

In cooperation with
NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

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

Part 4. Quantity and Quality of Ground-Water and Tributary Contributions to Stream Base Flow in Selected Main-Valley Reaches



Scientific Investigations Report 2004-5018

U.S. Department of the Interior
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Selected Main-Valley Reaches**

By Paul M. Heisig

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U.S. Department of the Interior
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Conversion Factors and Abbreviations

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
million gallons (Mgal)	3,785	cubic meter (m ³)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83). Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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

Part 4. Quantity and Quality of Ground-Water and Tributary Contributions to Stream Base Flow in Selected Main-Valley Reaches

By Paul M. Heisig

Abstract

Estimates of the quantity and quality of ground-water discharge from valley-fill deposits were calculated for nine valley reaches within the Pepacton watershed in southeastern New York in July and August of 2001. Streamflow and water quality at the upstream and downstream end of each reach and at intervening tributaries were measured under base-flow conditions and used in mass-balance equations to determine quantity and quality of ground-water discharge. These measurements and estimates define the relative magnitudes of upland (tributary inflow) and valley-fill (ground-water discharge) contributions to the main-valley streams and provide a basis for understanding the effects of hydrogeologic setting on these contributions. Estimates of the water-quality of ground-water discharge also provide an indication of the effects of road salt, manure, and human wastewater from villages on the water quality of streams that feed the Pepacton Reservoir. The most common contaminant in ground-water discharge was chloride from road salt; concentrations were less than 15 mg/L.

Investigation of ground-water quality within a large watershed by measurement of stream base-flow quantity and quality followed by mass-balance calculations has benefits and drawbacks in comparison to direct ground-water sampling from wells. First, sampling streams is far less expensive than siting, installing, and sampling a watershed-wide network of wells. Second, base-flow samples represent composite samples of ground-water discharge from the most active part of the ground-water flow system across a drainage area, whereas a well network would only be representative of discrete points within local ground-water flow systems. Drawbacks to this method include limited reach selection because of unfavorable or unrepresentative hydrologic conditions, potential errors associated with a large number of streamflow and water-quality measurements, and limited ability to estimate concentrations of nonconservative constituents such as nutrients.

The total gain in streamflow from the upper end to the lower end of each valley reach was positively correlated with the annual-runoff volume calculated for the drainage area of the reach. This correlation was not greatly affected by the proportions of ground-water and tributary contributions, except at two reaches that lost much of their tributary flow after the July survey. In these reaches, the gain in total streamflow showed a negative departure from this correlation.

Calculated ground-water discharge exceeded the total tributary inflow in each valley reach in both surveys. Ground-water discharge, as a percentage of streamflow gain, was greatest among reaches in wide valleys (about 1,000-ft wide valley floors) that contain permeable valley fill because tributary flows were seasonally diminished or absent as a result of streambed infiltration. Tributary inflows, as a percentage of streamflow gain, were highest in reaches of narrow valleys (200-500-ft wide valley floors) with little valley fill and high annual runoff.

Stream-water and ground-water quality were characterized by major-ion type as either (1) naturally occurring water types, relatively unaffected by road salt, or (2) road-salt-affected water types having elevated concentrations of chloride and sodium. The naturally occurring waters were typically the calcium-bicarbonate type, but some contained magnesium and (or) sulfate as secondary ions. Magnesium concentration in base flow is probably related to the amount of till and its carbonate content, or to the amount of lime used on cultivated fields within a drainage area. Sulfate was a defining ion only in dilute waters (with short or unreactive flow paths) with low concentrations of bicarbonate. Nearly all tributary waters were classified as naturally occurring water types.

Ground-water discharge from nearly all valley reaches that contain State or county highways had elevated concentrations of chloride and sodium. The mean chloride concentrations of ground-water discharge—from 8 to 13 milligrams per liter—did not exceed Federal or State standards, but were about 5 times higher than naturally occurring levels. Application of road salt along a valley

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bottom probably affects only the shallow ground water in the area between a road and a stream. The elevated concentrations of chloride and sodium in the base-flow samples from such reaches indicate that the concentrations in the affected ground water were high enough to offset the low concentrations in all unaffected ground water entering the reach.

Nutrient (nitrate and orthophosphate) concentrations in base-flow samples collected throughout the valley-reach network could not generally be used to estimate their concentrations in ground-water discharge because these constituents can be transformed or removed from water through biological uptake, transformation, or by adsorption on sediments. Base-flow samples from streams with upgradient manure sources or villages served by septic systems consistently had the highest concentrations of these nutrients.

Introduction

Maintenance of the quality of water from upstate reservoirs that provide New York City's water supply is a concern because degradation of water quality could result in the need for costly filtration, under the Surface Water Treatment Rule of the Safe Drinking Water Act (Public Law 104-82). A variety of land-use activities occur within reservoir watershed areas, including some that may adversely affect the water quality of streams that supply the reservoirs. The New York State Department of Environmental Conservation (NYSDEC) is charged, under the requirements of the Federal Clean Water Act, section 305(b), with providing data to the United States Environmental Protection Agency (USEPA) on the quality of surface waters and ground waters of New York State. The Pepacton Reservoir watershed in the western Catskill Mountains (fig. 1) was selected by NYSDEC for hydrologic investigation because it had received much less study than the neighboring, and more intensely farmed, Cannonsville Reservoir watershed to the west. In 2000, the U.S. Geological Survey (USGS), in cooperation with NYSDEC, began a 2-year study to evaluate the quality of ground-water discharge to streams in reaches of major valleys (this report) and in smaller upland basins (Heisig and Phillips, 2004; Phillips and Heisig, 2004) within the Pepacton watershed. Surficial geology and recharge estimates within the Pepacton watershed were addressed in a concurrent USGS study (Reynolds, 2004).

Base flow (dry-weather streamflow) is derived from ground-water discharge from springs and from direct seepage into stream channels. Therefore, any net change in stream-water quality between the upper and lower ends of a given stream reach (barring tributary inflow or point-source contamination) is a function of the composite water quality of ground water discharged to the stream within that reach. The quality of ground-water discharge will reflect the presence or absence of non-point sources such as road-deicing salts and

human and animal wastes, especially in the valley-bottom area of a reach.

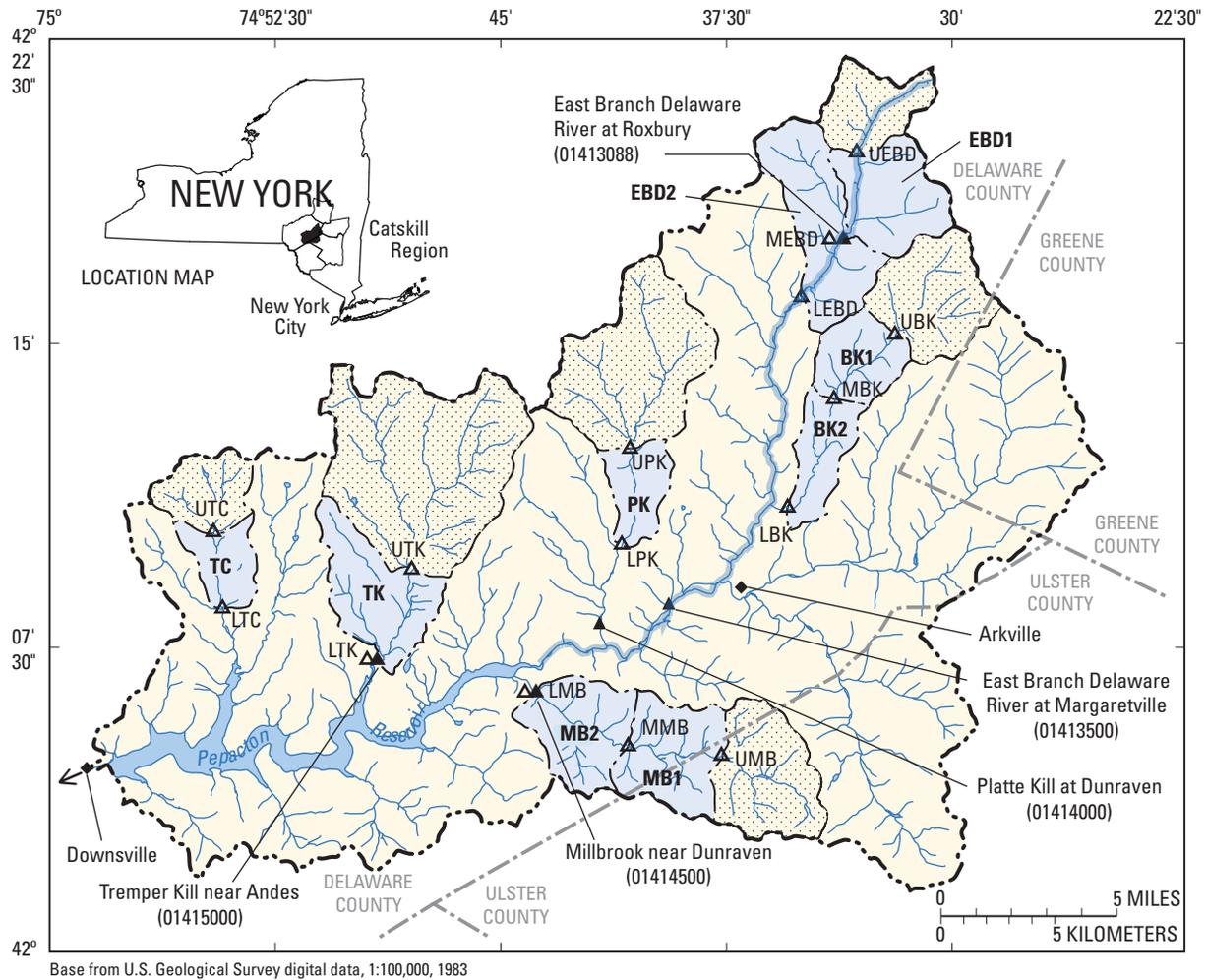
The quality of shallow ground water in valley-fill deposits could be estimated through chemical analysis of water samples collected from a network of wells at appropriate locations along valley streams, but the installation of a well network for evaluation of shallow ground-water quality throughout the Pepacton watershed would be prohibitively expensive. In addition, it also would provide data only from isolated points and would thereby give a limited representation of the spatial variations in ground-water quality within the watershed. Instead, the chemical composition of ground-water discharge from valley-bottom deposits across the watershed was estimated from surface-water measurements of flow and chemical quality. A base-flow sample can represent a composite sample of shallow ground-water discharge upstream of a sample site. Shallow ground water is susceptible to nonpoint-source contamination, especially in valley-bottom areas.

The study entailed (1) selection of nine valley-stream reaches, (2) measurement of streamflow and major-ion concentrations at the upstream and downstream ends of each reach, (3) measurement of streamflow and major-ion concentrations of tributary flow entering each valley reach (or estimation of major-ion concentrations from specific conductance measurements), and (4) application of these data to mass-balance equations to estimate the amount of ground-water discharge and the concentrations of the selected ground-water constituents. Streamflow measurements and water sampling were carried out during two base-flow surveys—July 10-17 and August 7-8, 2001.

The mass-balance technique used in this study was best suited for estimating concentrations of conservative (unreactive) constituents. This technique is unreliable for estimating concentrations of nonconservative (chemically reactive) constituents, or of constituents with small concentration ranges. This technique is also unlikely to detect individual or widely spaced point sources of contamination.

Purpose and Scope

This report (1) documents the results of base-flow sampling from selected reaches of nine major-valley streams and their associated tributaries; (2) presents calculated ground-water discharges within each reach for the July and August surveys of 2001; (3) evaluates ground-water discharge in relation to (a) annual runoff within the drainage area of each reach, and (b) the width and general permeability of unconsolidated material in the valley bottom (valley fill) within each reach; (4) classifies the chemical composition of base-flow samples and ground-water discharge according to water type (major ions) and interprets them in relation to land use, including roads, which are salted in the winter, and (5) relates the occurrence of selected constituents (chloride and sodium, nitrate, and orthophosphate) to their most likely sources.



EXPLANATION

- Study reach and associated drainage area
- Headwater drainage area
- Boundary of Pepacton Reservoir watershed
- East Branch Delaware River
- TK** Valley-reach designation
- Valley-reach measurement site
- U Denotes upstream site
- M Denotes middle site on adjacent valley reaches
- L Denotes downstream site
- (01413088) USGS Stream-gaging station and identifier
- National Weather Service station

STREAM NAMES

- TC Terry Clove Kill
- TK Tremper Kill
- MB Mill Brook
- PK Platte Kill
- BK Batavia Kill
- EBD East Branch Delaware River

Figure 1. Locations of valley-reach study sites, stream-gaging stations, and weather stations in the Pepacton Reservoir watershed in southeastern New York.

Previous Investigations

Previous investigations that pertain to water resources in the Pepacton watershed have described the geologic framework of the area, and the low-flow characteristics of streams and tributaries within the region. Bedrock and the thickness and type of glacial deposits and within the Pepacton Reservoir area was discussed by Fluhr (1953), and

ground-water resources of Delaware County were discussed by Soren (1963). Glacial geology and deglaciation in the western Catskill Mountains was discussed by Kirkland (1973) and Ozvath (1985). The effects of hydrology, geology, and geomorphology on low-flow characteristics of streams in the Delaware and Susquehanna River basins in New York were analyzed by Coates (1971). Infiltration of water from tributary streams as they enter larger valleys in the Susquehanna River Basin in New York was detailed by Randall (1978).

Acknowledgments

Thanks are extended to the landowners for access to their properties, and especially to Robert Bond and the Tuscarora Club for access to club lands in the Mill Brook basin. Thanks also are extended to State, county, and town highway superintendents that provided information on road-salt usage and practices. USGS staff members Daniel Edwards, Kevin Reisig, Thomas Suleski, and Brett Phillips, assisted in sample collection and stream-discharge measurements, and Krysta Button, Julia Guastella, Hannah Ingleston, and Patrick Phillips, processed the water samples.

Study Area

The Pepacton Reservoir watershed encompasses an area of 372 mi² within the western Catskill Mountains of southeastern New York. It is largely rural and is drained by the East Branch Delaware River, which is impounded in the Pepacton Reservoir by the dam at Downsville (fig. 1). Maximum relief is about 2,800 ft. Runoff (precipitation minus evapotranspiration) ranges from 22 to 40 in/yr; the highest rates are associated with the highest mountains along the southeastern and eastern edges of the watershed (Randall, 1996).

The bedrock consists of nearly flat-lying sandstone, siltstone, shale, and conglomerate of Devonian age that is overlain by discontinuous glacial and alluvial deposits (Fisher and others, 1970). Cliff-forming sandstone and conglomerate are commonly interbedded with less resistant shale and siltstone; this produces a step-like alternation of near-vertical and gentle slopes on upper hillsides. The most common glacial deposit in upland areas is till, which is nearly continuous on low slopes and thin or absent on steep hillsides. Thick till deposits are common on the lee (typically south) side of hills relative to the direction of ice movement during glaciation (Coates, 1966). Deposits within the main valleys (herein referred to as valley fill) typically consist of postglacial alluvium, including alluvial fans, and are underlain and locally bordered by stratified drift that was deposited by glacial meltwater as outwash or ice-contact deposits. Till commonly underlies the stratified drift above the bedrock surface (Fluhr, 1953).

Most streams in the large valleys flow over valley-fill deposits. Two exceptions are the Batavia Kill and especially Mill Brook, which flow over bedrock in their lower reaches near their confluence with the East Branch Delaware River (fig. 1). Mill Brook valley is oriented east-west and appears to contain thick till deposits that have shifted the stream course to the south side of the valley (A. Randall, USGS, oral communication, 2003). Bedrock has been exposed and incised by stream erosion along the lower 3 mi of Mill Brook (fig. 1).

The elevation difference between the Batavia Kill valley and East Branch Delaware River valley has resulted in headward erosion up the Batavia Kill valley and exposure of bedrock in a 0.25-mi reach of the channel.

Land use within the uplands differs considerably from that along the valley bottoms. The uplands are dominated by forest and former farmland that is reverting to forest, as well as low-density residential development and hayfields. Dairy farms were formerly widespread in these areas but now remain in only a few small upland subbasins. The valley-bottom areas, in contrast, have long been the focus of human activity because the soils are favorable for agriculture, the land is level and suitable for building and transportation, and the streams are a ready supply of water. The valley-bottom areas contain all of the villages and major roads, and much of the remaining farmland, including dairy farms and inactive farmland. Low-density residential development follows the main roads out of the villages.

Rainfall within the Pepacton watershed was measured at the National Weather Service stations at Arkville and Downsville (fig. 1) throughout the study. The maximum July and August monthly total rainfall differences between the two stations exceeded 1 in., and flows at stream-gaging stations within the watershed (fig. 1) differed in their response to storms (see fig. 4, further on). Rainfall at the Arkville station was 0.3 in. above the long-term mean (54 years of record) in July 2001 and 1.25 in. below the mean in August 2001 (Cornell University Northeast Regional Climate Center, written commun., 2002). Annual amounts of runoff from the drainage area of each of the nine stream reaches are summarized in table 1.

Approach and Methods

The amount of ground-water discharge and its chemical composition in each of nine valley reaches were determined with mass-balance calculations based on (1) the measured difference between streamflow at the upstream and downstream ends of each reach, (2) the measured difference between major-ion concentrations at the upstream and downstream ends of each reach, and (3) measured or estimated streamflow from tributaries to each reach (inflow) and measured or estimated chemical concentrations. Tributary concentration estimates were derived from specific conductance measurements. The streamflow measurements and water sampling were done during July 10-17 and August 7-8, 2001.

Average annual runoff, in inches, within each valley-reach area was derived from a map by Randall (1996). These values were multiplied by their respective drainage areas to obtain annual volumes (in cubic ft) of water available to streams.

Table 1. Drainage-area and runoff data on valley reaches in the Pepacton watershed in southeastern New York.[mi², square miles. Locations are shown in fig. 1.]

Reach identifier (see fig. 1)	Stream name	Drainage area of valley reach (mi ² *)	Drainage area above upstream end of reach (mi ²)	Reach area as percent of total drainage area above downstream end of reach	Length of reach (mi)	Reach drainage area per mile of reach length (mi ²)	Average annual runoff [†]	
							Inches [†]	Millions of cubic feet
TC	Terry Clove Kill	3.78	4.86	44	2.20	1.72	25.2	221
TK	Tremper Kill	8.84	24.36	26	2.85	3.10	23.0	472
PK	Platte Kill	4.15	15.84	21	2.80	1.48	24.0	231
MB1	Mill Brook	7.99	9.48	45	3.00	2.66	28.1	522
MB2	Mill Brook	7.73	17.47	30	3.10	2.49	25.6	460
BK1	Batavia Kill	5.22	9.02	36	2.50	2.09	25.8	313
BK2	Batavia Kill	4.8	14.24	26	3.45	1.39	24.7	275
EBD1	East Branch Delaware River	8	5.5	58	2.35	3.40	26.2	487
EBD2	East Branch Delaware River	10.26	13.5	44	2.15	4.77	26.2	625

* includes valley floor plus upland hillsides and tributary watersheds that drain to main-valley stream

† estimated runoff derived from Randall (1996)

Valley-Reach Selection

The nine valley reaches (fig. 1) were chosen to represent a wide range in the valley-bottom width and several types of land use. Reach length ranged from 2.15 to 3.45 mi (table 1). Valley-bottom widths ranged from about 200 ft in the bedrock-floored channel in the lower reach of Mill Brook (MB2) to about 1,500 ft in the lower reach of the East Branch Delaware River (EBD2). Land uses in selected reaches included dairy farms, an unsewered village, low-density residential development in formerly farmed areas and forested areas, and several types and lengths of roads. Reach selection was also based on the following hydrologic criteria:

1. *Valley-reach drainage area exceeds 20 percent of the total drainage area above the downstream valley-reach site.* Reaches with as small a headwater drainage area (the drainage area upstream from the valley reach, as delineated in fig. 1) as possible relative to the valley-reach drainage area were essential to minimize the uncertainty of the calculated streamflow gain within each reach. A large headwater drainage area would provide a large upstreamflow to the valley reach, and the uncertainty inherent in measurement of large flows could be nearly equal to the gain in flow within the reach. The valley-reach drainage areas (between the upstream and downstream sites) ranged from 21 to 59 percent of the total drainage area above the downstream end of each reach (table 1). The least reliable ground-water discharge estimates came from reaches with the largest headwater drainage areas. This criterion prevented use of the widest valley reach in the Pepacton watershed—the East Branch Delaware River valley just upstream of the Pepacton Reservoir.

2. *Minimal inflow from tributaries.* Minimizing the number of tributaries (and their drainage area) within a valley reach minimizes errors associated with streamflow measurements and thereby improves the reliability of the ground-water-discharge estimates.
3. *Absence of lakes or wetlands within the drainage area.* Surface-water bodies store stormwater and its associated water-quality characteristics and release it gradually downstream. Thus, a delayed stormwater contribution during base-flow periods would make base-flow quantity and quality unrepresentative of ground-water discharge.
4. *Absence of wastewater-treatment plants.* Effluent from wastewater-treatment plants, such as the facility on the East Branch Delaware River at Margaretville, makes base flow unrepresentative of ground-water-discharge quality and quantity.

Base-Flow Surveys

Surveys of streamflow and stream-water quality were completed during low base-flow conditions, when tributary flow, which represents base flow from upland areas, was minimal and most of the increase within the valley-stream reaches represented ground-water discharge from the valley-fill deposits. Base-flow conditions were assessed through data from USGS stream-gaging stations within the Pepacton watershed (fig. 2) on a reach-by-reach basis because rainfall amounts varied locally, and because valley-bottom width and permeability differed from reach to reach. The high evapotranspiration rates and dry tributary streambeds (especially in wide valleys) in summer decreased the magnitude of stormflows and thereby decreased the number

of days before base-flow conditions resumed after each storm compared to other times of year. Base-flow conditions were reached between 1 and 4 days after a storm.

The valley-reach surveys included streamflow measurements and water-quality sampling. They were conducted on July 10, 13, 16, 17, and August 7 and 8, 2001 (fig. 2).

July survey. A total of 14 valley-reach sites and 29 tributaries were visited. Streamflow was measured at all valley-reach sites and 18 tributaries; the other 11 tributaries were dry. Water samples were collected at all valley-reach sites and at six of the tributaries. Streamflow and specific conductance were estimated for an additional 10 small tributaries that were not visited. No ground-water-discharge or chemical-quality estimates were made for the two Mill Brook reaches because a half-hour rain shower (recorded as 0.01 in. at the two meteorological stations, but estimated to be locally higher) caused road runoff that entered the stream during the survey.

August survey. A total of 15 valley-reach sites and 34 tributaries were visited. Streamflow was measured at all valley-reach sites and 15 tributaries; the other 19 tributaries were dry. Water samples were collected at all valley-reach sites and at nine of the tributaries. Streamflow and specific conductance were estimated for three additional small tributaries that were not visited. An additional valley-reach stream-water sample was collected within the upper valley reach of Mill Brook (MB1), in which surface flow was lost along a nearly 2,000-ft reach of streambed adjacent to large alluvial fan. The major-ion composition of the re-emerging flow was nearly identical to that at the upstream valley-reach site (UMB).

Field Measurements

Discharge, specific conductance, pH, temperature, and dissolved oxygen concentration were measured at the upstream and downstream ends of each valley reach, and at or near the mouth of as many as 17 tributaries during each of the two survey periods. Discharge was measured with a current meter at main-valley streams and some large tributaries, and with a volumetric-measurement bag or bucket (with one or two replicate measurements) at small tributaries. Two teams of hydrologic technicians made measurements in each valley reach—one at the valley stream and one at the tributaries. This approach ensured that (1) the same individuals measured the same flow components, and (2) the time between upstream and downstream measurements was short (about 1 hour), to minimize the effect of fluctuations in discharge. Diurnal fluctuations in stream stage were not evident at any of the

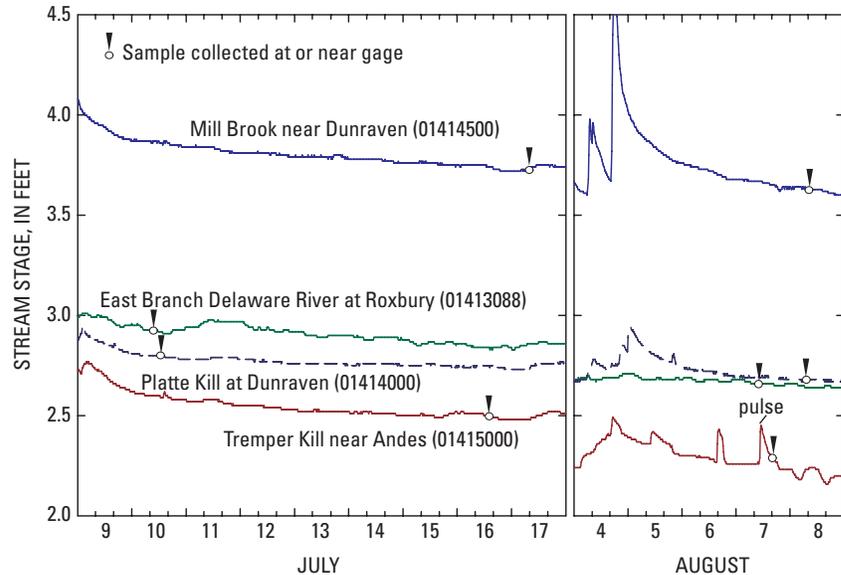


Figure 2. Stream stage at four USGS stream-gaging stations within the Pepacton watershed during the July and August 2001 valley-reach surveys. (Locations are shown in fig. 1.)

stream-gage sites. Errors in discharge measurements may have been as high as ± 8 to 10 percent, but probable errors at downstream sites were smaller (± 5 to 8 percent) because the greater stream widths allowed 30 or more measurement sections across the channels.

Water Sampling and Analysis

Water samples were collected at all 15 valley-reach measurement sites and at six to eight tributary sites in each of the two surveys. Two methods were used: equal-width-increment samples (Shelton, 1994) were collected at as many downstream valley-reach sites as feasible; grab samples were collected where the streams were too shallow and narrow for equal-width-increment samples. The grab-sample technique was used at all tributary sites and many of the upstream valley-reach sites.

The water samples were analyzed for major ions, nutrients (dissolved nitrogen species and dissolved orthophosphate), dissolved organic carbon (DOC), iron, manganese, and selected trace elements by the USGS National Water Quality Laboratory in Denver, Colo. Results are given in Butch and others (2002). Replicate and blank samples collected in this study and in the concurrent base-flow study of small subbasins in the Pepacton watershed (Heisig and Phillips, 2004) represented 8 percent of the samples. Differences between major-ion replicate analyses were acceptable; typically 5 percent or less, except for low potassium concentrations (0.5 mg/L), for which replicate samples differed by as much as 10 percent.

Estimation of Tributary Streamflow and Water Quality

The discharge and specific conductance values estimated for the one or two small, inaccessible tributaries in five of the valley reaches were based on values measured on the nearest tributaries with drainage basins of similar size. All estimated tributary discharges were small— 0.04 to 0.2 ft³/s in July and 0.02 to 0.05 ft³/s in August (table 2). Estimated tributary discharges averaged 7 percent of the total streamflow gain in the July survey, and 4 percent of the gain in the August survey.

Tributary water quality (major-ion concentrations) was estimated for all unsampled sites so that total, flow-weighted tributary water quality could be calculated for each valley reach and used in the mass-balance computations. Most small tributaries had low major-ion concentrations with narrow concentration ranges. Concentrations in unsampled tributaries were either (1) estimated from the regression relation of specific conductance to major-ion concentration for tributaries in drainage areas of similar land use, or (2) assigned on the basis of analytical results from nearby tributaries with similar specific conductance values (including tributaries sampled in the small-basin companion study (Heisig and Phillips, 2004).

Major-ion concentrations were estimated for 31 percent of all tributary flow for July and 10 percent of all tributary flow for August. The chemical composition of ground water in these areas is largely unaffected by road salt; hence, calcium and bicarbonate were typically the dominant ions (Heisig and Phillips, 2004). Concentrations of nutrients (nitrate and orthophosphate) in tributaries were not estimated because of their nonconservative nature and their unpredictable source concentrations from farmed areas. Concentrations of nonconservative constituents were subject to losses from biological uptake, chemical transformation, or sorption on sediments. Most tributaries for which major-ion concentrations were estimated drain small, largely undeveloped (forested) subbasins, although some contain farms, former farmland, and short stretches of roads.

Regression values (r^2) for the relation of specific conductance to calcium, magnesium, acid-neutralizing capacity (ANC), and potassium concentration in tributaries ranged from 0.67 to 0.98. Values for chloride and sodium concentration where road salt had affected base-flow chemistry were within the lower part of the r^2 range. Chloride and sodium concentrations below 1.5 mg/L did not show any correlation with specific conductance, nor did sulfate concentrations in any range. Therefore, the concentration

Table 2. Discharge increases in valley-reach streams, contributions from tributaries, and calculated ground-water discharge to valley reaches in Pepacton watershed in Catskill region of southeastern New York, July and August 2001.

[All streamflow and ground-water-discharge values in cubic feet per second. Est., estimate. A dash indicates no measurement made.]

Reach identifier* in fig. 1	July 2001 Survey				August 2001 Survey			
	Increase in discharge from upstream to downstream measurement site	Total tributary flow to reach (values in parentheses are est. percentage of total flow)	Calculated ground-water discharge (values in parentheses are est. ground-water contribution, as percentage of streamflow gain)	Potential percent error in ground-water discharge (assuming $\pm 10\%$ error in flow measurements that minimize and maximize ground-water-discharge est.)	Streamflow gain from upstream to downstream measurement sites	Total tributary flow to reach (values in parentheses are est. percentage of total)	Calculated ground-water discharge (values in parentheses are est. ground-water contribution as percentage of streamflow gain)	Potential percent error in ground-water discharge (assuming $\pm 10\%$ error in flow measurements that minimize and maximize ground-water-discharge est.)
TC	1.22	0.20(100)	1.02 (84)	± 22	0.60	0.05 (100)	0.55 (92)	± 16
TK	2.15	0.78 (19)	1.37 (64)	± 90	1.23**	0.05 (0)	1.18 (96)	± 44
PK	1.25	0.24 (21)	1.01 (81)	± 79	0.61	0.13 (16)	0.48 (79)	± 74
MB1	--	--	--	--	2.02	0.47 (9)	1.55 (77)	± 51
MB2	--	--	--	--	1.89	0.64 (0)	1.25 (66)	± 95
BK1	0.82	0.27 (19)	0.55 (67)	± 108	0.90	0.10 (0)	0.80 (89)	± 36
BK2	1.55	0.04 (100)	1.51 (97)	± 53	0.69	0.00 (0)	0.69 (100)	± 63
EBD1	3.57	0.66 (0)	2.91 (82)	± 25	0.87	0.02 (0)	0.85 (98)	± 15
EBD2	4.44	0.00 (0)	4.44 (100)	± 33	2.38	0.00 (0)	2.38 (100)	± 19

* Stream -name abbreviations:

TC Terry Clove Kill MB Mill Brook BK Batavia Kill
TK Tremper Kill PK Platte Kill EBD East Branch Delaware River

** True value may be as much as 0.3 cubic feet per second lower than this value because an upstream water release of unknown origin had not completely passed the downstream gage at the time of flow measurement.

estimates for these constituents represent either individual or the average concentrations in nearby tributaries.

The streamflow and chemical data for all tributaries were compiled, and all tributary flows within each valley reach were summed (total tributary inflow), their composite chemical concentrations were calculated as flow-weighted means (See appendix). Charge balances (the percent difference between the total negative charge of anions and the total positive charge of cations) were used as a check of the reasonableness of the major-ion-chemistry results. Charge balances for all valley reaches were acceptable (within ± 5 percent).

Mass-Balance Calculation of Ground-Water Quality

Major-ion concentrations of ground water in each valley reach were calculated from the July and August streamflow measurements and chemical data through the following mass-balance equation:

$$Q_{gw} C_{gw} = Q_{dn} C_{dn} - Q_{up} C_{up} - Q_{trib} C_{trib} \quad (\text{Equation 1})$$

Where:

Q_{gw} = ground-water discharge to the valley stream

C_{gw} = concentration of constituent in ground water

Q_{dn} = streamflow at downstream valley-stream site

C_{dn} = concentration of constituent at downstream valley-stream site

Q_{up} = streamflow at upstream valley-stream site

C_{up} = concentration of constituent at upstream valley-stream site

Q_{trib} = sum of tributary flows within a valley reach (tributary inflow)

C_{trib} = flow-weighted mean concentration of constituent among tributaries

A major-ion concentration in ground water C_{gw} equals:

$$C_{gw} = \frac{Q_{dn} C_{dn} - Q_{up} C_{up} - Q_{trib} C_{trib}}{Q_{gw}}$$

Individual major-ion results within each reach were combined and expressed as a major-ion water type (Appendix), defined by the ions that constituted at least 10 percent of the total cations (calcium, magnesium, sodium, and potassium) or the total anions (bicarbonate, chloride, sulfate, and nitrate), in milliequivalents per liter.

Potential Errors in Estimates of Ground-Water Discharge and Water Type

Errors in estimates of ground-water discharge and, ultimately, major-ion water type, were largely related to (1) uncertainties in the upstream and downstream streamflow measurements, and (2) the difference between the upstream and downstream streamflow measurements relative to the magnitude of the flows. For instance, a potential uncertainty of

± 10 percent in streamflow measurement in valley streams with large flows would require a proportionately large difference between upstream and downstream streamflow measurements to overcome the effect of this uncertainty.

The actual errors in the streamflow measurements are unknown; therefore, a worst-case potential error (in percent) was calculated for each ground-water-discharge estimate. Ground-water discharges were recalculated from combinations of ± 10 -percent adjustments in streamflow that maximized and minimized the ground-water estimates. Ground-water-discharge estimates were maximized when the upstream and tributary inflow values were adjusted to 10 percent smaller than the measured values, and the downstream streamflow was adjusted to 10 percent greater than its measured value. The ground-water-discharge estimates were minimized when these negative and positive adjustments were reversed. Thus, the maximum and minimum ground-water discharges represent the same percent departure from the initial estimate and differ only in sign. Potential errors ranged from ± 15 to ± 108 percent and were generally smaller in August than in July because the smaller upstream and tributary flows in August generally resulted in an increase in the percentage of base flow contributed by ground-water discharge (table 2).

The potential-error results allow a comparison of the uncertainty of the ground-water discharge estimates among valley reaches within and between the two surveys. Small differences between upstream and downstream streamflow, and large flow magnitudes, contribute to high potential errors (table 2). The actual ranges of percent error are probably smaller than indicated, however, because these estimated uncertainty values used extreme-opposite biases among the streamflow measurements. Opposite biases are unlikely because (1) valley-stream measurements are probably biased in the same direction if the channel geometries within a given reach are similar; (2) the downstream-measurement errors are probably smaller than ± 10 percent because the channels at the downstream sites are larger than at the upstream sites and, thus, provide better measurement conditions; and (3) volumetric measurements of tributary flows are more likely to underestimate streamflow than to overestimate it; therefore, a negative bias is most likely.

The effects of errors in ground-water-discharge estimates on water-type determinations were evaluated through data collected in August 2001 from four valley reaches (BK1, BK2, MB2, EBD2), which represent the range of land uses in valley-bottom areas within the watershed. Potential errors in ground-water discharges at these reaches ranged from ± 19 to ± 95 percent. Ground-water types were calculated from the maximum and minimum ground-water discharges, based on ± 10 -percent errors in streamflow measurements. If no change in water type occurred over this error range, the estimates were considered insensitive to the range of streamflow-measurement errors, and no further analysis was done. If a change in water type was indicated, the sensitivities of water-type results to streamflow errors smaller than ± 10 percent (± 5 , ± 3 percent) were evaluated.

Results of this sensitivity evaluation indicated that water type changed little, if at all, within any reach except the one (MB2) with the highest potential error (± 95 percent). All changes in water type coincided only with positive (+) changes in ground-water discharge. The water types shifted from (1) unaffected water to water containing chloride (or sodium), or (2) water containing chloride as a secondary anion to water with chloride as the dominant anion. No change in water type was indicated for the valley reaches with potential ground-water-discharge errors of ± 19 percent (EBD2) and 63 percent (BK2). The water type for the valley reach with a ± 36 -percent potential error (BK1) changed to a chloride-dominated type only at the $+10$ -percent streamflow-measurement error. Water type at the valley reach with a ± 95 -percent potential error (MB2) changed to a chloride or sodium-affected water in response to $+10$, $+5$, and $+3$ percent increases in streamflow measurement error. In summary, water type remained stable over relatively large changes in ground-water-discharge estimates, except where those changes approached 100 percent of the original discharge value.

Ground-Water and Tributary Contributions to Stream Base Flow in Selected Main-Valley Reaches

The quantity and quality of ground-water and tributary contributions to valley-stream base flow provide basic hydrologic information on 1) the proportions of tributary flow from upland areas and ground-water discharge from valley-bottom areas and 2) the interaction between the shallow, most active part of the ground-water flow system (affected by human activities) and surface water in valley-bottom settings. Water-quality and land-use data indicate a connection between land-use practices and the quality of shallow ground water and base flow in the main-valley streams studied.

Quantity of Water

Analysis of the streamflow measurements from the valley-reach surveys revealed three patterns in the total and individual quantities of ground-water discharge and tributary inflow to main-valley streams: (1) the streamflow gain in a given valley reach was chiefly a function of the volume of annual runoff (precipitation minus evapotranspiration) in the valley-reach drainage area, (2) ground-water discharges were consistently greater than tributary flows in all valley reaches in both surveys, and (3) tributary inflows were strongly affected by upland drainage area size, main-valley width, permeability of valley-fill deposits, and local annual runoff. These observations are described in the following paragraphs.

Relation Between Streamflow Gain and Annual Runoff Volume

A general positive relation was found between streamflow gain within the valley reaches and annual runoff volume, regardless of the proportions of ground-water discharge and tributary inflow (fig. 3). Annual runoff represents the annual amount of water available for streamflow (stormflow plus base flow). Local differences in precipitation and evapotranspiration cause runoff differences of as much as 5 in. among the drainage areas of the nine valley reaches (Randall, 1996). The total volume of runoff from each valley reach, expressed in millions of cubic feet per year (table 1), is the average annual runoff volume, in inches, multiplied by the drainage area of the valley reach. This includes the valley floor, the adjacent unchanneled uplands, and the drainage areas of upland tributaries.

A study in central New England (Wandle and Randall, 1994) reported that low-flow discharge (base flow) in streams was largely a function of the amount of water available to the upstream drainage area and the amount of permeable stratified drift at land surface relative to the amount of less-permeable unconsolidated material within the drainage area. The extent of stratified drift relative to the size of valley-reach drainage areas in the Pepacton watershed does not vary greatly; this may explain why annual runoff volume, not amount of stratified drift, appears to be the major control on streamflow gain along the valley reaches.

Negative departures from the trend line for streamflow gain as a function of annual runoff volume for the July and August surveys (fig. 3) are probably due to one or more of the following factors: (1) large potential errors in ground-water-discharge estimates, (2) low rainfall within the Tremper Kill subbasin, and (3) complete loss of flow in large tributaries during the 3 to 4 weeks between the two surveys. The relatively small July streamflow gains at the Tremper Kill (TK) and upper Batavia Kill (BK1) valley reaches are consistent with the large potential errors in the ground-water-discharge estimates for these reaches (table 2, fig. 3). Specifically, BK1 is the only valley reach in which the streamflow gain in July was less than the streamflow gain in August—an anomaly that might be ascribed to over-measurement of discharge at the upstream (BK1) site. The downstream-site measurement appears reasonable because it serves as the upstream site for valley reach BK2, which plots on the trend line in figure 3.

The relatively small streamflow gains within the Tremper Kill (TK) valley reach in July, and particularly in August, may also reflect smaller rainfall amounts in this subbasin than in the others. Localized thunderstorms are common during the summer, and monthly rainfall totals for July and August at the two weather stations (fig. 1) differed by more than 1 in. (Cornell University Northeast Regional Climate Center,

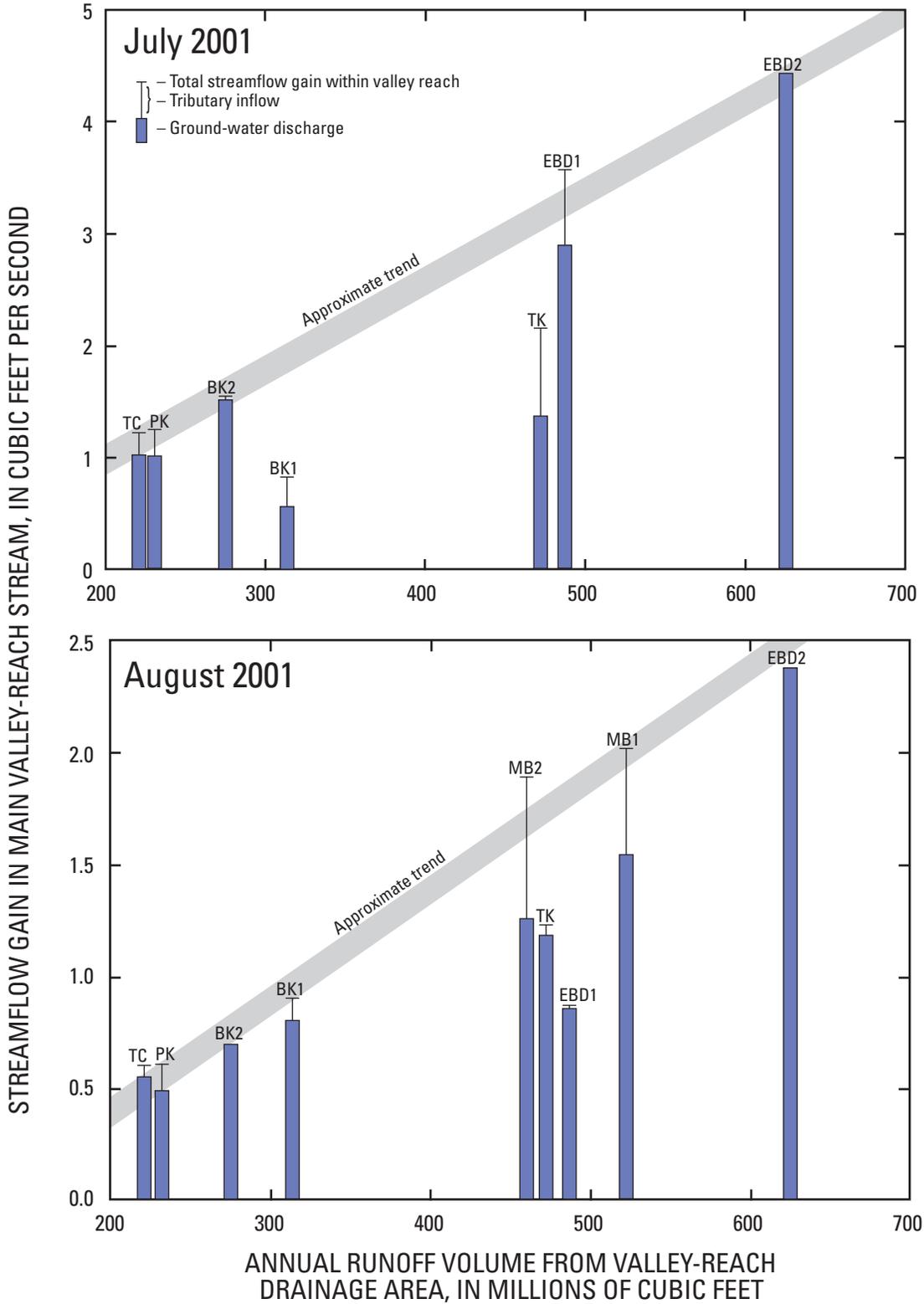


Figure 3. Total streamflow gain within the nine valley reaches as a function of annual runoff volume from their respective valley-reach drainage areas (not including headwater drainage area upvalley from valley reach), Pepacton watershed, southeastern N.Y., July and August 2001. (Locations are shown in fig. 1.)

written commun., 2002). Precipitation was not recorded within the Tremper Kill subbasin, but streamflow data were available from USGS stream-gaging stations (figs. 1, 2) on the Tremper Kill, Platte Kill, Mill Brook, and East Branch Delaware River at Margaretville (Butch and others, 2002). The July and August 2001 monthly means of daily mean discharges at these sites were compared with the corresponding monthly means for the period of record at each of these stream-gaging stations; the results indicate that Tremper Kill means were 6 to 14 percent lower than the means for the other subbasins in July, and 8 to 17 percent lower in August; this supports the other evidence that rainfall in the Tremper Kill subbasin was less than in the surrounding subbasins during this study.

The reach with the largest negative departure from the August trend line for streamflow gain as a function of annual runoff (fig. 3) was the upper East Branch Delaware River valley reach (EBD1), which had plotted close to the trend line in July. The decrease in streamflow gain between the two surveys coincided with the loss of all flow from the largest tributary to the reach and the loss of much of the flow from another large tributary. This observation suggests that as tributary flows ceased to reach the valley stream and the point of zero flow migrated upstream toward the main-valley wall, so did the ground-water mound that exists beneath the flowing tributary (Randall, 1978). Ground-water mounds are maintained by the infiltration of stream water to the water table. The dissipation of the mound under dry sections of streambeds thereby decreased ground-water discharge in addition to the loss of tributary discharge to the valley stream.

Ground-Water Discharge in Relation to Tributary Inflow

Ground-water discharge from valley deposits exceeded the inflow from tributaries in all valley reaches (fig. 4) and decreased from July to August in all but one valley reach (BK1). Tributary inflow decreased more than ground-water discharge, causing the ground-water-discharge contribution to increase as a percentage of streamflow gain in a valley reach (table 2). The decrease in tributary inflow reflects the seasonal decreases in: (1) flow from upland sources and (2) the amount of tributary flow lost through streambed infiltration (Randall, 1978). Infiltration losses are typically greatest where a tributary crosses permeable material within a wide main valley before joining the valley stream. Tributary flow that infiltrates permeable deposits near the valley stream can move rapidly toward the valley stream as ground water; thus, a loss of tributary flow through infiltration near the valley stream would result in an increase in ground-water discharge to the valley stream.

Differences in Tributary Inflow Among Valley Reaches

Differences in tributary-inflow contributions (base flow from upland areas) to the valley streams correspond to differences in width and permeability of valley-fill deposits, size of drainage area, and annual runoff volume. Tributaries entering wide valleys with permeable valley fill (outwash, ice-contact, or alluvial deposits) are likely to lose more water through streambed infiltration than those entering narrow valleys or valleys that contain only poorly permeable valley fill (thin alluvium over till). Similarly, valley reaches with large upland drainage areas and (or) large annual runoff volumes will have greater tributary inflow than valley reaches with small upland drainage areas and low annual runoff volumes. For example, no tributary flow reached the stream in reach EBD2 in July or in August 2001 (fig. 4). One large tributary lost all flow to streambed infiltration before reaching the valley stream because it has an exceptionally long (nearly 0.5 mi) channel that traverses permeable valley-fill material within the main valley. Large tributaries to valley reaches TK and EBD1 contributed most of the tributary inflow to the valley streams in July, but these contributions decreased in August more than in the other valley reaches when their flow decreased to, or below, the infiltration capacity of the streambeds. The four valley reaches with narrow valley bottoms and relatively small upland drainage areas (BK2, BK1, TC, PK) had relatively small tributary inflows in July and August, but two other reaches with narrow valley bottoms (MB1, MB2) had the largest tributary inflows of the August survey. Reaches MB1 and MB2 have somewhat larger drainage areas, greater annual runoff volumes, and more tributaries than the four aforementioned valley reaches (fig. 1, table 1). Unmeasured tributary flows to MB1 and MB2 were probably greater in July than in August because tributary inflows in nearly all other valley reaches were greatest in July.

Quality of Water

The chemical quality of ground-water discharge and tributary inflows that entered valley streams during the July and August surveys was measured or calculated for all reaches except the two Mill Brook reaches (MB1, MB2) in July and the Tremper Kill (TK) reach in August. The Mill Brook reaches were temporarily affected by runoff from a local storm, and the Tremper Kill was temporarily affected by an unexplained 6-hour spike in discharge (fig. 2). Water-quality estimates were largely limited to major ions, which are more conservative (less reactive) than nutrients (such as nitrate and orthophosphate). Most major ions are derived largely from

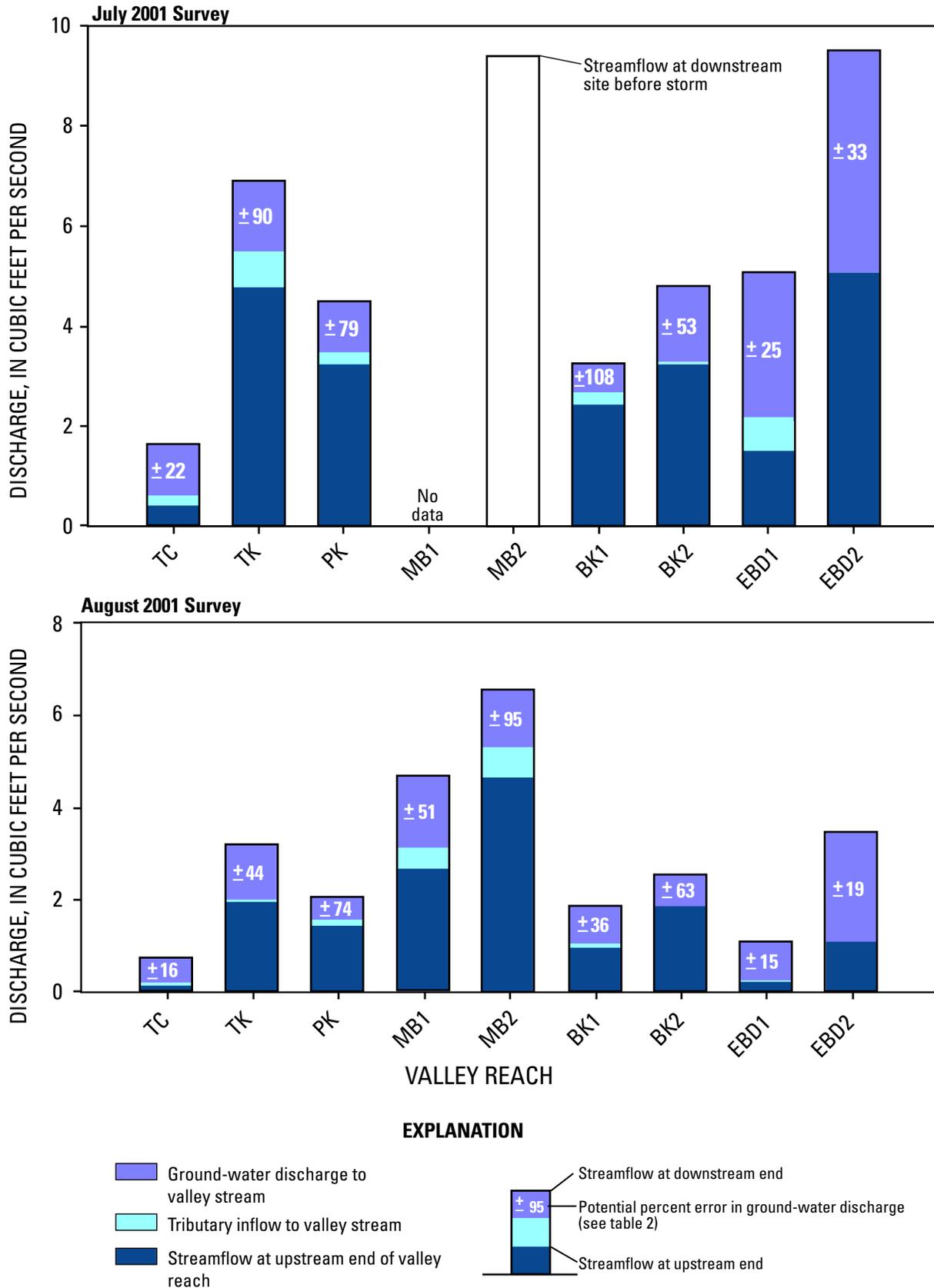


Figure 4. Ground-water-discharge and tributary-inflow contributions to total streamflow gain in the nine valley reaches, Pepacton watershed in southeastern New York, July and August 2001. (Locations are shown in fig. 1.)

natural sources, but sodium and chloride are derived mainly from road salt applied to State and county roads during winter.

Nitrate and orthophosphate are a concern because they can contribute to downstream reservoir eutrophication. Ground-water contributions of nitrate were calculated for only four valley reaches, however, and no calculations for orthophosphate were made because 1) their nonconservative nature (loss or retention due to biological activity and (or) sorption on sediments) in hyporheic zones and in streams, and 2) their unpredictable concentrations in tributaries, especially in farmed areas, introduce unacceptable uncertainties into budget calculations. The principal sources of these nutrients in ground water are human waste from septic systems, particularly in villages, and animal wastes, such as cow manure applied to cultivated fields and pastures.

General Water-Type Classification

The water components (tributary inflow, ground-water discharge, and flow in valley streams) in each valley reach were classified as one of six chemical water types according to their major-ion concentrations (fig. 5 and appendix). Water-type designation reflects the specific ions that constituted at least 10 percent (in milliequivalents per liter) of the cations and anions (herein referred to as “defining ions”). The cations can include calcium (Ca), sodium (Na), magnesium (Mg), and potassium (K), and the anions can include bicarbonate (HCO_3), chloride (Cl), sulfate (SO_4), and nitrate (NO_3). For example, sodium and chloride represent at least 10 percent of the cations and anions, respectively, in the two water types that are most affected by leachate from road-deicing salts, and represent less than 10 percent of the cations and anions, respectively, in the other four water types, which are largely unaffected by road-salt leachate.

The four water types for which sodium and chloride are not defining ions all have Ca and HCO_3 as defining ions; the presence or absence of Mg and SO_4 as defining ions determines the specific water type (fig. 5). Magnesium concentration varies locally within streams in the Pepacton watershed and is probably associated with the till composition (carbonate minerals) and thickness within the watershed and, in some agricultural areas, with the amount of lime (crushed limestone) that is applied to fields. Base-flow SO_4 concentrations in most small tributaries and in Mill Brook were generally low; SO_4 was a defining ion only in dilute waters with low HCO_3 concentrations. The specific conductance of these dilute waters (unaffected by road salt) was less than 70 $\mu\text{S}/\text{cm}$ in all samples. Dilute waters represent either a short ground-water residence time, or a longer residence time in relatively unreactive aquifer material. Bicarbonate (HCO_3) concentration in ground water typically increases (evolves) with increasing residence time or increased reactivity (carbonate mineral content) of the surrounding aquifer material until it eventually becomes the only defining anion.

Waters Affected By Road Salt and Nutrients

The principal source of sodium and chloride to shallow ground water is road salt that is applied most heavily along major roads in winter, which subsequently infiltrates to the water table over time. The principal sources of nutrients in ground water are cow manure that is applied to cultivated fields, and human waste that is discharged from septic systems, particularly in villages.

Chloride and Sodium Sources and Concentrations

Chloride and (or) sodium become defining ions only in waters affected by road salt. Chloride may be more abundant than bicarbonate in some instances. Ground waters affected by road salt began as one of the four naturally occurring water types (largely unaffected by road salt), but became chemically altered by salt leachate as they flowed beneath roadway areas (fig. 6). The amount of chloride and sodium in ground water that discharges to streams is related to the type of roads and the road mileage within the drainage area (Heisig, 2000; Heisig and Phillips, 2004). Annual salt-application rates are highest on State roads (40 tons per mile of two-lane road) and county roads (32 tons per mile of two-lane road), and are lowest on town roads (1 to 12 tons per mile of two-lane road) (Heisig and Phillips, 2004). Many of the State and county roads in the Pepacton watershed parallel the major streams. The type of roads that follow the main-valley streams within each valley reach, and those in the upgradient drainage area of each valley reach, are indicated in figure 5; these roads represent nonpoint sources of salt leachate and affect only shallow ground water in the area between the road and the stream (fig. 6). The elevated sodium and chloride concentrations between roads and streams are commonly sufficient to shift the mean chemical quality of the overall ground-water discharge from a naturally occurring type to one with chloride and sodium as defining ions (fig. 5).

The estimated chloride concentrations in ground-water discharge from valley-stream reaches that contain a State or county road averaged from 8 to 13 mg/L—about 5 times higher than naturally occurring levels (fig. 5) – but these concentrations do not pose health or regulatory concerns because they do not approach the New York State drinking-water maximum contaminant level (MCL) for chloride (250 mg/L). No MCL has been established for sodium, but health guidelines suggest less than 20 mg/L for severely restricted sodium diets and less than 270 mg/L for moderately restricted sodium diets (New York State Department of Health, 2001). The chloride concentrations of ground-water discharge calculated in this study represent the mean of three ground-water components (fig. 6): (1) shallow, high-chloride ground water entering from a small area on one side of a valley, (2) deeper, low-chloride ground water entering on that side of the valley, and (3) shallow and deep low-chloride ground water entering from the other side of the valley (fig. 6). The chloride and sodium concentrations of salt-affected shallow ground

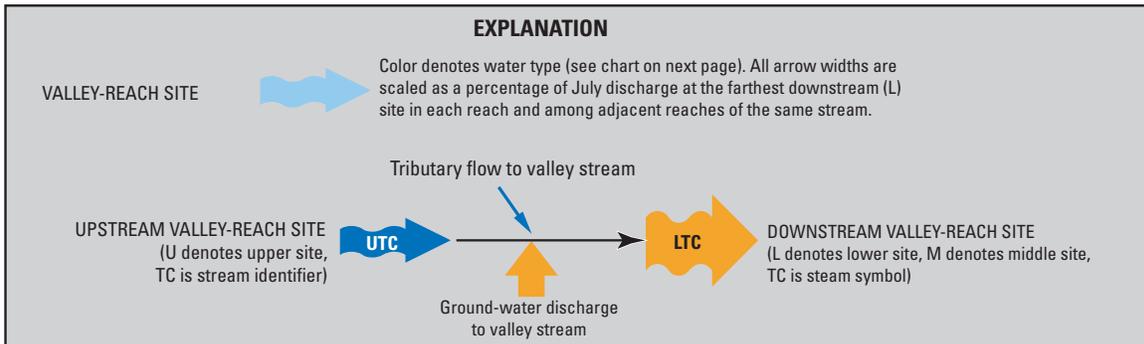
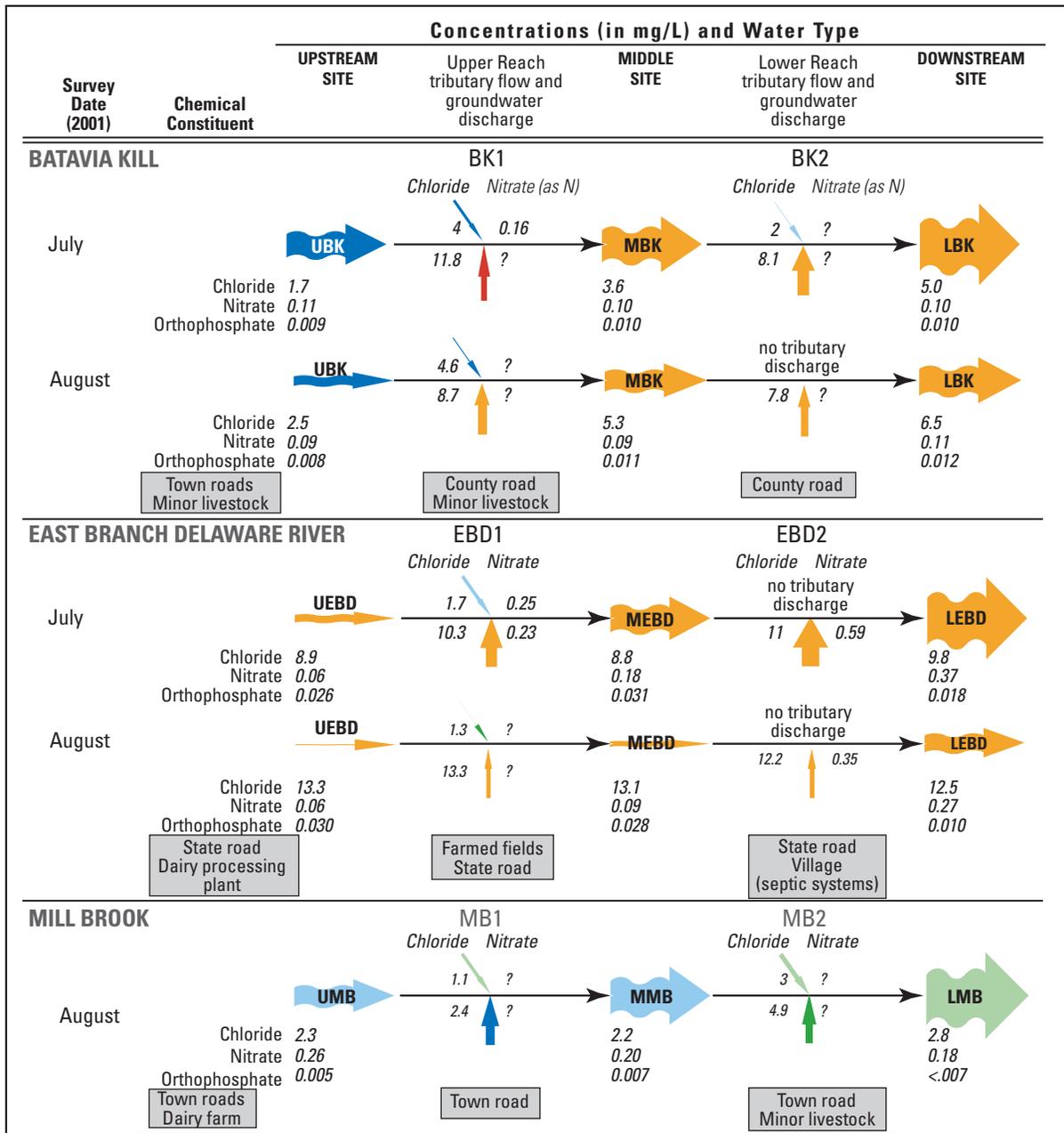


Figure 5. Relative discharge magnitude, water type, concentration of chloride, nitrate, and orthophosphate in streamflow and ground-water discharge, and land uses that might affect ground-water quality in each reach studied in Pepacton watershed, southeastern N.Y., July and August 2001. (Site locations are shown in fig. 1.).

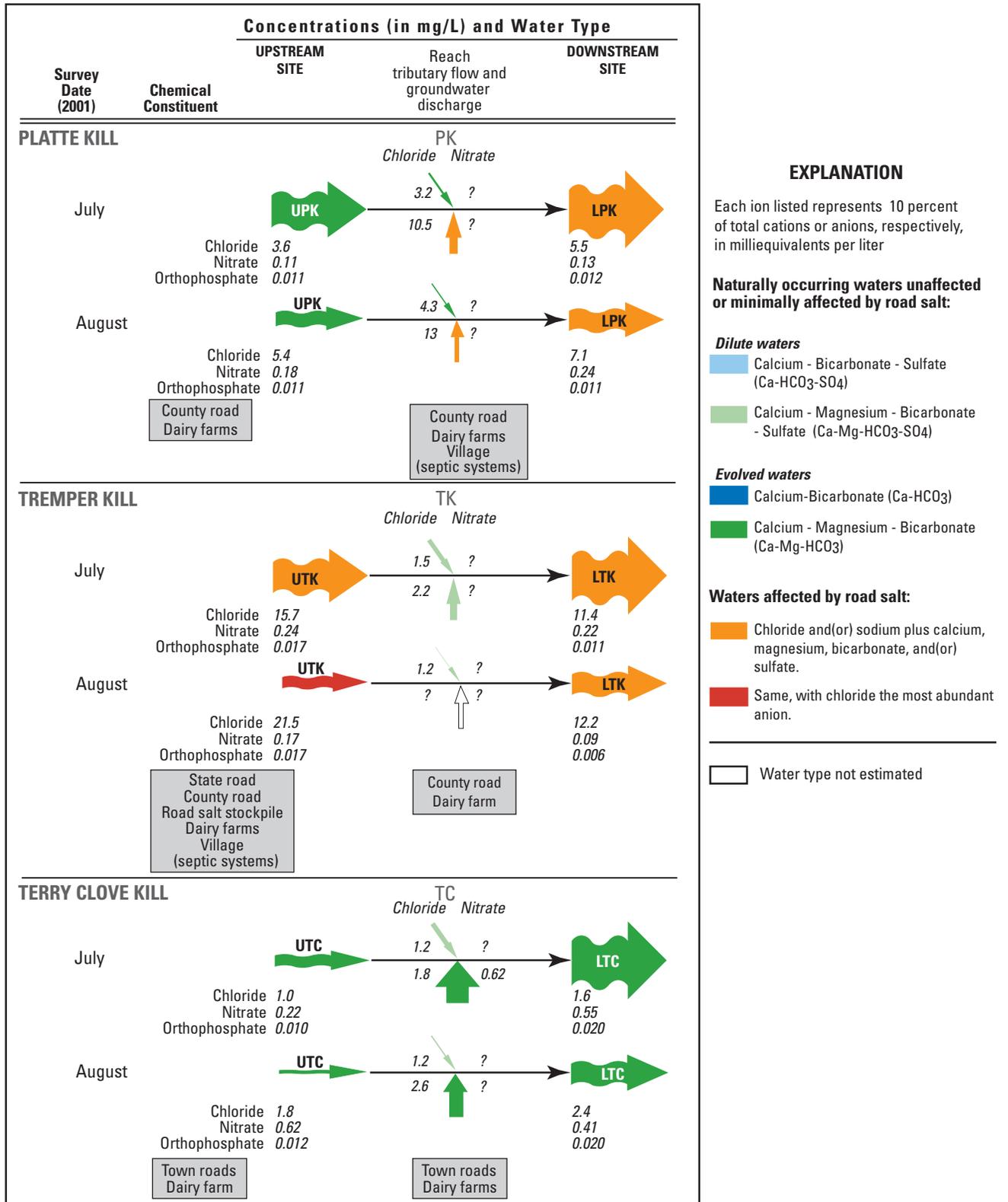
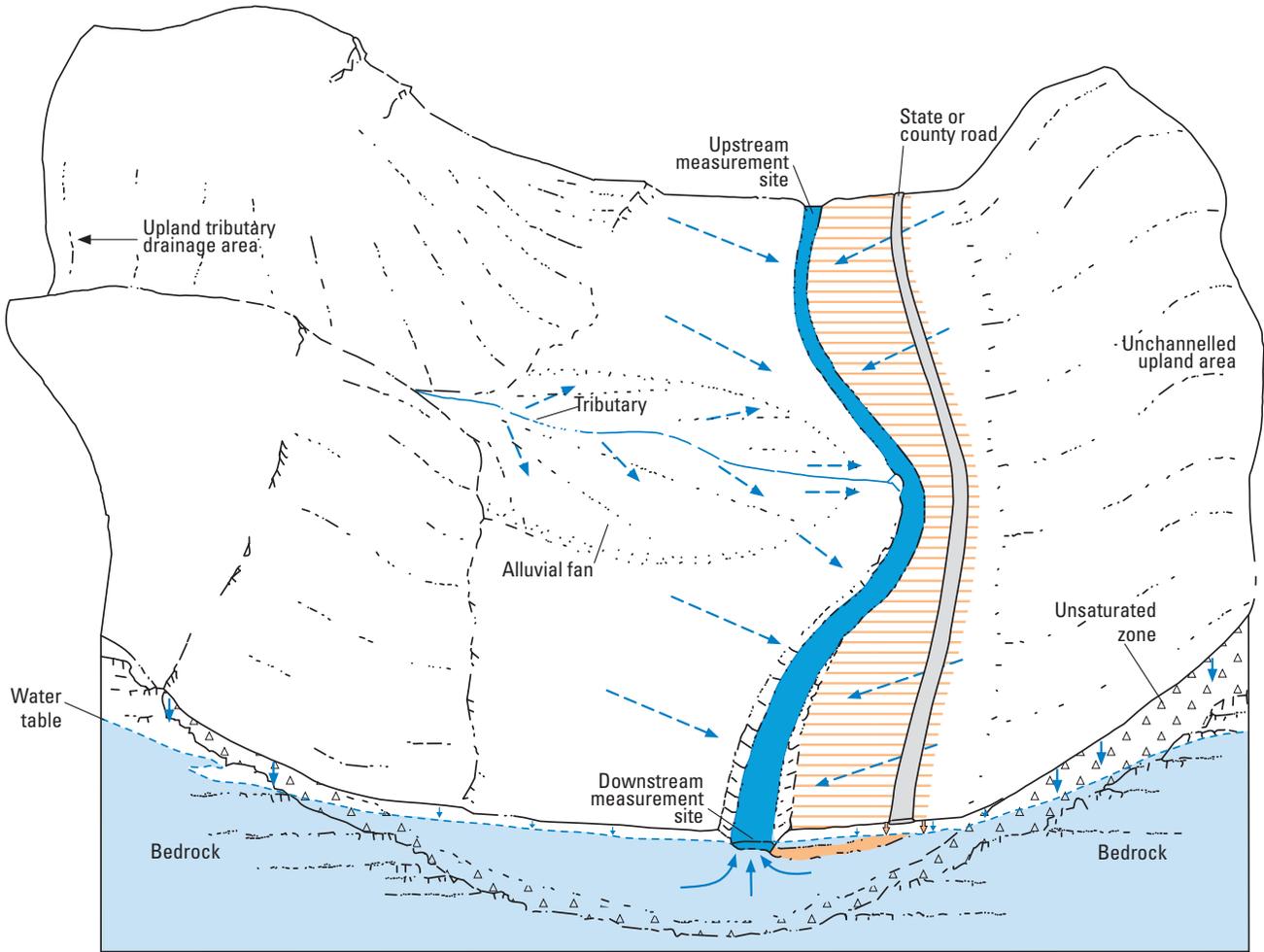


Figure 5. (Continued) Relative discharge magnitude, water type, concentration of chloride, nitrate, and orthophosphate in streamflow and ground-water discharge, and land uses that might affect ground-water quality in each reach studied in Pepacton watershed, southeastern N.Y., July and August 2001. (Site locations are shown in fig. 1.).



Not to Scale

EXPLANATION

-  **Unsaturated deposits**
-  **Saturated deposits** -- blue indicates low-chloride ground water; orange indicates ground water affected by road salt
-  **Area underlain by ground-water affected by road salt**
-  **Till** -- unsorted, poorly permeable clay-to boulder-size sediments
-  **Stratified valley-fill deposits** -- glacial ice-contact and outwash deposits and recent flood-plain (alluvial) deposits; generally permeable
-  **Bedrock** -- interbedded sandstone, siltstone, and shale
-  **Infiltrating water** -- blue indicates low-chloride water; orange indicates road-salt contaminated water
-  **Ground-water flow path**
-  **Direction of ground-water flow beneath land surface**
-  **Stream**

Figure 6. Generalized valley reach (upland tributary drainage area is omitted) showing migration of road-salt leachate to shallow ground water and the adjacent valley stream.

water in some localities may be as high as a few hundred mg/L (Massachusetts—Granato and others, 1995; Ohio—Jones and Sroka, 1997). Other effects of road salt can include corrosion of metal on bridges, damage to vegetation, decreased biodiversity along roads and nearby streams, decreased soil permeability, and toxicity to fish and birds (Environment Canada and Health Canada, 2000).

Ground-water discharge in all valley reaches that contain State or county roads was estimated to have elevated chloride concentrations (8-13 mg/L) except the Tremper Kill (TK) reach (fig. 5), which contains a county road; ground-water discharge to this reach during the July survey had an estimated chloride concentration of only about 2 mg/L. This anomaly has two possible explanations:

1. The county road largely follows the lower hillsides, well above the valley bottom, and the stream generally flows along the opposite side of the valley. Limited storm runoff from this road likely infiltrates to the water table because storm drains and ditches probably divert most runoff directly to tributaries or the stream, where it flows downstream as part of stormflow before the resumption of base-flow conditions. Also, salt leachate that infiltrates to the water table at some distance from the stream probably becomes entrained in deeper flow paths, with longer residence times, than leachate that becomes ground water in areas close to the stream and, thus, may not yet have reached the valley stream.
2. The large potential error in the quantity of ground water discharging to the Tremper Kill (table 2, fig. 4) indicates a large uncertainty in concentration estimates; therefore, 2 mg/L could be an under estimate of the actual value.

The water types indicated for nearly all valley-reach, tributary inflow, and ground-water discharge waters in each reach did not change from July to August, and none shifted to or from road-salt-affected types (fig. 5). All valley reaches except the Terry Clove Kill and the two Mill Brook reaches, which contain only town roads, had at least one streamflow component affected by road salt. The tributary contributions to streamflow gain in all reaches were classified as naturally occurring water types, largely unaffected by road salt, which is consistent with the absence of State and county roads in the tributary drainage areas.

Nitrate and Orthophosphate Sources and Concentrations

Streamflow in many of the valley reaches showed either little increase, or even a decrease, in nitrate (NO_3) and orthophosphate (PO_4) concentrations from the upstream site to the downstream site; therefore, the nitrate concentration in ground-water discharge could be estimated only for valley reaches with little or no tributary inflow and a relatively large downstream increase in nitrate concentration. Only four estimates of nitrate concentration (mg/L as N) in ground-water discharge were made, and no estimate of orthophosphate concentration was made.

Large nitrate increases within a valley reach indicate a nitrogen source within that reach, but two factors— dilution by tributary inflow and the potential for biological uptake or transformation of nitrate, indicate that the concentrations obtained through the mass-balance calculation for ground water entering a reach represents a lower limit of the true average nitrate concentration. The reaches for which nitrate concentrations in ground-water discharge were calculated were the two East Branch Delaware River reaches (EBD1, EBD2) and the Terry Clove Kill reach (TC) during the July survey, and EBD2 during the August survey. All of these reaches contain nutrient sources within their valley-bottom areas; the EBD2 reach contains a village served by septic systems, and the others contain cultivated fields or dairy farms (fig. 5). The estimated concentrations of nitrate in ground water entering these reaches ranged from 0.23 to 0.62 mg/L as N. The value for each reach represented an average for the entire reach; the concentrations in shallow ground water immediately downgradient from the sources would presumably have been higher than the average for the reach.

Nutrient concentrations (NO_3 , PO_4) in most of the main-valley reaches were low (fig. 5). The highest concentrations of both nutrients were consistently found within the Terry Clove Kill and the two East Branch Delaware River valley reaches. The elevated concentrations are generally attributable to dairy farming and septic-waste disposal within the upstream drainage areas, but an evaluation of the intensity of these practices was beyond the scope of this study; such an evaluation would require data on livestock and septic-system density and locations of sources relative to the valley stream, and the drainage area associated with each valley reach. Nevertheless, the results of this study indicate that livestock and human waste contribute nutrients to ground water that discharges to main-valley streams in the Pepacton watershed.

Summary

Streamflow measurements and water-quality data were collected at nine main-valley reaches and their tributaries in the Pepacton Reservoir watershed in the Catskill Mountains during base-flow periods in July and August of 2001. The data were used in mass-balance equations to estimate the quantity and major-ion concentrations of ground water entering main-valley streams from adjacent valley-fill deposits. This information provides a general indication of the major-ion concentrations of shallow ground water that discharges to streams in six main valleys within the Pepacton watershed. Estimation of nutrient concentrations (nitrate and orthophosphate) in ground water by this method was limited or precluded by the nonconservative behavior of these constituents.

Total gains in streamflow between the upstream and downstream valley-reach sites were closely related to the volume of annual runoff from the respective valley-reach

drainage areas, regardless of the proportion of ground-water discharge to tributary inflow within a reach. Ground-water discharge exceeded tributary inflow in all valley reaches. The proportions of ground-water discharge and tributary inflow in the valley reaches reflected the width and permeability of valley-fill deposits. Stream reaches in narrow valleys without extensive valley fill tended to receive the largest proportions of tributary inflow and the smallest proportions of ground-water discharge, whereas tributary inflow to wide valleys with extensive valley fill was the smallest proportion of stream gain because of losses through streambed infiltration. Ground-water discharge was the largest proportion of streamflow gain in reaches of wide valleys.

The major-ion composition of water from valley-stream sites, tributary inflow, and ground-water discharge in each reach was evaluated. All waters ranged from naturally occurring waters with little or no indication of human effect, to water types affected by road salt. Naturally occurring water types were typically a calcium-bicarbonate type. Nearly all ground-water-quality estimates and base-flow samples from main-valley reaches that contain State or county highways indicated road-salt-affected water types. Mean concentrations of chloride in ground-water discharge (8-13mg/L) were typically about 5 times higher than the naturally occurring concentrations (less than 2 mg/L). Application of salt to a road in a valley bottom affects only the shallow ground water in the area between the road and the stream, but the concentrations in the water entering the stream can be sufficiently large to elevate the mean chloride concentration of ground-water discharge in the reach.

Estimation of nitrate and orthophosphate concentrations in ground-water discharge was not possible because these nutrients are nonconservative and their concentrations in unsampled tributaries that pass through dairy-farm areas could not be reliably estimated. However, stream-water samples collected downstream from manure sources or villages served by septic systems consistently had the highest nutrient concentrations.

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Appendix

Appendix A . Valley-stream discharge at sampling sites and tributary discharge and ground-water flow into reach, with major-ion water type and major-ion concentration of each during baseflow-sampling surveys in Pepacton Reservoir watershed in southeastern New York, July and August 2001.

[Concentrations in milligrams per liter except as specified. $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25° Celsius. \geq greater than or equal to, $<$ less than. Dash indicates no data or no estimated value. Analyses by U.S. Geological Survey, Denver, Colo. Locations are shown in fig. 1.]

Valley stream	Site or flow-component identifier*	USGS station identifier	Discharge or f/w (ft ³ /s)	Major-ion water type	Specific conductance (mS/cm)	Sodium (Na)	Potassium (K)	Magnesium (Mg)	Calcium (Ca)	Chloride (Cl)	Sulfate (SO ₄)	Bicarbonate (HCO ₃)	Orthophosphate (PO ₄) as P	Nitrate (NO ₃) as N
July 2001 Survey														
Batavia Kill	UBK	0141309740	2.42	Ca-HCO ₃	55	2.1	0.41	1.2	6.6	1.7	4.5	24	0.009	0.107
	BK1 trib		0.27	Ca-HCO ₃	94	3.5	0.48	1.9	12.0	4.0	4.6	41	--	0.160
	BK1 gw		0.55	Ca-Na-Cl-HCO ₃	101	6.7	1.02	1.4	7.8	11.8	7.4	16	--	--
	MBK	01413098	3.24	Ca-Na-HCO ₃	66	3.0	0.52	1.3	7.3	3.6	5.0	24	0.010	0.097
	BK2 trib		0.04	Ca-HCO ₃ -SO ₄	50	2.0	0.45	0.9	6.0	2.0	5.3	18	--	--
	BK2 gw	1.51	Ca-Na-HCO ₃ -Cl	98	5.3	0.36	1.7	9.8	8.1	5.6	40	--	--	
	LBK	01413099	4.79	Ca-Na-HCO ₃	76	3.7	0.47	1.4	8.1	5.0	5.2	29	0.010	0.102
East Branch Delaware	UEBD	01413070	1.50	Ca-Na-HCO ₃ -Cl	106	7.9	0.45	1.5	10.2	8.9	3.7	38	0.026	0.057
	EBD1 trib		0.66	Ca-HCO ₃ -SO ₄	49	1.9	0.45	0.9	6.0	1.7	5.3	18	--	--
	EBD1 gw	2.91	Ca-Na-HCO ₃ -Cl	112	9.3	0.68	1.6	10.4	10.3	5.6	38	--	\geq 0.23	
	MEBD	01413088	5.07	Ca-Na-HCO ₃ -Cl	102	7.9	0.58	1.5	9.8	8.8	5.0	35	0.031	0.180
	EBD2 trib		0.00	--	--	--	--	--	--	--	--	--	--	--
	EBD2 gw		4.44	Ca-Na-HCO ₃ -Cl	126	7.7	0.8	1.9	12.0	11.0	6.7	35	--	\geq 0.59
	LEBD	01413092	9.51	Ca-Na-HCO ₃ -Cl	113	7.8	0.68	1.7	10.8	9.8	5.8	35	0.018	0.370
Mill Brook	UMB	01414308	4.93 (rain)	Ca-HCO ₃ -SO ₄	52	1.2	0.38	1.0	6.8	1.9	5.5	21	0.008	0.276
	MB1 trib		(rain)	--	--	--	--	--	--	--	--	--	--	--
	MB1 gw		(rain)	--	--	--	--	--	--	--	--	--	--	--
	MMB	01414340	8.34 (rain)	Ca-HCO ₃ -SO ₄	48	1.2	0.38	1.1	6.0	1.9	5.3	18	0.004	0.211
	MB2 trib		(rain)	--	--	--	--	--	--	--	--	--	--	--
	MB2 gw		(rain)	--	--	--	--	--	--	--	--	--	--	--
	LMB	01414500	9.52	Ca-Mg-HCO ₃ -SO ₄	52	1.5	0.42	1.3	6.3	2.0	5.5	21	0.004	0.191
Platte Kill	UPK	10413936	3.23	Ca-Mg-HCO ₃	72	3.0	0.65	1.8	7.7	3.6	4.9	29	0.011	0.110
	PK trib		0.24	Ca-Mg-HCO ₃	72	2.5	0.31	1.7	7.5	3.2	4.9	31	--	--
	PK gw		1.01	Ca-Na-HCO ₃ -Cl	130	7.0	0.8	2.3	10.2	10.5	6.1	38	--	--
	LPK	01413945	4.48	Ca-Na-Mg-HCO ₃	85	4.1	0.71	2.0	8.9	5.5	5.5	32	0.012	0.130
Tremper Kill	UTK	01414865	4.71	Ca-Na-HCO ₃ -Cl	125	8.7	1.03	2.5	9.2	15.7	5.8	32	0.017	0.236
	TK trib		0.78	Ca-Mg-HCO ₃ -SO ₄	55	1.7	0.34	1.8	5.7	1.5	5.6	23	--	--
	TK gw		1.37	Ca-Mg-HCO ₃ -SO ₄	60	1.7	0.57	1.9	6.0	2.2	6.4	18	--	\geq 0.110
	LTK	0141500	6.86	Ca-Na-Mg-HCO ₃ -Cl	104	6.5	0.86	2.3	8.2	11.4	5.9	28	0.011	0.218
Terry Clove Kill	UTC	01415438	0.41	Ca-Mg-HCO ₃	67	1.6	1.1	2.1	7.2	1.0	5.3	30	0.010	0.216
	TC trib		0.20	Ca-Mg-HCO ₃ -SO ₄	55	1.8	0.75	1.7	6.0	1.6	5.3	20	--	--
	TC gw		1.02	Ca-Mg-HCO ₃	79	2.2	1.56	2.5	8.2	1.8	7.0	32	--	\geq 0.620
	LTC	01415465	1.63	Ca-Mg-HCO ₃	74	2.0	1.37	2.3	7.7	1.6	6.4	30	0.020	0.552

* Prefix U, upper site; M, middle site; L, lower site.
trib (tribuary) estimates refer to all tributaries entering valley reach; gw (ground water) estimates refer to entire valley reach

Appendix A (continued) . Valley-stream discharge at sampling sites and tributary discharge and ground-water flow into reach, with major-ion water type and major-ion concentration during baseflow-sampling surveys in Pepacton Reservoir watershed in southeastern New York, July and August 2001.

Valley stream	Site or flow-component identifier*	USGS station identifier	Discharge or flow (ft ³ /s)	Major-ion water type	Specific conductance (mS/cm)	Sodium (Na)	Potassium (K)	Magnesium (Mg)	Calcium (Ca)	Chloride (Cl)	Sulfate (SO ₄)	Bi-carbonate (HCO ₃)	Ortho-phosphate (PO ₄) as P	Nitrate (NO ₃) as N
August 2001 Survey														
Batavia Kill	UBK	0141309740	0.94	Ca-HCO ₃	67	2.5	0.58	1.3	7.8	2.5	4.5	30	0.008	0.091
	BK1 trib		0.1	Ca-HCO ₃	113	4.0	0.51	2.2	14.3	4.6	4.7	55	--	--
	BK1 gw		0.8	Ca-Na-HCO ₃ -Cl	80	4.8	0.77	1.3	7.2	8.7	6.3	22	--	--
	MBK	01413098	1.84	Ca-Na-HCO ₃ -Cl	75	3.6	0.66	1.4	7.9	5.3	5.3	28	0.011	0.087
	BK2 trib		0	--	--	--	--	--	--	--	--	--	--	--
	BK2 gw	0.69	Ca-Na-HCO ₃ -Cl	83	4.7	0.74	1.4	8.0	7.8	6.1	26	--	--	
LBK	01413099	2.53	Ca-Na-HCO ₃ -Cl	86	4.2	0.66	1.6	8.9	6.5	5.4	33	0.012	0.107	
East Branch Delaware	UEBD	01413070	0.21	Ca-Na-HCO ₃ -Cl	145	9.8	0.97	2.0	13.2	13.3	3.6	52	0.030	0.062
	EBD1 trib		0.02	Ca-HCO ₃ -SO ₄	57	1.8	0.39	1.1	7.0	1.3	5.4	24	--	--
	EBD1 gw		0.85	Ca-Na-HCO ₃ -Cl	140	12.2	0.95	1.9	11.6	13.3	5.2	53	--	--
	MEBD	01413088	1.08	Ca-Na-HCO ₃ -Cl	139	11.6	0.94	1.9	11.8	13.1	4.9	52	0.028	0.090
	EBD2 trib		--	--	--	--	--	--	--	--	--	--	--	--
	EBD2 gw	2.38	Ca-Na-HCO ₃ -Cl	123	7.2	0.98	1.9	11.7	12.2	6.8	38	--	≥ 0.35	
LEBD	01413092	3.46	Ca-Na-HCO ₃ -Cl	128	8.6	0.97	1.9	11.7	12.5	6.2	43	0.010	0.266	
Mill Brook	UMB	01414310	2.65	Ca-HCO ₃ -SO ₄	59	1.3	0.5	1.1	7.4	2.3	5.4	21	0.005	0.261
	MB1 trib		0.47	Ca-Mg-HCO ₃ -SO ₄	46	1.0	0.45	1.4	5.0	1.1	5.5	18	--	--
	MB1 gw		1.55	Ca-HCO ₃ -SO ₄	48	1.6	0.62	1.2	6.1	2.4	6.0	20	--	--
	MMB	01414340	4.67	Ca-HCO ₃ -SO ₄	54	1.3	0.5	1.2	6.3	2.2	5.4	21	0.007	0.204
	MB2 trib		0.64	Ca-Mg-HCO ₃ -SO ₄	62	2.4	0.48	1.6	6.0	3.0	5.8	24	--	--
	MB2 gw	1.25	Ca-Mg-HCO ₃	87	3.4	0.98	2.0	8.7	4.9	5.2	32	--	--	
LMB	01414500	6.56	Ca-Mg-HCO ₃ -SO ₄	61	1.8	0.59	1.4	6.8	2.8	5.4	23	< 0.007	0.184	
Platte Kill	UPK	10413936	1.42	Ca-Mg-HCO ₃	89	3.3	0.99	2.1	8.9	5.4	5.3	35	0.011	0.176
	PK trib		0.13	Ca-Mg-HCO ₃	90	3.5	0.36	2.4	9.3	4.3	4.7	38	--	--
	PK gw		0.48	Ca-Na-HCO ₃ -Cl	149	8.0	1.64	3.1	14.0	13.0	9.3	45	--	--
	LPK	01413945	2.03	Ca-Mg-Na-HCO ₃ -Cl	103	4.4	1.1	2.4	10.1	7.1	6.2	38	0.011	0.237
Tremper Kill	UTK	01414865	1.94	Ca-Na-Cl-HCO ₃	146	10.7	1.47	2.8	10.3	21.5	6.6	35	0.017	0.167
	TK trib		0.05	Ca-Mg-HCO ₃ -SO ₄	65	1.9	0.19	2.3	7.1	1.2	6.7	31	--	--
	TK gw		1.18	--	--	--	--	--	--	--	--	--	--	--
	LTK	0141500	3.17	Ca-Na-Mg-HCO ₃ -Cl	106	6.3	1.08	2.4	8.5	12.2	6.2	30	0.006	0.094
Terry Clove Kill	UTC	01415438	0.12	Ca-Mg-HCO ₃	76	1.8	2.68	2.0	7.6	1.8	6.5	30	0.012	0.615
	TC trib		0.05	Ca-Mg-HCO ₃ -SO ₄	65	1.9	0.19	2.3	7.1	1.2	6.7	31	--	--
	TC gw		0.55	Ca-Mg-HCO ₃	84	2.5	1.7	2.6	8.5	2.6	7.2	35	--	--
	LTC	01415465	0.72	Ca-Mg-HCO ₃	82	2.4	1.82	2.5	8.3	2.4	7.1	34	0.020	0.408