|------|--|------|--|------|-----------------------------------|------|--------------------------------------|------|
| | January | June | January | June | January | June | January | June | January | June |
| mean | 1.46 | 1.62 | .662 | 1.47 | .713 | .526 | .344 | .591 | .302 | .242 |
| median | 1.43 | 1.69 | | | .775 | .567 | | | .175 | .119 |
| maximum | 2.27 | 2.40 | | | .996 | .743 | | | .674 | .902 |
| minimum | .708 | .692 | | | .30 | .183 | | | .102 | .938 |

IV. WATER QUALITY (CONTINUED)

G. Pesticides

Six pesticide compounds were detected in base-flow samples.

Samples from 10 of the 12 sites sampled for pesticides in November 2001 contained at least one pesticide. The concentrations of these pesticides were at least an order of magnitude below any New York State or Federal limit.

Information on the distribution and concentrations of pesticides in ground water and surface water in the study area is scant, but recent studies in other parts of New York have shown seasonal trends in pesticide concentrations in ground water and correlations between pesticide occurrence and land use (Eckhardt and others, 1999, 2001; Phillips and others, 1998, 1999a, 1999b).

Base-flow samples were collected at 12 sites in November 2001 (fig. 4G) and analyzed for the 113 pesticides or their degradates listed in table 6.

(Degradates are the degradation products of parent compounds.) The concentrations of all pesticides detected were at least an order of magnitude below any New York State or Federal limit. However, samples were collected in November, several months after the summer applications to fields, lawns, roads, and utility rights-of-way; this indicates that the compounds detected in base flow were derived from a sustained ground-water contribution and are probably not the result of direct runoff from land surface.

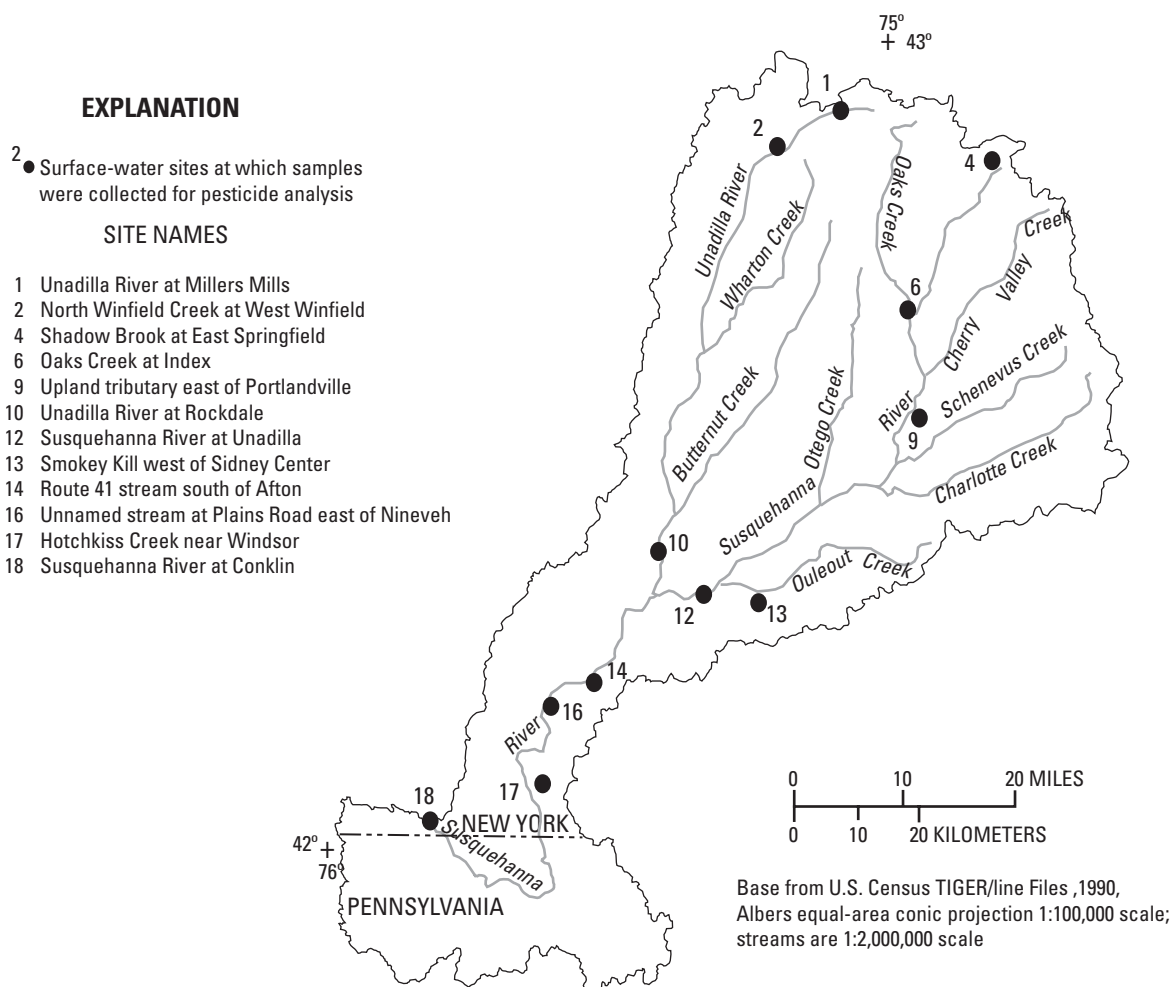


Figure 4G. Locations of the 12 sites in the upper Susquehanna River Basin, N.Y., where water samples were analyzed for pesticides, November 2001. (USGS station numbers are given in table 1.)

Table 6. Pesticides for which base-flow samples collected from 12 sites in upper Susquehanna River Basin in November 2001 were analyzed.

[Boldface type indicates compound detected in this study. Asterisk indicates degradation product.]

| Compounds for which samples were analyzed | | |
|---|------------------------------|---------------------|
| 2,4-D | Deisopropylatrazine * | Metribuzin |
| 2,4-D methyl ester * | Deethyldeisopropylatrazine * | Molinate |
| 2,4-DB | Diazinon | Napropamide |
| 2,6-Diethylaniline * | Dicamba | Neburon |
| 2-Hydroxyatrazine * | Dichlorprop | Nicosulfuron |
| 3-(4-chlorophenyl)-1-methyl urea * | Dieldrin | Norflurazon |
| 3-Hydroxycarbofuran * | Dimethenamid ESA * | Oryzalin |
| 3-ketocarbofuran * | Dimethenamid OA * | Oxamyl |
| Acetachlor ESA * | Dinoseb | Oxamyl oxime * |
| Acetachlor OA * | Diphenamid | p,p'-DDE * |
| Acifluorfen | Diuron | Parathion |
| Alachlor ESA * | Disulfoton | Parathion-methyl |
| Alachlor OA * | EPTC | Pebulate |
| Alachlor | Ethalfuralin | Pendimethalin |
| Aldicarb | Ethopropos | cis-Permethrin |
| Aldicarb sulfone * | Fenuron | Phorate |
| Aldicarb sulfoxide * | Flufenacet OA * | Picloram |
| alpha-HCH | Flufenacet ESA * | Prometon |
| Atrazine | Flumetsulam | Propachlor |
| Bendiocarb | Fluometuron | Propanil |
| Benfluralin | Fonofos | Propargite |
| Benomyl | Imazaquin | Propham |
| Bensulfuron-methyl | Imazethapyr | Propiconazole |
| Bentazon | Imidacloprid | Propyzamide |
| Bromacil | Lindane | Propoxur |
| Bromoxynil | Linuron | Siduron |
| Butylate | MCPA | Simazine |
| Carbaryl | MCPB | Sulfometuron methyl |
| Carbofuran | Malathion | Tebuthiuron |
| Chloramben methyl ester * | Metalaxyl | Terbacil |
| Chlorimuron-ethyl * | Methiocarb | Terbufos |
| Chlorothalonil | Methomyl | Terbuthylazine |
| Chlorpyrifos | Methomyl oxime * | Thiobencarb |
| Clopyralid | Methyl azinphos | Tri-allate |
| Cycloate | Metsulfuron-methyl | Tribenuron-methyl |
| Dacthal | Metolachlor | Triclopyr |
| Dacthal mono-acid * | Metolachlor ESA * | Trifluarlin |
| Deethylatrazine * | Metolachlor OA * | |

IV. WATER QUALITY (CONTINUED)

H. Detected herbicides

All six of the pesticide compounds detected were agricultural herbicides.

Two of the compounds (atrazine and deethylatrazine) were found in samples from every stream in which a pesticide was detected.

The six pesticide compounds that were detected were agricultural herbicides—a class of pesticides used to control broadleaf weeds and grasses in fields, lawns, utility right-of-ways, and other areas. These herbicides and their degradates are usually highly soluble and can move through the hydrologic system in surface runoff or ground water. Their toxicity to humans is relatively low compared to that of insecticides (Ware, 1983), which are used more extensively than pesticides in residential and urban areas (Templeton and others, 1998) and were not detected in this study. The measured concentrations did not exceed any New York State or Federal regulatory limits (table 7).

Ten of the 12 streams that were sampled for pesticides contained at least one of these herbicides, and one of these streams (site 16, forested) contained all six compounds (fig. 4H). Two of the compounds (atrazine and deethylatrazine) were found in samples from all 10 of the streams in which a pesticide was detected.

Atrazine is one of the most commonly used pesticides in the nation (Koplin and others, 1998; Larson and others, 1999) and has been the pesticide detected most frequently in previous ground-water and surface-water studies in the United States as a result of its wide-spread use (Barbash and Resek, 1996). Its maximum concentration during this study was 0.073 µg/L. Deethylatrazine is a degradate of atrazine and was detected at a maximum concentration of 0.024 µg/L.

Metolachlor ESA, the ethanesulfonic acid degradate of metolachlor, was detected in samples from nine sites and had a maximum concentration of 1.26 µg/L. Metolachlor was detected in samples from six sites, and metolachlor OA, the oxanilic acid

degradate of metolachlor, was detected in samples from three sites; the maximum concentrations were 0.417 µg/L and 1.19 µg/L, respectively. Alachlor ESA, a degradate of alachlor, was detected in samples from two sites; the maximum concentration was 0.08 µg/L.

The pesticide analyses indicate a correlation between atrazine and deethylatrazine concentrations and land use. Samples from the four subbasins with the highest percentages of agricultural land (sites 1, 2, 4, and 14; table 1) had the highest concentrations of atrazine plus deethylatrazine (fig. 4H). Samples from two of the subbasins dominated by forested land with virtually no agricultural land (sites 9 and 17; table 1) contained no pesticides. The anomalously high pesticide detections at sites 14 and 16 are discussed in the next section (IV-I).

Metolachlor did not show a strong correlation with land use; it was detected in samples from two agricultural sites, one forested site, and all three main-stem river sites sampled (fig. 4H). Metolachlor ESA and OA, where detected, were at higher concentrations than metolachlor. Similarly, alachlor was not detected, but its degradate, alachlor ESA, was detected in samples from two sites. Concentrations of parent compounds can exceed those of their degradates if the parent compounds are flushed into streams by precipitation soon after application (Eckhardt and others, 2001), but the summer of 2001 in the study area was dry, and the pesticide sampling was not until November. Thus, the lack of precipitation allowed the parent compounds time to break down into their degradation products within the soils, from which the degradation products were transported to ground water before the November sampling.

Table 7. Sites and concentrations at which herbicides were detected in November 2001 base-flow samples from upper Susquehanna River Basin, and Federal or State concentration limit (USEPA, 2000). [Site locations are shown in fig. 4G and listed in table 1. Dash indicates no limit has been established. µg/L, micrograms per liter.]

| Name | Sites | Maximum detected concentration (µg/L) | Federal or State limit (µg/L) |
|-----------------|------------------------------------|---------------------------------------|-------------------------------|
| Alachlor ESA | 12, 16 | 0.08 | -- |
| Atrazine | 1, 2, 4, 6, 10, 12, 13, 14, 16, 18 | 0.073 | 3.0 |
| Deethylatrazine | 1, 2, 4, 6, 10, 12, 13, 14, 16, 18 | 0.024 | -- |
| Metolachlor | 2, 10, 12, 14, 16, 18 | 0.417 | 50 |
| Metolachlor ESA | 1, 2, 4, 6, 10, 12, 14, 16, 18 | 1.26 | 50 |
| Metolachlor OA | 10, 14, 16 | 1.19 | 50 |

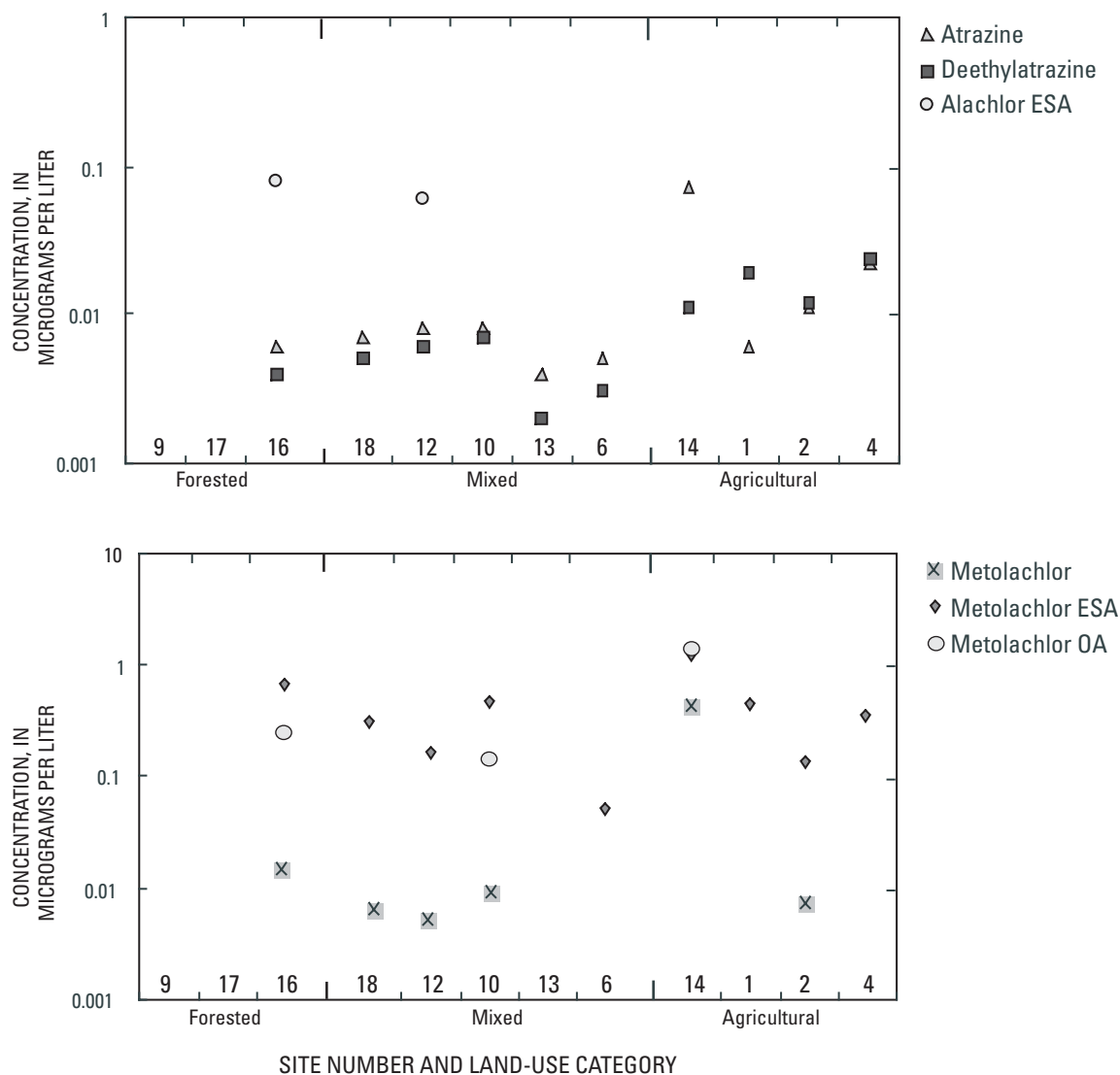


Figure 4H. Concentrations of the six herbicides detected (atrazine, deethylatrazine, alachlor ESA, metolachlor, and its two metabolites) in relation to land use at the 12 sites sampled under base-flow conditions in the upper Susquehanna River Basin, N.Y., November 2001. (Site locations are shown in fig. 4G.)

IV. WATER QUALITY (CONTINUED)

I. Two streams with anomalous salt and herbicide concentrations

Two streams sampled during this study contained chemicals in concentrations indicative of deicing salt and herbicide applications within the subbasin.

Samples from two streams near Interstate 88 in the southern part of the study area had higher concentrations of iron, manganese, sodium chloride, and several pesticides than the other sites.

Two small tributaries to the Susquehanna River in the south-central part of the study are—sites 14 (agricultural) and 16 (forested)—that were sampled in January and June 2001 for nutrient and common inorganic constituent analyses (table 2) and in November 2001 for pesticide analysis (table 6) showed higher concentrations of sodium, chloride, manganese, iron, and the herbicides atrazine, metolachlor, metolachlor ESA, and metolachlor OA than all other sites sampled.

The elevated sodium and chloride concentrations in these two streams are probably the result of road salting on Interstate 88 (I-88), a major four-lane divided highway that crosses the drainage area of each stream less than 0.5 mi upstream from the sampling sites. Construction of I-88 in the 1970s entailed the channelizing of many natural drainages and the routing of many channels through culverts beneath the highway. The new drainage patterns may increase the runoff of precipitation and might also channel highway runoff toward these streams.

Deicing salt (NaCl) is initially applied to I-88 at rates of 225 to 270 lb/mi per lane during snowstorms; if a second application is required, 115 to 270 lb/mi per lane is applied (New York State Department of Transportation, 1994). The high concentrations of sodium and chloride in the June base-flow samples from these streams, as well as the January samples, indicate that road salt is probably reaching these streams as dissolved sodium and chloride in ground water throughout the year.

These two streams also had the highest concentrations of four herbicides (atrazine, metolachlor, and the two metolachlor degradates) of all streams sampled (fig. 4I), although the concentrations did not exceed State or Federal limits. Pesticides are applied to transportation rights-of-way along I-88 to control the growth of broad-leaf

weeds and grasses (Edward Capria, New York State Department of Transportation, Chenango County Division, oral commun., 2002). A utility corridor (powerline) runs just east of I-88 in the headwaters of these two sites; thus, the application of herbicides along this corridor, as well as along the highway, could be the principal source of these constituents in the two streams. Runoff from cornfields that surround the stream above site 14 also could be contributing some of the metolachlor and atrazine.

Base-flow samples from sites 8, 14, and 16 (locations shown in fig. 1) also had higher concentrations of iron and manganese than samples from the other sites (fig. 4I). These indicate anoxic, acidic conditions probably caused by the decay of organic matter that would dissolve iron and manganese minerals within the alluvial and glacial deposits, and once the water bearing these minerals discharges to the stream, the iron and manganese would precipitate, either through redox reactions (higher redox potential within the stream water than within the alluvial material), or through iron-converting bacteria along the streambank, which live in the interface between anoxic conditions of the riparian soil and the oxygenated surface-water environment (Hem, 1992, p. 83-89).

The mean concentrations of sodium, chloride, iron, manganese, and the four herbicides at sites 14 and 16 are plotted in relation to those at all other sites in figure 4I. The concentrations of these constituents at both sites are shown to exceed those at the other sites, and the manganese concentration at sites 14 and 16 exceeded the U.S. Environmental Protection Agency's SMCL (secondary maximum contaminant level) of 50 µg/L, as did the iron concentration at sites 8 and 14 (SMCL 300 µg/L) (U.S. Environmental Protection Agency, 2000).

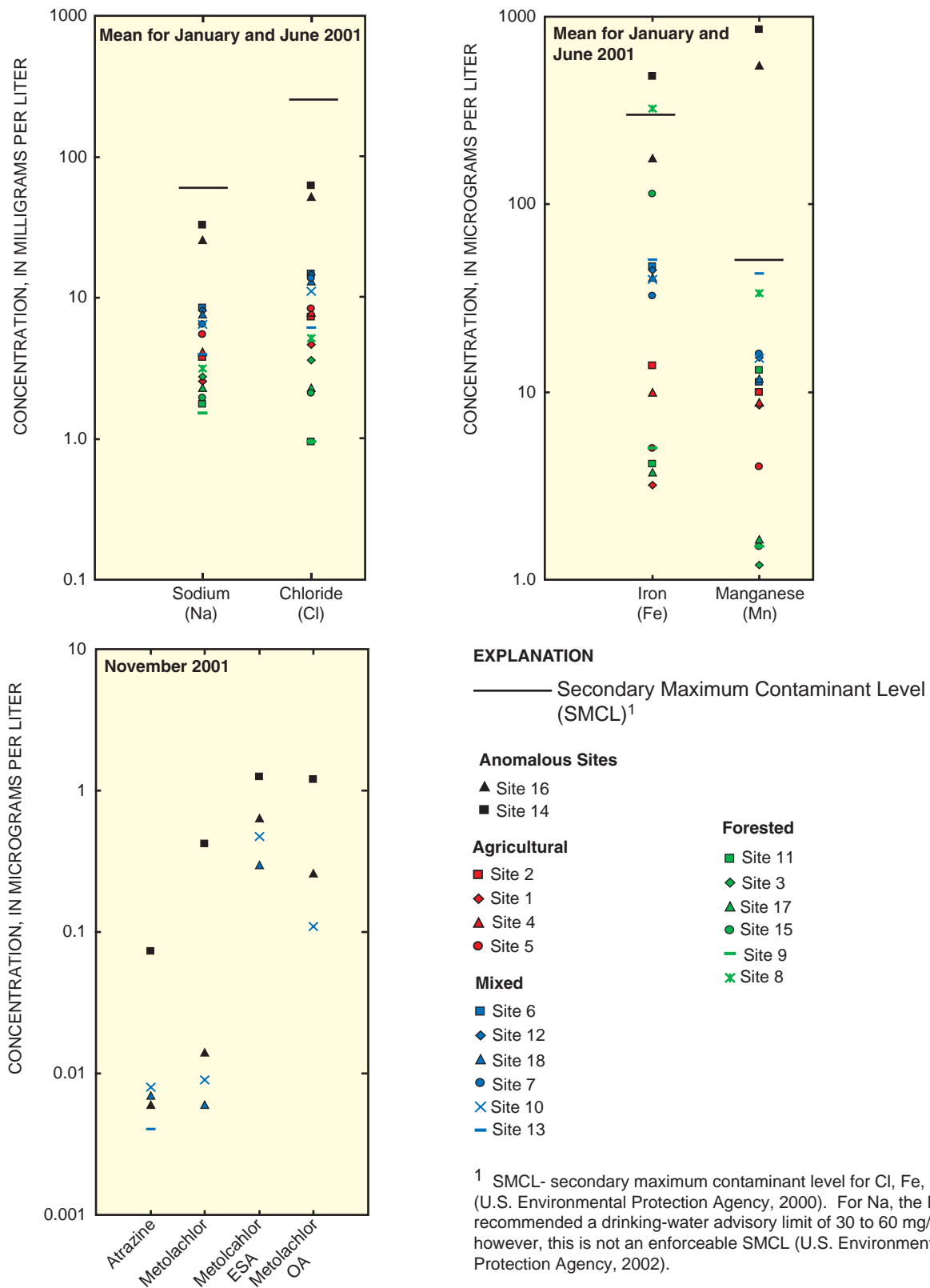


Figure 4I. Concentrations of sodium, chloride, iron, manganese, and four herbicides detected in base-flow samples from sites 14 and 16 in relation to those at all other sites and in relation to Federal water-quality standards. (Site locations are shown in fig. 1.)

V. AGE DATING OF WELL WATER TO DETECT INDUCED INFILTRATION

A. Dating technique

Chlorofluorocarbons, known as CFCs, can be used to indicate the age of ground water and, thus, the potential for induced infiltration of river water to nearby wells.

Four municipalities in the study area have production wells near the Susquehanna River. CFC concentrations in water from these wells were used to calculate the age of the water and the potential for induced infiltration from the river.

The yield of a pumped well finished in a sand and gravel aquifer can be greatly increased through induced recharge from a nearby surface-water body, but most surface water contains microorganisms and other contaminants that can be hazardous to humans. Most of these contaminants can be filtered out by aquifer material before reaching the well, but the pumped water must be sampled routinely to ensure complete removal of contaminants. Therefore, a well's potential for induced infiltration of river water is a concern to local water managers.

A pilot study was conducted in a 30-mi reach of the study area (fig. 5) in February 2001 to calculate the age of ground water at four production wells in an effort to assess whether these wells are inducing infiltration of river water. The age of ground water, defined as the number of years from infiltration at the water table to discharge from a pumping well or natural spring, can be used for other purposes, including calculation of recharge rates, refinement of hydrologic models, assessment of the potential for contamination from local sources, and detection of river water that infiltrates into the aquifer. The chemical quality of ground water affected by infiltration of river water is intermediate between that of the river and that of the aquifer.

Chlorofluorocarbons (CFCs) are synthetic industrial compounds that occur in the atmosphere and in precipitation. CFC concentrations in precipitation, and in ground water recently derived from precipitation, correspond to that in the contemporaneous atmosphere. Atmospheric CFC concentrations have been recorded since about 1945

(Plummer and Busenberg, 2000); therefore, comparison of CFC concentrations in a water sample with the historical records of atmospheric CFC concentrations can indicate the year in which that water entered the water table (since about 1945). River water has an age of zero because it is in constant contact with the atmosphere.

The accuracy of an estimated age depends in part on the degree to which transport through the aquifer affected the CFC concentrations; for example, chemical processes such as microbial degradation and sorption can decrease the concentrations (Plummer and Busenberg, 2000). For this reason, the estimated age of the water is normally referred to as "model age" or "apparent age."

CFC concentrations in water samples from the four wells were used to indicate the water's age and the presence of river water. Extremely young water (less than 1 year) would indicate induced recharge from the river, but this interpretation would need to be compared with other data, such as well logs, microbial and other chemical analyses of the water, and seasonal changes in water temperature at the wells (Winslow and others, 1965; Randall, 1977, 1981; and Miller, 2000). The four wells tap glacial sand and gravel aquifers (table 8). Their distances from the river are as follows: Unadilla, 95 ft; Sidney, 110 ft; Otego, 65 ft; Afton, 450 ft. All samples were collected in February 2001 and analyzed through standard techniques (Kendall and Caldwell, 1998; Plummer and Busenberg, 2000). Results are summarized in the following section.

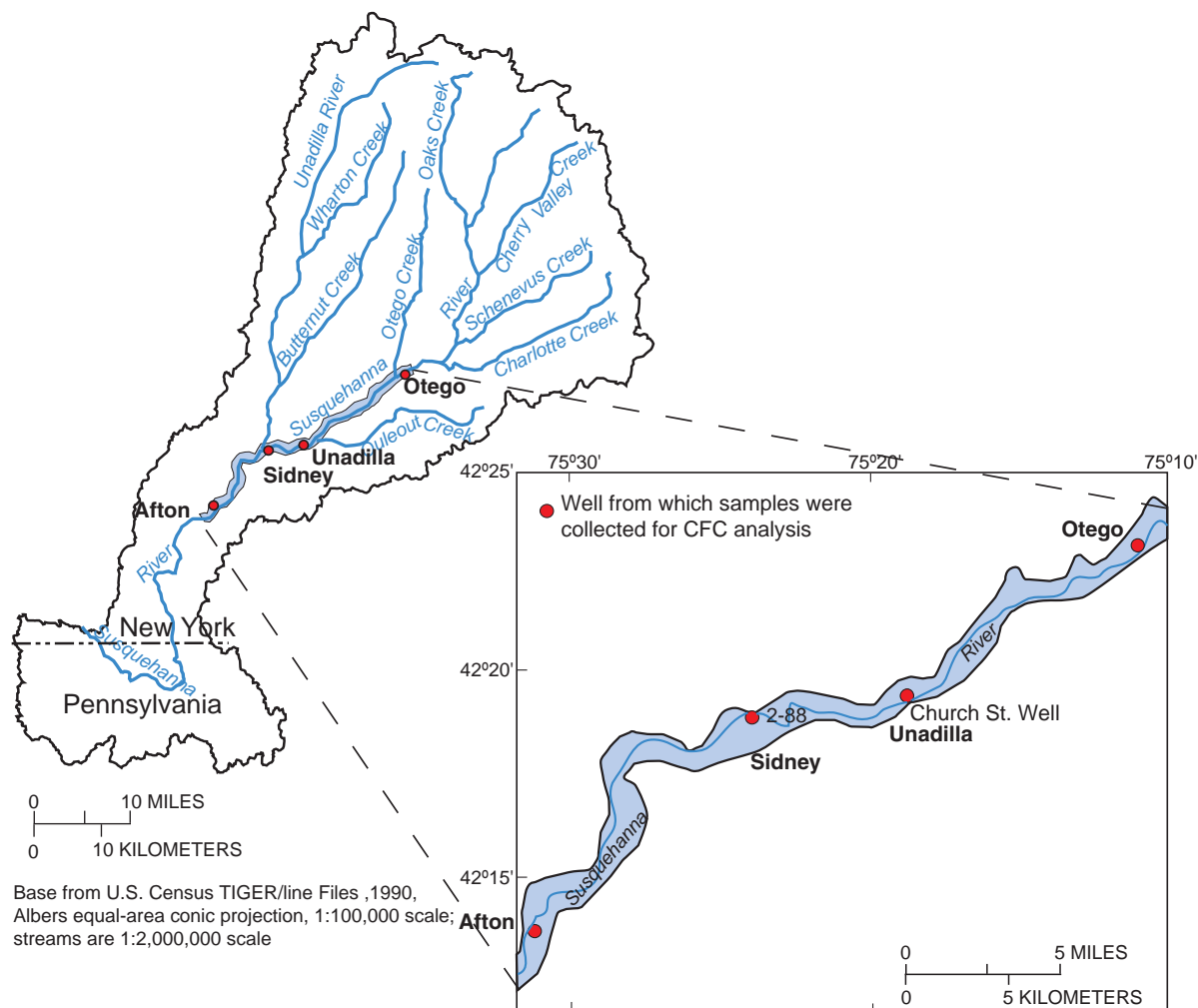


Figure 5. Locations of wells near Susquehanna River that were used for chlorofluorocarbon (CFC) analysis. (Site descriptions are given in table 8.)

Table 8. Data on the four production wells sampled for chlorofluorocarbons (CFCs) to estimate potential for induced infiltration of water from Susquehanna River in study area, February 2001. [Distance is in feet; well depths and screened intervals are in feet below land surface. Dashes indicate sample contamination. Well locations are shown in fig. 5.]

| Well | Distance from river | Well depth | Screened interval | Type of aquifer* | Lithology | Infiltration from river |
|--|---------------------|------------|-------------------|------------------|--|-------------------------|
| Village of Unadilla Church Street well | 95 | 99 | 89-99 | C | 0-14 ft, clay; 14-49 ft, sand and gravel; 49-62 ft, clay and gravel; 94-98 ft, sand & gravel; 98-106 ft, till; 106-108 ft, bedrock. | -- |
| Village of Sidney well 2-88 | 110 | 95 | 75-95 | U | 0-5 ft, fine sand; 5-54 ft, sand and gravel; 54-62 ft, fine to coarse sand; 62-95 ft, sand and gravel. | -- |
| Village of Otego well | 65 | 78 | 63-78 | C | 0-3 ft, fill; 3-25 ft, clay; 25-50 ft, clay & gravel; 50-63 ft, sand and clay; 63-66 ft, gravel; 66-68 ft, till; 68-80 ft, gravel, fine sand and clay. | No |
| Village of Afton well | 450 | 133 | 123-133 | C | 0-10 ft, sand & gravel; 10-20 ft, sand; 20-30 ft, gravel; 30-98 ft, fine sand, silt and clay; 98-110 ft, sand & gravel; 110-119 ft, silty gravel; 119-134 ft, sand & gravel; 134-137 ft, sand with trace gravel; 137-185 ft, unknown; 185 ft, bedrock. | No |

* C, confined; U, unconfined

V. AGE DATING OF WELL WATER TO DETECT INDUCED INFILTRATION (CONTINUED)

B. Results and Interpretation

Water from the Otego production well is probably 26 to 43 years old, and water from the Afton production well is probably 37 to 50 years old. The age of water from the other wells could not be ascertained because the samples contained CFCs from urban sources.

CFCs have three major forms—CFC-12 (dichlorodifluoromethane), which was first used in 1931 as an alternative to ammonia and sulfur dioxide in refrigeration and other industrial applications; CFC-11 (trichlorofluoromethane), first used in 1936 for air conditioners and refrigeration, insulation, propellants in aerosol cans, and as solvents; and CFC-113 (trichlorotrifluoro-methane), first used in the mid-1950s for semiconductor chip manufacturing in vapor degreasing and cold immersion cleaning of electronic components (Plummer and Friedman, 1999). If all three CFC forms indicate a similar age, that value can be considered fairly reliable. The certainty is diminished if only two of the CFC forms are used or yield similar values. If only one form can be used, the value is not considered reliable.

The feasibility of using CFCs as tracers of recent recharge and indicators of ground-water age was first recognized in the 1970s (Plummer and Busenberg, 2000). Ground-water dating with CFC-11, CFC-12, and CFC-113 is possible because (1) their amounts in the atmosphere over the past 50 years have been reconstructed, (2) their solubilities in water are known, and (3) concentrations in air and young water are high enough that they can be measured. Age is determined from CFCs by relating their measured concentrations in ground water back to known historical atmospheric concentrations and/or to calculated concentrations expected in water in equilibrium with air. Water samples for CFC analysis can be collected from domestic, irrigation, monitoring, and municipal wells, and from springs. A closed path is established between the well or pump to a valve system that is used to fill glass ampoules with water, creating a headspace with CFC-free, ultra-pure nitrogen gas. The samples are then transported to the U.S. Nuclear Regulatory Commission-licensed USGS laboratory for analysis of CFC content by gas chromatography to a detection limit of 0.3 parts per quadrillion.

CFC contamination of ground water—that is, the presence of CFCs from sources other than the atmosphere, can occur in developed areas from local sources such as septic-tank effluent, leaking sewerlines, industrial wastes, and induced recharge

from rivers carrying sewage-treatment-plant effluent. Samples that contain CFCs from local sources yield ages that are too young—sometimes impossibly young if the concentrations exceed those set by air-water equilibrium. Samples from three of the four wells sampled were contaminated by one or more forms of CFCs from nonatmospheric sources (table 9). The Otego production-well samples showed CFC-113 contamination, the Sidney samples showed CFC-12 and CFC-113 contamination and possibly CFC-11 contamination, and the Unadilla production well showed contamination by all three CFC forms. Only the Afton production well showed no CFC contamination.

Water pumped by the Afton production well is from a confined aquifer and was indicated to range from 37 to 53 years old; it is probably about 50 years old because CFC-11 and CFC-12 indicated ages of 50 and 53 years, respectively (table 9). This relatively old age indicates that pumping from this confined aquifer does not induce recharge from the Susquehanna River, 450 ft away. The lack of induced infiltration would indicate that the confining unit, which consists of 68 ft of fine sand, silt, and clay (table 8) is continuous and extensive, and (or) that the confined aquifer is recharged by downward infiltration from the overlying unconfined aquifer far from the well and river.

Water pumped from the Otego well was indicated to range from 26 to 43 years old (table 9), but the uncertainty is large because the age ranges indicated by the CFC-11 and CFC-12 analyses (43 and 26 years, respectively) differ considerably. Age based on CFC-113 was not available in the Otego analysis because the samples showed contamination. The relatively old age of water at this well indicates that little or no infiltration of river water is induced by pumping, probably because the aquifer is confined by a clay layer 10 to 25 ft thick (table 8) that underlies the river and overlies the aquifer.

No reliable age could be inferred from the CFC data for the Sidney and Unadilla wells because the samples reflect contamination, probably from local sources within the contributing area of these wells.

Table 9. Concentrations of CFCs in water samples from four production wells on the Susquehanna River in February 2001 and the calculated model ages of the water (time of recharge).

[Values are in parts per trillion per volume (pptv). C, contaminated with CFCs from nonatmospheric sources. Well locations are shown in fig. 5.]

| Well location | Concentration in solution as indicated by | | | Concentration in atmosphere, as indicated by | | | Model ground-water age | | | Ground-water age and date of recharge |
|---------------------------------|---|--------|---------|--|--------|---------|------------------------|--------|---------|---|
| | CFC-11 | CFC-12 | CFC-113 | CFC-11 | CFC-12 | CFC-113 | CFC-11 | CFC-12 | CFC-113 | |
| Village of Afton | 3.4 | 3.2 | 4.1 | 1.2 | 5.1 | 3.5 | 50.0 | 53.0 | 37.0 | 37 to 50 years. Late 1940's to early 1960's |
| Village of Otego | 19.8 | 135 | 0.0 | 7.2 | 214 | 0.0 | 43.0 | 26.0 | C | 26 to 43 years. Mid-1970's with degradation of CFC-11 and(or) CFC-113, or possible CFC-12 contamination of 1950's water |
| Village of Sidney, well 2-88 | 519 | 2910 | 3520 | 188 | 4610 | 3020 | 19.0 | C | C | Probably early 1980's; contamination precludes reliable estimate |
| Village of Unadilla, Church St. | 979 | 1270 | 987 | 355 | 2010 | 848 | C | C | C | All samples contaminated. |

SUMMARY AND CONCLUSIONS

Base flow is an approximation of the quality of shallow ground water and constitutes more than 60 percent of total annual flow of streams within the upper Susquehanna River Basin. Nitrate, inorganic chemical constituents, and pesticide concentrations reflect land use and carbonate content of bedrock upstream of the 18 sampling sites.

Base flow from 18 streams in the upper Susquehanna River Basin from Millers Mills to Conklin, N.Y., was sampled and analyzed several times during 2001 for common ions, nutrients, and pesticides to characterize the quality of shallow ground water. The CFC concentrations of water from four production wells were measured to estimate the age and the potential for induced infiltration from the river.

The upper Susquehanna River Basin is mainly rural. It is about 26 percent agricultural land and about 71 percent undeveloped, forested land and contains one city (Oneonta) and several small villages. The northernmost part is underlain by carbonate (limestone) bedrock; the rest is underlain by noncarbonate siltstone, sandstone, and noncalcareous shale.

Base flow (the ground-water component of streamflow) of a stream is an approximation of the chemical quality of shallow ground water within the stream's drainage area. Hydrograph-separation analyses of the 1941-93 discharge records of four streams with streamflow-gaging stations indicated that base flow constitutes more than 60 percent of total annual flow in streams of the study area. Hence, the chemical quality of baseflow is an important factor influencing the total stream flow that leaves the upper Susquehanna River Basin and eventually empties into Chesapeake Bay.

Base-flow samples were analyzed for pH, alkalinity, specific conductance, dissolved solids, and common inorganic cations and anions. The predominant cations in the samples were calcium, magnesium, and sodium; the predominant anions were chloride, sulfate, and bicarbonate. Base-flow quality was found to reflect land use and the presence or absence of carbonate bedrock and carbonate-rich glacial deposits in the subbasins. The 18 subbasins were categorized by predominant land use according to whether they were predominantly agricultural,

forested, or a mixture of both, and whether they were dominated by carbonate or noncarbonate rocks.

Base-flow samples collected in January and June 2001 from agricultural subbasins underlain by carbonate bedrock contained higher concentrations of most inorganic constituents than base flow from the forested subbasins that lack carbonate material. The largest subbasins, which contain a mixture of agricultural and forested land as well as a mixture of carbonate and noncarbonate rock, had intermediate concentrations of most inorganic constituents.

Median nitrate (NO_3^-) concentrations were lowest in base-flow samples from forested subbasins and highest in samples from agricultural subbasins; concentrations in samples from sites from large subbasins with mixed land use were intermediate. Nitrate concentrations in the forested and mixed subbasins were lower in summer than in winter as a result of the increased biological activity, reduced recharge, and denitrification in the soil and streams during the growing season. The agricultural subbasins generally showed the opposite—higher nitrate concentrations in the early summer than in the winter—probably as a result of fertilizer and manure applications near these streams.

Pesticides were detected in 10 of the 12 streams sampled in November 2001 for pesticide analysis. Only 6 of the 113 compounds for which samples were analyzed were detected; these were metolachlor and its two degradates (metolachlor OA and metolachlor ESA), atrazine and its degradate (deethylatrazine), and alachlor ESA. The highest concentrations of atrazine plus deethylatrazine were in samples from the four streams with the largest percentage of agricultural land in their drainage areas. No pesticides were detected in samples from the two streams that drain subbasins with nearly 100 percent forested land. Pesticide concentrations at main-stem river sites representing mixed land use generally were intermediate between those of the agricultural and the forested subbasins. No pesticides were detected at concentrations that exceeded New York State or Federal water-quality standards.

Two small streams had unusually high concentrations of sodium, chloride, iron, manganese, and metolachlor and its two degradates. These two sites probably receive runoff from a nearby utility right-of-way to which herbicides are applied, as well as from Interstate 88, which crosses the headwaters of both streams and to which road salt is applied in the



Upland stream (site 9 in table 1) in upper Susquehanna River Basin, N.Y., during base-flow conditions, June 2001.

winter. The elevated iron and manganese concentrations in these streams may result from anoxic conditions in the source aquifers. Anoxic, acidic conditions caused by decaying organic matter would allow iron and manganese minerals within the unconsolidated deposits in the valley to dissolve readily. Once the water discharges into the stream, iron and manganese oxidize and precipitate.

Concentrations of chlorofluorocarbons (CFCs) in ground-water samples from two of four wells sampled in villages near the Susquehanna River indicate the age of the water in these wells and the likelihood that these wells are inducing some surface water from the river. Water in the Otego well is probably 26 to 43 years old; water in the Afton well is probably 37 to 50 years old. These apparent old ages indicate that neither well induces surface-water infiltration from the river, probably because both are confined by a layer of fine-grained material. No

reliable age could be estimated from water samples from the production wells at Sidney and Unadilla because the samples contained CFCs from local sources.

The data presented in this report demonstrates the importance of understanding the water quality of base flow in the upper Susquehanna River Basin. Most chemical constituents for which analyses were done were below any State or Federal water-quality standards, though 2 streams had manganese concentrations above the USEPA SMCL and 2 had iron concentrations above the USEPA SMCL. This data can be used by water managers throughout the study area for comparisons of the concentrations of chemical constituents in production wells with the baseflow concentrations, or in possible future stormflow studies to compare base-flow to stormflow concentrations.

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