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Editor

Acidic Deposition and Aquatic Ecosystems

Regional Case Studies

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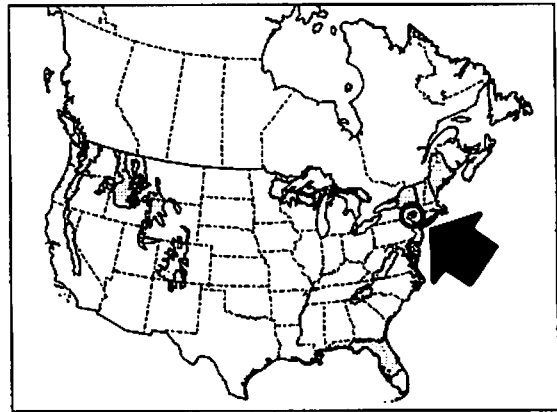# Catskill Mountains

John L. Stoddard and Peter S. Murdoch

ABSTRACT. The Catskill region of New York experiences the highest rates of acidic deposition of any region of the United States with low acid neutralizing capacity (ANC) surface waters. Surface waters are represented almost entirely by streams, whose chemical compositions are strongly affected by discharge. Many streams exhibit ANC ≤ 0 μeq L^{-1} during high-flow events; a few are acidic at baseflow. The sum of Ca^{2+} and Mg^{2+} concentrations exceeds ANC in all streams by a consistent 120 to 140 μeq L^{-1}; differences between ANC and [Ca^{2+} + Mg^{2+}] are attributable mainly to high SO_4^{2-} concentrations, which result from acidic deposition. Nitrate concentrations increase during high-flow events. Depressed ANC values during snowmelt and storms are the result of dilution of base cations, relatively consistent SO_4^{2-}, and increased NO_3^- levels.

Site-specific studies indicate that stream SO_4^{2-} is matched very closely by SO_4^{2-} concentrations in precipitation, when adjusted for dry deposition and evapotranspiration. Stream nitrate yield is exceeded by atmospheric deposition on an annual basis. Biological processes may play important roles in controlling the amount of NO_3^- supplied to Catskill streams during high-flow events.

Long-term monitoring data (1922 to the present) indicate that ANC values are increasing, largely as a result of an increasing trend in base cations. Sulfate concentrations are decreasing, but any positive effect this might have on ANC is balanced by a sharply increasing trend in NO_3^-. Limited data indicate that acidic deposition has had no deleterious effects on Catskill stream biota.

Introduction

The Catskill Mountains of southeastern New York (Chapter 5, Eilers and Selle, this volume) have become a focus of research into the effects of acidic deposition for several reasons. The region experiences higher rates of acidic deposition than any other region in the Northeast (Northeast Overview Section, Driscoll, this volume), and contains several streams with low acid neutralizing capacity (ANC) at baseflow (Murdoch 1988). Streams in the Catskill region supply drinking water for millions of people in the New York City metropolitan area, and Catskill streams have been historically renowned for trout fishing. This chapter summarizes the results of studies conducted by numerous federal, state, and municipal agencies, which indicate that surface waters of the Catskill region have undergone significant chemical changes as a result of acidic deposition.

Surface waters in the Catskill region are represented almost entirely by streams. Only two lakes sampled by the U.S. Environmental Protection Agency (EPA) Eastern Lake Survey (ELS) were
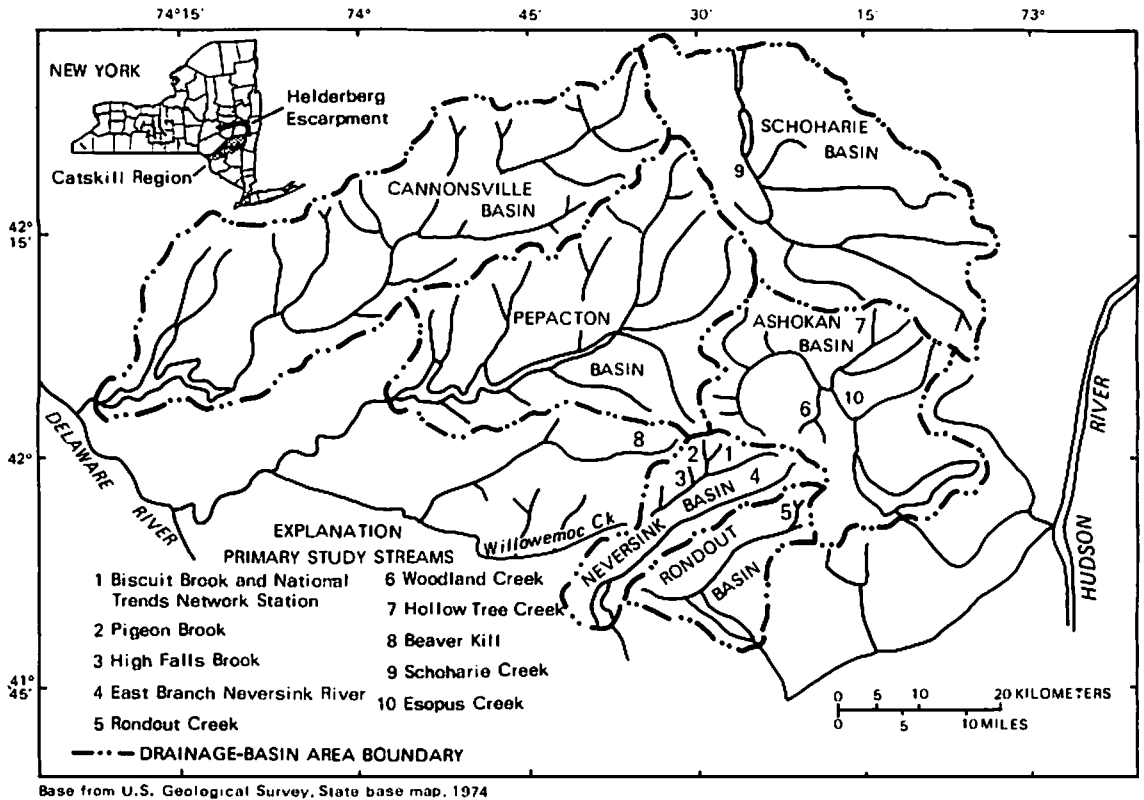
FIGURE 8.1. Map of the Catskill Mountains showing regional boundaries and boundaries of major drainage basins. Also indicated are locations of Long-Term Monitoring (LTM) sites, the Biscuit Brook intensive study and NTN site, and historical data sites on Schoharie and Esopus Creeks.

located within the boundaries of the Catskill region as defined here. As a result, much of the information presented in this chapter is derived from research and monitoring of streams in the region by the U.S. Geological Survey (USGS), the New York City Department of Environmental Protection (NYCDEP), and the EPA.

The USGS has been monitoring stream and precipitation chemistry in the Catskill region since 1983, in cooperation with the NYCDEP during 1985-88 and the EPA during 1983-86. A monitoring station for measuring continuous discharge is being operated at Biscuit Brook in the headwaters of the Neversink River (Figure 8.1). Samples for analyzing stream chemistry are collected at this site weekly, as well as during selected storms and snowmelt. Seven other streams have been sampled and their discharge measured 10 to 12 times

per year since 1983 as part of the EPA Long-Term Monitoring (LTM) project. An additional 58 streams (for a total of 66) were sampled seasonally during 1985-87 by USGS and NYCDEP. A National Trends Network (NTN) station adjacent to Biscuit Brook monitors precipitation chemistry and volume weekly. Six Catskill streams were sampled during the EPA's National Stream Survey (NSS) in 1986.

In addition to these recent sampling programs, the NYCDEP has monitored selected chemical variables at approximately 25 stream sites, beginning in 1915 at the earliest site. The USGS has collected water quality data on the Esopus Creek in the Ashokan Basin (Figure 8.1) as part of its Hydrologic Benchmark program since 1967, and also maintains several continuous discharge gauges on large streams throughout the region.

Regional Characteristics

Physiography and Geology

The Catskill Mountains, which form the northeastern end of the Appalachian Plateau (Rich 1934), are the uplifted remnants of a massive Devonian delta that fed into a shallow inland sea to the west. The high ridges are predominantly erosional remnants, and the physiography suggests that the relief is due largely to stream action. The northern, eastern, and western boundaries of the mountain region are defined by the limestone sequences of the Helderberg escarpment, the Hudson River valley, and the Delaware River valley, respectively (Figure 8.1). The southern Catskill boundary is less distinct but can be generally defined by the Delaware River and Rondout Creek valleys.

The Catskill region contains six major watersheds: Esopus Creek (in the Ashokan Basin) and Rondout Creek, which drain east to the Hudson River; Schoharie Creek, which drains north to the Mohawk River; the upper Delaware River and the Willowemoc-Beaverkill systems, which drain west to the main Delaware River; and the Neversink River, which drains south and subsequently to the Delaware River (Figure 8.1). All these streams except the Willowemoc and Beaverkill feed impoundments that provide water for New York City.

Bedrock Composition

Bedrock in the Catskills generally consists of 60% sandstones and interspersed conglomerates and 40% mudstone or siltstone. Quartz makes up approximately 70% of the bedrock detrital material; rock fragments from metamorphic terrane to the east constitute up to 48% of the matrix material (Ethridge 1977). The mineral composition is fairly uniform throughout the region. Muscovite is a common accessory mineral and amphibole is present in small quantities. Calcite and hematite are the primary cement materials, but the amount of interstitial cement is small (Way 1972). Way (1972) reported pyrite and calcite in the shales along the Catskills' southern boundary, and in the area just northeast of the Catskills, but pyrite has not been reported within the Catskill Mountain region.

Surficial Deposits

The surficial deposits of the Catskill Mountains are more varied than the bedrock. Although the last period of continental glaciation (Wisconsinan) ended 14,000 year ago, local alpine-type glaciation continued in many of the headwater valleys. The glacial ice persisted to varying degrees across the area, depending on basin topography, orientation, and the subclimate created by the continental ice margin just to the north. Glacial deposits in headwater valleys are a combination of continental glacier-derived material deposited perpendicular to the direction of regional ice movement and reworked or secondarily scoured alpine glacier-derived material deposited perpendicular to each valley.

Thick drift, deposited and compressed under the glacial ice sheets, and thinner till, deposited as the glaciers melted and retreated, have been reported from repeated glaciations in the main valleys of most Catskill watersheds by Rich (1934). Thin till and exposed bedrock are predominant in the headwater streams, and thick drift is common along valley bottoms. Depth of drift and till varies from a few centimeters along and near ridges, to more than 40 m at the base of the Schoharie basin (Figure 8.1). Holocene alluvial deposits on modern flood plains extend well into many headwater valleys. Glacial striae and stratified deposits indicate that the continental ice sheet flowed downvalley in the Beaverkill and both branches of the Neversink, but upvalley in the Schoharie, Rondout, and Esopus basins. Ice travelled southeastward in the western Catskills, but the valleys containing headwater streams were last occupied by local glaciers moving downslope.

Morainal loops are common in the Catskills (Rich 1934). These consist of unstratified drift deposited at the end of local valley glaciers and are concave upvalley. They have been mapped midway up the Biscuit Brook basin and in the headwaters of the upper East Branch Neversink and Beaverkill basins. Deltaic materials (clays and fine gravels), deposited in ice-impounded lakes by glacial streams, are found in several headwater basins, particularly along the ridge between the Schoharie and Esopus basins (Figure 8.1), where glacial lakes once formed.

Rich (1934) reported that glacial deposits in the lower East Branch Neversink valley (Figure 8.1)

FIGURE 8.2. View of Rondout Creek above Red Brook during snowmelt. Stream channel incised to bedrock, mixed hardwood and hemlock forest, steep slopes, and thin soils are typical of headwater streams in the Catskill Mountains.

are older than Wisconsinan, and dissection of till by streams in this valley is more advanced than would seem possible unless the area had been exposed longer than other valleys to the north. The postglacial flood plains there are wide, and tributary alluvial fans are large. Surficial material in the Catskills consists primarily (> 90%) of local rock and sediment (Parker et al. 1964), but there is a great deal of local variability in the percentage of exotics, particularly carbonate-bearing sediments.

Soils

The soils of the Catskill Mountains are generally categorized as belonging to the Arnot-Oquaga-Lackawanna association; these soils range from excessively well drained to well drained and are on predominantly steep slopes (Tornes 1979). Soils in the basins that have been studied vary locally, but they are predominantly shallow boulder soils on steep slopes conducive ·to rapid precipitation runoff and are moderately to extremely acidic. The Lackawanna soils in the East Branch Neversink and upper Rondout watersheds contain a fragipan at a depth of 45 to 90 cm. In watersheds containing deltaic deposits, the deposits are generally overlain by Hoosic soils, which are deep and excessively well-drained soils on glacial outwash, and Valois soils, which are deep, well-drained soils developed on till. The soils inherit their character largely from the surficial materials on which they have developed.

Vegetation and Land Use

Vegetation in the Catskill Mountains is primarily hardwood forest that includes mostly American beech (*Fagus granidifolia*), sugar maple (*Acer sacharum*), and yellow birch (*Betula alleghaniensis*). Many watersheds contain first-growth forest at elevations above 730 m (Kudish 1985). Before settlement of the area during 1840–90, the Catskill forests were primarily eastern hemlock (*Tsuga canadensis*). The primary industry was bark peeling of hemlock for tanneries, and hemlock trunks were generally left to rot. Hemlock groves remain

throughout the region, primarily along stream banks (Figure 8.2). No major forest fires were reported after the 1840s (Kudish 1985).

The upper watersheds became a state preserve in 1870. Most of the lower watersheds (below 450 m elevation) are privately owned and are in agricultural, recreational, or residential use. Anthropogenic effects are least evident in the Rondout, Beaverkill, and Neversink valleys. The valleys of the east and west branches of the Delaware River and the Schoharie River are primarily agricultural; the valley of the Esopus Creek contains several villages and scattered residential areas.

Local Sources of Air Pollution

Sources of air pollution within 50 km are negligible or nonexistent in the Catskill region. Approximately 8.9×10^6 kg of SO_2 and 9.96×10^5 kg of nitrous compounds are emitted annually from sources within a 50 km radius of the NTN station at Biscuit Brook (John Robertson, U.S. Military Academy, 1986, written communication), but most of these sources are to the south and east, and do not contribute significantly to SO_4^{2-} and NO_3^- deposition in the Catskills. The nearest large point source of pollutants is in the area of Kingston, New York, located approximately 40 km due east and downwind of the Catskills. Winds in the Catskills are generally from the west and northwest. The closest potential upwind center for air pollution is Binghamton, New York, about 130 km to the west. Automobile emissions within the region are probably insignificant, but airborne dust from road salt may contribute Na^+ and Cl^- to Catskills watersheds.

Climate

The Catskill Mountains have cold winters and moderately cool to warm summers. Average annual air temperature at Slide Mountain weather station at Winisook Lake is 5°C (National Oceanic and Atmospheric Administration data, 1950–82). Heavy dew is common during the early morning throughout the freeze-free period.

Long-term records of precipitation indicate a very uniform seasonal distribution. Parker et al. (1964) analyzed 30 years (1921–50) of data from Roxbury, New York, in the headwaters of the Pepacton basin (Figure 8.1). Monthly mean precipitation
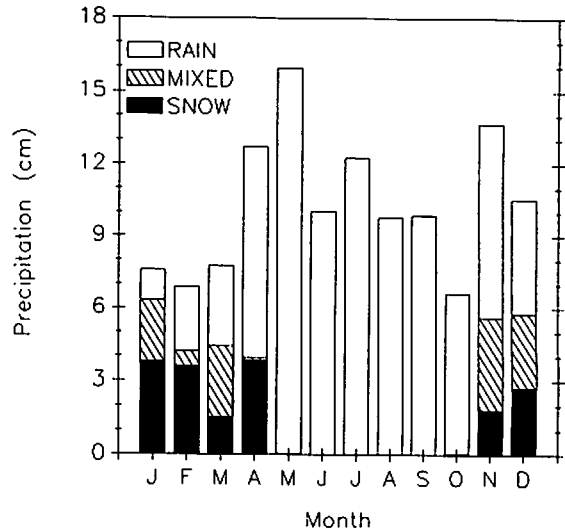

FIGURE 8.3. Mean monthly precipitation at the Biscuit Brook NTN site, 1983–86.

values varied from a minimum of 19 cm in February to a maximum of 25 cm in June. At the Biscuit Brook NTN station, precipitation was greatest during early spring and late fall during 1983–86 (Figure 8.3), but the seasonal distribution of precipitation volume has been variable, at least since the NTN station was established in 1983. Parker et al. (1964) note that yearly minima and maxima are both most likely to occur in late summer and early fall, when thunderstorms and hurricanes can deliver large but unpredictable volumes of precipitation to the region.

Annual volumes of precipitation vary both areally and with elevation. The greatest annual volumes are in the central, high-elevation zones (e.g., Slide Mountain and Frost Valley in Table 8.1). Parker et al. (1964) indicate that maximum precipitation for the region falls in the upper East Branch watershed of the Neversink River (150 to 160 cm yr⁻¹ for the period 1921–55), and minimum volumes fall in the northernmost Catskills (90 to 100 cm yr⁻¹). The region receives storms from the south, along the Atlantic coast, and from the west. This characteristic probably is responsible for the greater precipitation volumes at low-elevation Catskill sites (e.g., Downsville and Grahamsville in Table 8.1) than at central New York sites (e.g., Ithaca). High-elevation sites in the central Catskills receive more

TABLE 8.1. Annual precipitation (in cm) at Biscuit Brook and other stations in the state of New York.[a]

Location[b]	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	Mean
1. Upper Neversink River	175	172	183	159	202	131	168	134	180	149	165
2. Lower Biscuit Brook	167	156	165	126	173	111	–	–	–	135	148
3. Finger Lakes	104	113	118	81	92	80	99	80	90	105	96
4. Taconic Plateau	151	134	137	88	116	98	126	112	135	130	123
5. Western Catskills	139	131	138	104	125	103	97	96	117	131	118
6. Southern Catskills	144	136	139	111	130	88	104	101	–	116	107
7. Western Adirondacks	145	173	159	127	118	120	121	116	125	119	132

[a] Data from National Oceanic and Atmospheric Administration.
[b] Specific monitoring stations are: 1. Slide Mountain Station at Winisook Lake; 2. Frost Valley; 3. Cornell University at Ithaca; 4. Grafton; 5. Downsville Dam at Downsville; 6. Grahamsville; and 7. Big Moose.

precipitation than high-elevation sites in the Adirondack Mountains (e.g., Big Moose in Table 8.1). From a 10-year average of annual precipitation (1975–84), stations just outside the Catskill Mountains to the west and south received 32% and 46% less volume, respectively, than the Slide Mountain station (Figure 8.1; Table 8.1) (Murdoch 1988). Precipitation at the Biscuit Brook NTN station averaged 145.1 cm yr^{-1} for water years (WY) 1984–86 (water year = October 1 through September 30); average annual snowfall at Biscuit Brook was 21.3 cm (snow water equivalence) for the same period (Figure 8.3).

Evapotranspiration (ET) estimates for 1983–86 indicate that about 57 cm of water (40%) leaves the Biscuit Brook watershed annually as ET (ET = total annual precipitation inputs − total annual stream outputs). This value is comparable to estimates for the Catskills and the northeastern United States, based on long-term precipitation and stream dis-

charge data (Knox and Nordenson 1955), and to estimates for the Adirondack Mountains, based on empirical equations (Murdoch et al. 1987).

Chemistry of Atmospheric Deposition

Average concentrations of major constituents in precipitation collected at the NTN station at Biscuit Brook were similar to those observed at other monitoring stations in the Northeast, but precipitation volumes were greater (Table 8.2) (see also Northeast Overview Section). Average volume-weighted precipitation pH at Biscuit Brook was 4.25 during 1983–86 and weekly values ranged from 3.25 to 5.92 (Murdoch 1988).

Data for precipitation at the Biscuit Brook NTN station during 1983–87 may have been affected by the drought that occurred during 1984 and 1985, and these data may be atypical, over the long term, for the Catskill region. Hydrogen ion concentra-

TABLE 8.2. Volume-weighted mean concentrations and pH in weekly precipitation samples from Biscuit Brook and other NADP/NTN stations in northeastern United States, 1984–85.[a]

	Biscuit Brook (New York)		Leading Ridge (Pennsylvania)		Hubbard Brook (New Hampshire)	Huntington (New York)	
	1984	1985	1984	1985	1984	1984	1985
C_B							
$(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+})$	14.3	7.8	15.0	11.5	10.6	10.5	9.6
NH_4^{+}	8.9	8.9	17.8	13.3	9.4	10.0	10.0
H^{+}	43.7	50.1	70.7	60.2	38.8	37.5	42.3
SO_4^{2-}	41.2	45.0	69.2	56.4	34.5	36.8	39.7
NO_3^{-}	21.9	21.9	35.9	28.5	20.6	20.1	23.8
Cl^{-}	5.4	3.4	5.3	5.1	4.5	3.1	2.8
pH	4.36	4.30	4.15	4.22	4.41	4.43	4.37
Volume	133	122	113	107	125	109	102

[a] Concentrations are in $\mu eq\ L^{-1}$; volumes are in cm. Data are from NADP/NTN Coordinator's Office 1986, 1987.
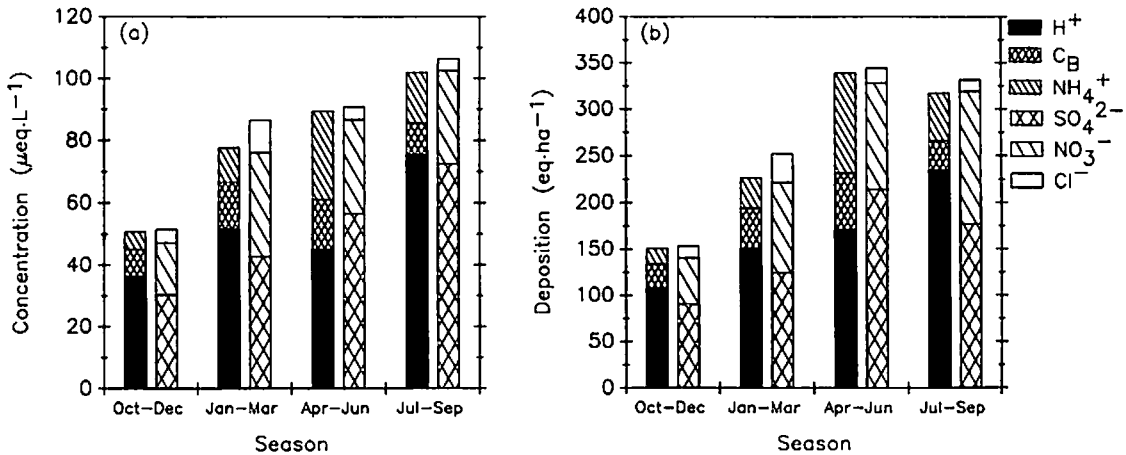
FIGURE 8.4. Mean seasonal concentrations (a), and mean deposition (b), of major ions in precipitation at the Biscuit Brook NTN site, 1983-86.

tions at Biscuit Brook were lower than the 15-year volume-weighted average (1963-77) at Hubbard Brook Experimental Forest (HBEF) in New Hampshire, but higher than those for the dry periods at Hubbard Brook in 1980 and 1981 (Glass and Loucks 1986). Similarly, Cl^- and SO_4^{2-} concentrations at Biscuit Brook during WY 1984-86 were slightly lower than the Hubbard Brook 15-year average, but similar to the 1980-81 concentrations.

The NTN station at Hills Creek in northcentral Pennsylvania, approximately 160 km southwest of the Catskills, recorded slightly higher concentrations of all constituents during WY84 than were recorded at Biscuit Brook (Lynch et al. 1985). The station at Leading Ridge, in southwestern Pennsylvania, received substantially higher SO_4^{2-} concentrations than Biscuit Brook during both WY84 and WY85 (Table 8.2) (Barker and Witt 1990). This pattern of an eastward decrease in SO_4^{2-} concentrations in precipitation is consistent with a hypothesized midwestern source of SO_4^{2-}.

The 1983-86 data on chemical concentrations in precipitation at the Biscuit Brook NTN station show no consistent seasonal trends (Figure 8.4a). Concentrations of H^+ and SO_4^{2-} are highest in summer, whereas NO_3^- concentrations are highest in winter and summer. Wet deposition of acid anions is highest in spring, when volumes are greatest (Figure 8.3); wet deposition of H^+ is highest in summer, when concentrations are highest. Wet deposition of Cl^- is greatest in late winter, which suggests that

dust carrying road salt may be entering the watersheds of Catskill headwater streams. Hydrogen accounted for 64% of the cation load at Biscuit Brook during 1983-86, and NH_4^+, the next most abundant cation, accounted for 20%. Of the anion load, SO_4^{2-} accounted for 60% and NO_3^- for 33%.

The chemical loading rates (wet deposition only) observed at Biscuit Brook during 1983-86 are within the range of those observed at Hubbard Brook Experimental Forest in New Hampshire, and at Woods Lake in the Adirondack Mountains. Annual NO_3^- loading during 1963-77 at Hubbard Brook ranged from 108 to 500 eq ha^{-1} (Likens 1985). Nitrate loading at Biscuit Brook was 447 eq ha^{-1} in WY84 and 341 eq ha^{-1} in WY85. The wet deposition of acid anions, NH_4^+, and H^+, was slightly greater at Biscuit Brook than at Hubbard Brook during a period when precipitation volume was similar at both sites (124 cm yr^{-1} from December 1980 through November 1982 at Hubbard Brook and 130 cm yr^{-1} during WY85 at Biscuit Brook), but the base cation concentrations were similar (Glass and Loucks 1986). The ranges in chemical concentrations and deposition rates observed in the central Catskills during the period of record (1983-86) were therefore similar to those at other monitoring stations in the Northeast that have longer periods of record. Long-term annual precipitation averages indicate that the Catskills receive greater precipitation volume, however, and may therefore have received greater annual chemi-

cal loads historically. Reconstructions of SO_4^{2-} deposition rates suggest that the Catskill region has received substantially greater loads of SO_4^{2-} in wet deposition than any other case study region (Chapter 3, Husar et al., this volume).

No direct measurements of dry deposition to the Catskill region have been made, and any estimates must therefore be based on data from other regions. Summers et al. (1986) give estimates of dry/wet deposition ratios for SO_4^{2-} in eastern North America that vary from 0.25:1 to 0.8:1, but point out that values for regions located at great distances from sources are likely to be at the low end of this range. Galloway et al. (1983b) reported a SO_4^{2-} dry:wet ratio of 0.42 (i.e., dry deposition is 30% of wet) for three Adirondack watersheds—a ratio that agrees well with an estimated ratio of 0.5 used in ILWAS model simulations (Appendix B). The Catskill region is similar to the Adirondacks region in terms of both elevation and concentrations of acid anions in wet deposition, and should therefore exhibit similar dry/wet deposition ratios. We use a ratio of 0.5 in constructing chemical budgets for Biscuit Brook (see Processes Influencing Surface Water Chemistry), which is sufficient to balance inputs and outputs of SO_4^{2-} and Cl^-.

Inputs of acid anions from clouds and fog represent unknown, but potentially important, inputs to the Catskill region. Weathers et al. (1986) reported on the chemistry of one particularly intense cloud/fog water event at Mohonk Mountain, on the southeastern border of the Catskill Mountains. Sulfate concentrations during this event were $1,100\ \mu eq\ L^{-1}$, and NO_3^- concentrations were $950\ \mu eq\ L^{-1}$ (approximately 25 to 40 times the concentrations in wet deposition; Table 8.2). Because these measurements were made on samples from active collectors, it isn't possible to estimate deposition rates for this event. Lovett et al. (1982) suggest that fog may make a significant contribution to rates of acidic deposition in subalpine areas of the eastern United States.

Regional Surface Water Chemistry

Ion Composition of Streams at High and Low Flows

A survey of 66 streams throughout the Catskill Mountains was conducted in a cooperative effort by USGS and NYCDEP during 1985–87 (referred to hereafter as the USGS/NYCDEP survey). Most of the sites chosen for this study were headwater streams, and emphasis was placed on sampling in areas thought to have the lowest streamwater ANC values. A few large streams were also included from each of the six major drainage basins (Figure 8.1). Each stream was sampled 6 to 12 times at discharges ranging from baseflow to high flows during snowmelt and/or storms (Murdoch and Barnes in press). A subset of these streams was sampled 10 to 12 times per year from August 1983 through 1986 (referred to hereafter as the LTM network).

The sampling in the USGS/NYCDEP survey was not intended to produce a statistically random selection of streams, and so any conclusions made about regional characteristics (i.e., proportion of streams with ANC $\leq$ 0) should be considered approximations, at best. Whenever conclusions of this type are made, they are based on a modified dataset. Several sites were dropped from the complete dataset, in order to minimize the bias associated with larger numbers of sampled streams in low ANC basins, leaving an approximately equal number of sites in each of the six basins.

Frequency distributions of key characteristics (watershed area, pH, ANC, sum of base cations ($C_B = Ca^{2+} + Mg^{2+} + Na^+ + K^+$), SO_4^{2-}, and NO_3^-) in the USGS/NYCDEP survey are shown in Figure 8.5. The plotted chemical data are mean values for each stream, partitioned into high- and low-flow periods to show the effect of stream discharge on the distribution of chemical characteristics in the region. The majority of streams (70%) drain watersheds < 2,000 ha (Figure 8.5a). As mentioned previously, sites were also included at low elevations in each major drainage basin, and some of these larger streams have drainage areas as large as 8,600 ha.

The pH levels showed a strong dependence on stream discharge (Figure 8.5d). At baseflow, 8% of the streams in the modified USGS/NYCDEP dataset had pH values < 5.5. During high flows, this proportion increased to 18%, and the pH distribution became bimodal. The majority of streams exhibited circumneutral pH at high flows, and very few had pH values between 5.0 and 6.0. All the streams sampled had pH values between 4.0 and 8.0 during both baseflow and high-flow periods.

Acid neutralizing capacity is also very dependent on stream discharge. Eight percent of streams had negative ANC at baseflow, and 16% had negative ANC at high flows (Murdoch and Barnes in
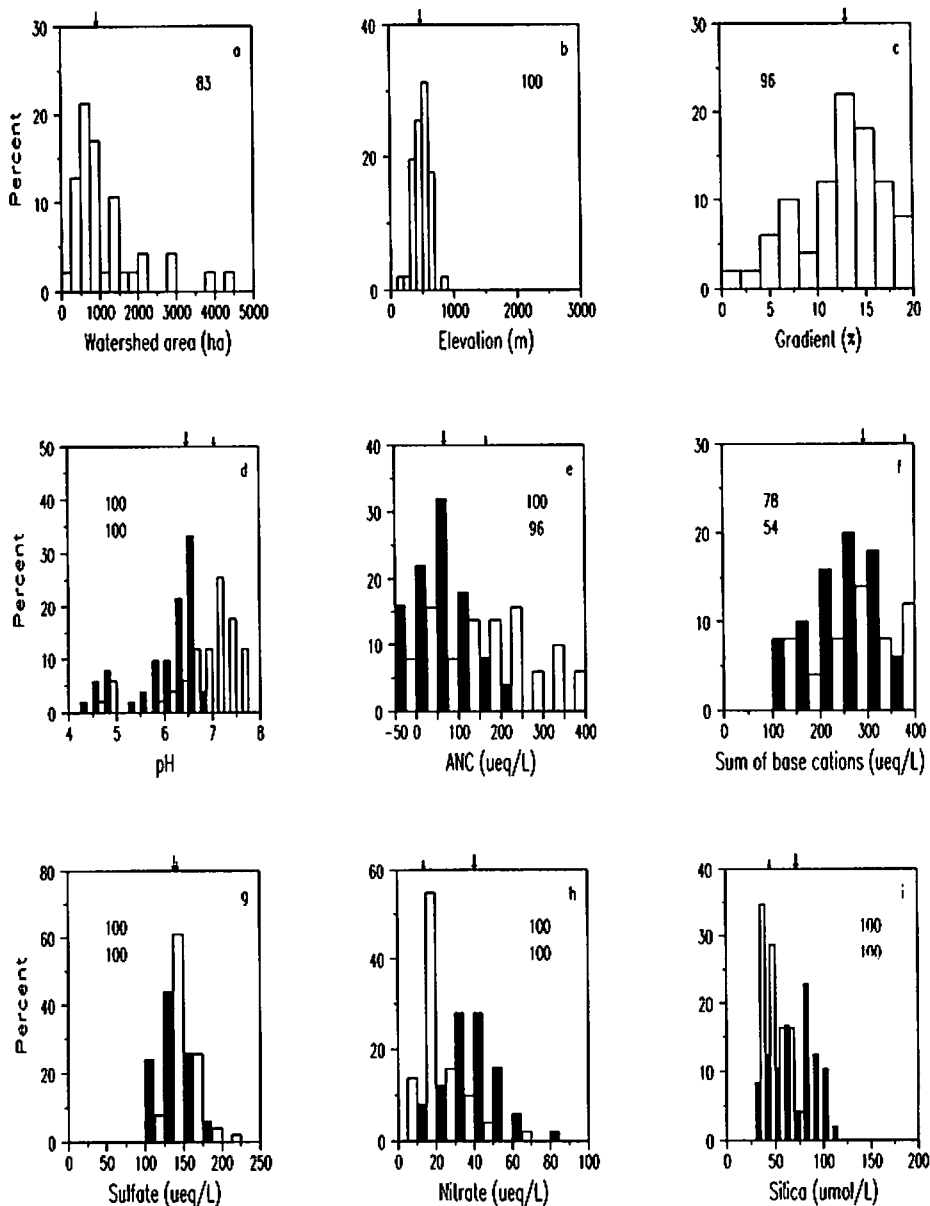
FIGURE 8.5. Histograms of watershed characteristics and streamwater chemistry for the modified USGS/ NYCDEP stream survey. Data are from 51 streams, distributed more or less evenly among the 6 major drainage basins. Data for chemical variables are subdivided into results for baseflow (clear bars) and high-flow (solid bars) periods. In order to show both high-flow and baseflow values, bars are only half the width of actual intervals (e.g., 24% of streams had SO_4^{2-} concentrations between 100 and 125 μeq L^{-1} at high flow; at baseflow 8% of streams had SO_4^{2-} between 100 and 125). Values in upper part of box are percentage of stream samples (high flow and baseflow), with values in the graphed range. Arrows indicate median values for each variable; larger arrow is for high-flow values, smaller arrow is for baseflow values.

press; Figure 8.5e). The range of observed ANC values changed at high discharges. At baseflow, the sampled streams (excluding the four largest watersheds with areas > 20,000 ha) exhibited a range in ANC of 408 μeq L^{-1} (from −18 to 390 μeq L^{-1}), with a relatively even distribution. At high flows, the range in ANC decreased to 236 μeq L^{-1} (from −35 to 201 μeq L^{-1}); the distribution shows a very strong mode at a value < 100 μeq L^{-1}.

The range in base cation (C_B) concentrations also decreased at high flows, but not to the extent that ANC values did (Figure 8.5f). Again excluding the four largest watersheds, baseflow C_B exhibited a range of 605 µeq L⁻¹ (from 110 to 715 µeq L⁻¹); the range decreased to 398 µeq L⁻¹ (from 100 to 498 µeq L⁻¹) at high flows. The decrease in the range of C_B and ANC, and in absolute concentrations of C_B and ANC, indicates that substantial dilution occurs during high-flow events. Dilution of C_B cannot explain all the change in ANC at high flows, however, because the range in ANC decreases more than the range in C_B. Dilution should act uniformly on base cation and ANC concentrations; the difference in response to high-flow events suggests that other ions contribute to the decline in ANC.

Some dilution of SO_4^{2-} concentration occurs during high flows, although SO_4^{2-} values at all rates of discharge remained generally in the 100 to 180 µeq L⁻¹ range (Figure 8.5g). The range in observed SO_4^{2-} is much smaller than that of ANC and C_B. The narrow range of SO_4^{2-} concentrations observed at both baseflow and high flows suggests an atmospheric, rather than geologic, source for SO_4^{2-} in the Catskills (see further discussion in section entitled Spatial Variability in Stream Chemistry).

Nitrate concentrations were higher during high flows than during baseflow (Figure 8.5h), unlike SO_4^{2-} and the other chemical variables discussed in the previous paragraphs. Modal NO_3^- values increased from < 20 µeq L⁻¹ at baseflow to near 50 µeq L⁻¹ during snowmelt and stormflows, and concentrations as high as 70 µeq L⁻¹ were common. Elevated NO_3^- concentrations during snowmelt have also been observed in the Adirondack Mountains (Peters and Driscoll 1987) and at Hubbard Brook (Likens et al. 1977), and have been identified as the main cause of episodic ANC declines in chronically acidified Adirondack lakes (Driscoll and Shafran 1984, Driscoll et al. 1987b, Schofield et al. 1985). The source of NO_3^- during stormflows and snowmelt periods is unclear, but some combination of NO_3^- storage in the snowpack (Galloway et al. 1980) and nitrification in the soil (Rascher et al. 1987, Peters and Driscoll 1987) is likely.

Comparisons of the Catskill stream data with data from Hubbard Brook in New Hampshire and from Adirondack lake outlets show the streams of all three regions to have similar SO_4^{2-} and NO_3^-

concentrations (Murdoch and Barnes in press). Average SO_4^{2-} concentrations at Hubbard Brook (Likens et al. 1977) and in Adirondack lake outlets (Driscoll and Newton 1985) were 130 and 136 µeq L⁻¹, respectively, compared to 139 µeq L⁻¹ in the Catskill streams. Average NO_3^- concentrations observed in the Catskill streams (31 µeq L⁻¹) were identical to those observed at Hubbard Brook, but higher than those in the Adirondack lake outlets (between 4 and 29 µeq L⁻¹); this may be due in part to the greater uptake of NO_3^- in lakes than in stream environments.

Silica concentrations in Catskill streams had a broad range of values (from 30 to 130 µmol L⁻¹) during high flows and a narrower range (from 30 to 90 µmol L⁻¹) during baseflow (Figure 8.5i). A shift toward less uniform silica concentrations among streams during high flows could be explained by the changes in relative contributions of groundwater as flow rises in each watershed. The increase in silica concentrations with increased flow in some streams suggests transport of rapidly weathered or dissolved silica from the shallow groundwater or soil environments, or a contribution of colloidal silica during conditions of rapid runoff.

The results of the USGS/NYCDEP survey compare well with the results of the National Stream Survey (NSS), although the similarity may well be coincidental (Table 8.3). The NSS used a probability-based sampling design, which randomly selected stream reaches that drained watersheds with areas < 155 km² (Kaufmann et al., 1988); site selection for the USGS/NYCDEP survey was not random, and was deliberately biased toward streams in areas with a high probability of exhibiting low ANC. Only six stream reaches in the NSS sample were within the boundaries of the Catskill region, making the calculation of population estimates problematic. Despite these difficulties, NSS population estimates for the Catskills (6% of upstream reach ends with ANC ≤ 0 and 5% with pH ≤ 5 at spring baseflow) and estimates for the modified USGS/NYCDEP survey (8% with ANC ≤ 0 and pH ≤ 5 at baseflow, 16% of ANC values ≤ 0 and 18% of pH values ≤ 5 at high flows) were remarkably close (Kaufmann et al. 1988; Chapter 17, Baker et al., this volume). Sulfate values for the two surveys were also similar (Table 8.3), but SO_4^{2-} was relatively uniform across the Catskill region and site selection is unlikely to have a large

TABLE 8.3. Median values (first and third quartiles in parentheses) of key variables in data sets used in this chapter.[a]

Data set	N	pH units	ANC µeq L⁻¹	SO₄²⁻ µeq L⁻¹	Ca²⁺ µeq L⁻¹	DOC µmol L⁻¹	NO₃⁻ µeq L⁻¹	Ca²⁺+Mg²⁺ µeq L⁻¹
USGS/NYCDEP	51	6.60	119	142	208	–	28	287
		(6.02–6.74)	(28–176)	(131–154)	(131–267)		(23–35)	(204–366)
NSS (Kaufmann et al. 1988)								
Downstream end								
Sample	6	6.97	104	149	172	87	16	250
		(6.81–7.18)	(60–204)	(134–159)	(147–260)	(58–113)	(15–18)	(225–341)
Population	161	7.18	204	159	259	91	18	341
		(7.07–7.32)	(123–218)	(155–166)	(183–273)	(57–113)	(17–18)	(263–351)
Upstream end								
Sample	6	6.57	54	144	164	83	20	234
		(6.32–6.93)	(37–111)	(130–158)	(100–193)	(58–100)	(18–23)	(163–267)
Population	161	6.59	58	158	193	95	23	255
		(6.59–6.93)	(58–171)	(148–169)	(186–267)	(49–100)	(22–48)	(255–341)
LTM	8	5.54	17	121	116	158	26	158
		(5.08–5.99)	(10–29)	(119–126)	(87–155)	(117–250)	(22–31)	(130–188)

[a] Values for the USGS/NYCDEP survey are based in survey of 66 streams, later modified to include an even number of sites in each major basin. NSS values are population estimates for upstream and downstream ends of six stream reaches sampled at spring baseflow within the Catskill region boundaries. Long-Term Monitoring (LTM) sites are a low ANC subset of the USGS/NYCDEP survey streams, which were sampled more intensively.

effect on these estimates. Nitrate was substantially lower in the NSS, probably because the samples were intentionally collected at baseflow when NO_3^- concentrations were low (Figure 8.5h); when only baseflow samples were considered, the median NO_3^- concentration for the modified USGS/NYCDEP survey was 14 µeq L⁻¹. The use of spring baseflow samples may be the major weakness of the NSS sampling approach, because it failed to identify the importance of NO_3^- to streamwater chemistry at high flows in the Catskills (Figure 8.5h; see also the section entitled Processes Influencing Surface Water Chemistry).

Spatial Variability in Stream Chemistry

The lowest values for pH and ANC in the Catskills region are found in the two southernmost basins (Figure 8.6a,b), the Neversink and Rondout (Figure 8.1). Acid neutralizing capacity becomes a small fraction of C_B in the low pH, low ANC streams (Figure 8.6c). To investigate these patterns, mean concentrations of major ions were calculated for each of the six major drainage basins of the Catskill region (Murdoch and Barnes in press; Table 8.4). Analysis of these mean concentrations within each of the basins indicates that:

- Concentrations of base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) differed markedly among the basins.
- ANC and pH values differed markedly among the basins and generally followed the pattern of Ca^{2+} concentrations.
- Concentrations of SO_4^{2-} and NO_3^- were relatively uniform among the basins.

Streams containing the highest concentrations of all ions except H^+ and aluminum were found in the westernmost basin (Cannonsville). Calcium and Mg^{2+} concentrations there were two to three times higher than in the two southernmost basins (Neversink and Rondout), but SO_4^{2-} concentrations in the Cannonsville basin were only 27% higher than in the Neversink basin and 14% higher than in the Rondout basin. Nitrate, like SO_4^{2-}, was relatively uniform across the region, but the highest concentrations were in the westernmost basins (Murdoch and Barnes in press). Higher Ca^{2+}, Mg^{2+}, SO_4^{2-}, and NO_3^- concentrations in the Cannonsville and Pepacton basins were undoubtedly due, to some degree, to greater agricultural land use in these basins. The higher Na^+ and Cl^- concentrations in the northern and western basins, which are more heavily populated, were at least partly due to greater use of road salt in these than in the southern and eastern basins.
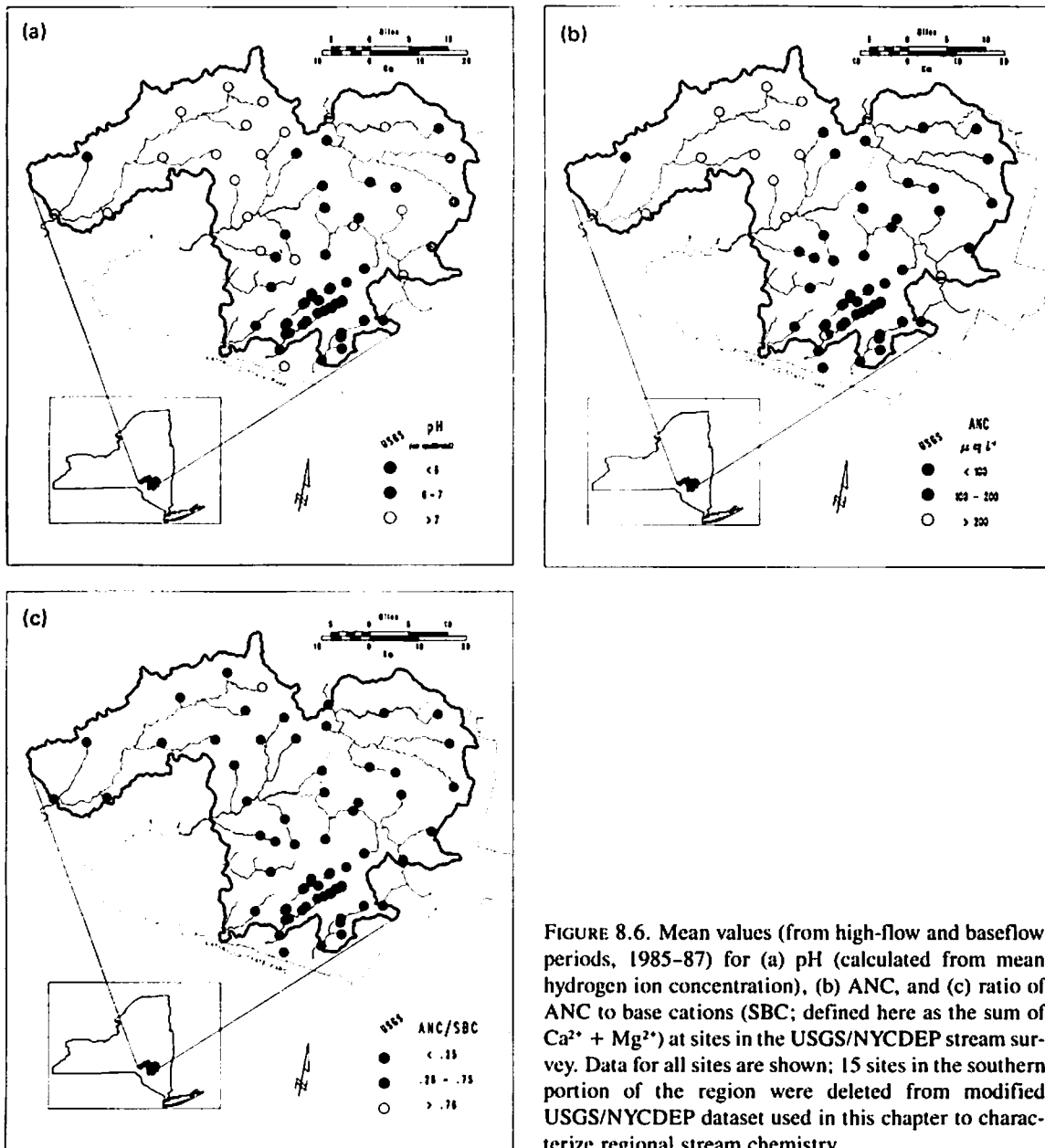
FIGURE 8.6. Mean values (from high-flow and baseflow periods, 1985-87) for (a) pH (calculated from mean hydrogen ion concentration), (b) ANC, and (c) ratio of ANC to base cations (SBC; defined here as the sum of $Ca^{2+} + Mg^{2+}$) at sites in the USGS/NYCDEP stream survey. Data for all sites are shown; 15 sites in the southern portion of the region were deleted from modified USGS/NYCDEP dataset used in this chapter to characterize regional stream chemistry.

The local differences in ANC among the major drainage basins are clearly related to the base cation concentrations of streams, and not to differences in acid anion concentrations. The source of base cations in each stream, particularly Ca^{2+} and Mg^{2+}, therefore plays an important role in controlling the stream's response to acidic deposition. Three hypothetical causes of local differences in base cation concentration are discussed in the following sections.

Calcium and Magnesium Content of Bedrock

Calcium and Mg^{2+} content of bedrock in the Catskill region may increase westward. The Catskill bedrock materials were deposited in a westward-

TABLE 8.4. Mean concentrations of key chemical variables in six major drainage basins of Catskill region, 1985–87.[a]

Drainage basin	Number of sites	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	NO_3^-	Cl^-	ANC	Al
Ashokan	10	6.57	224	83	66	8	141	26	58	141	2
Cannonsville	8	6.82	333	131	114	25	161	37	74	275	2
Neversink	23	5.05	114	51	24	8	127	26	24	13	18
Pepacton	9	6.92	268	80	52	11	151	37	47	164	2
Roudout	5	5.74	124	63	41	12	141	26	38	21	10
Schoharie	8	6.54	218	72	74	9	148	24	58	119	3

[a] Basin means are calculated by: (1) calculating mean high-flow and baseflow values for each site, (2) calculating means for each site from high-flow and baseflow means, and (3) calculating means for each basin from overall means at each site. Aluminum (total dissolved) concentrations are in μmol L^{-1}; all others except pH are in μeq L^{-1}.

developing delta, on the edge of a shallow sea that covered much of what is now central New York (Ethridge 1977). The western edge of that delta would therefore have been under marine influences and would have incorporated salts and carbonates. This pattern would be expected to produce greater amounts of carbonate and Na^+ in the Cannonsville basin, followed by the Pepacton basin. This expectation is borne out by Ca^{2+} and ANC values in these basins (Table 8.4). These marine influences would also be expected to contribute some gypsum to the bedrock and would therefore lead to elevated SO_4^{2-} concentrations (in addition to Ca^{2+}) in the westernmost basins. The highest SO_4^{2-} concentrations in the region are indeed found in the Cannonsville and Pepacton basins (Table 8.4). Differences in ANC among the Neversink, Ashokan, and Schoharie basins are not explained by this hypothesis, however, and data are not available to support any of these suppositions.

Limestone Fragments Deposited by Glaciation

Glaciation may have deposited more limestone fragments in the north Catskills than in the south. Given the glacial deposition patterns previously described, debris from the limestone escarpments north and northeast of the Catskill region could have been deposited by the ice on the leeward side (away from the prevailing direction of ice movement) of any high topographic features the ice encountered (Murdoch and Barnes in press). Deposition would have been greatest at the first ridge encountered and would have decreased over successive ridges. The Neversink and Rondout basins, the

farthest from the limestone source, would therefore have received a smaller percentage of the limestone fragments than the northern basins. This is consistent with Ca^{2+} and ANC values in these basins (Table 8.4). Recent studies of till stratigraphy in the western Catskills revealed cobbles of Adirondack origin in the Cannonsville basin but not in the Pepacton basin (D. Ozvath, Lafayette University, written communication). If material from the Adirondack Mountains was transported to the Catskill region, limestone fragments from the closer Helderberg escarpments could also have been transported, and like the Adirondack cobbles, would diminish southward. The control of surface water ANC by small amounts of "exotic" carbonate in till has been documented in the Catoctin Mountains in Maryland (Katz et al. 1985), the Precambrian Shield of Ontario (Hornbrook et al. 1986), and the Cascade Mountains of Washington (Drever and Hurcomb 1986).

Differences in Water Residence Time in Surficial Materials

The thickness, distribution, and permeability of surficial material may also differ among the basins. Because these largely determine the residence time of water in a basin, they may in turn have a significant effect on the base cation concentrations in Catskill streams. The preceding hypothesis suggests that the northernmost basin (Schoharie) should have received the greatest percentage of carbonate; yet its streams have the lowest Ca^{2+} concentrations of the northern basins (Table 8.4). This may be because the Schoharie valley, which is
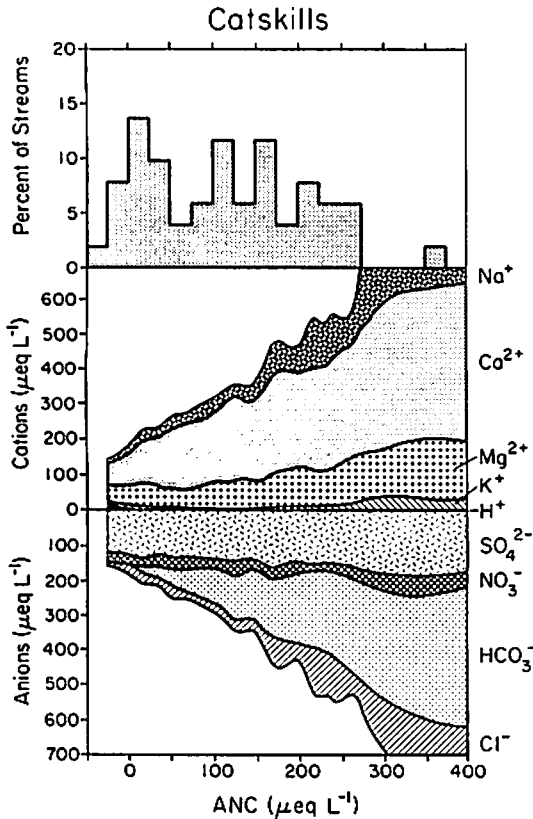
FIGURE 8.7. Spline diagrams of major anion and cation concentrations as a function of ANC for streams in modified USGS/NYCDEP dataset. These plots differ from most others in this book in including NO_3^-, and excluding organic acid anions.

FIGURE 8.8. Relationship between Na^+ and Cl^- in Catskill streams sampled in the USGS/NYCDEP survey. 1:1 line is shown.

Murdoch 1985), and could, therefore, be a determinant of ANC in Catskill streams.

Relations Among Chemical Variables

Spline diagrams of major ionic compositions across the range of ANC values observed in the Catskill streams (Figure 8.7) illustrate the uniformity of stream chemistry in the region. Relative cation concentrations are consistent across the entire range of ANC, and the dominance of cations follows the pattern $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > H^+$. Sulfate concentrations are high throughout the observed ANC range, and SO_4^{2-} is the dominant anion at ANC values < 130 μeq L^{-1}. Above 130 μeq L^{-1}, HCO_3^- becomes the dominant anion. Chloride becomes important stoichiometrically above ANC values of 150 μeq L^{-1}, in parallel with increased concentrations of Na^+. In all the streams sampled, Na^+ and Cl^- were found in a nearly 1:1 stoichiometric ratio (Figure 8.8), suggesting a strong influence of road de-icing salts on the concentrations of these ions. Because Na^+ in Catskill streamwater results primarily from road salt, and because K^+ is only a minor cation (Figure 8.7), we substitute the sum of Ca^{2+} and Mg^{2+} for C_B in many of the following discussions. However, throughout the chapter we are consistent in using C_B to refer to the sum of all base cations, and we use "$[Ca^{2+} + Mg^{2+}]$" when discussing only Ca^{2+} and Mg^{2+}.

oriented toward the north, underwent more glacial scouring and greater deposition of lake clay over the till than did the other northern basins (Murdoch and Barnes in press). Even though the carbonate content of the till may be as high (or higher) in the Schoharie basin as in the southern basins, the carbonate may have been less accessible for weathering during the postglacial period. The thickness and permeability of surficial deposits may therefore differ among the major basins, and the carbonate content of the bedrock and till in the Catskill basins could have less effect on the base cation concentrations of surface water than the thickness, permeability, and transmissivity of the surficial material. Till thickness has been shown to have strongly affected the buffering capacity of surface waters in the Adirondacks (Peters and
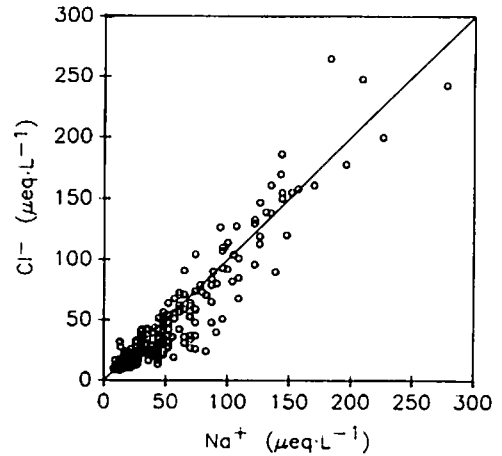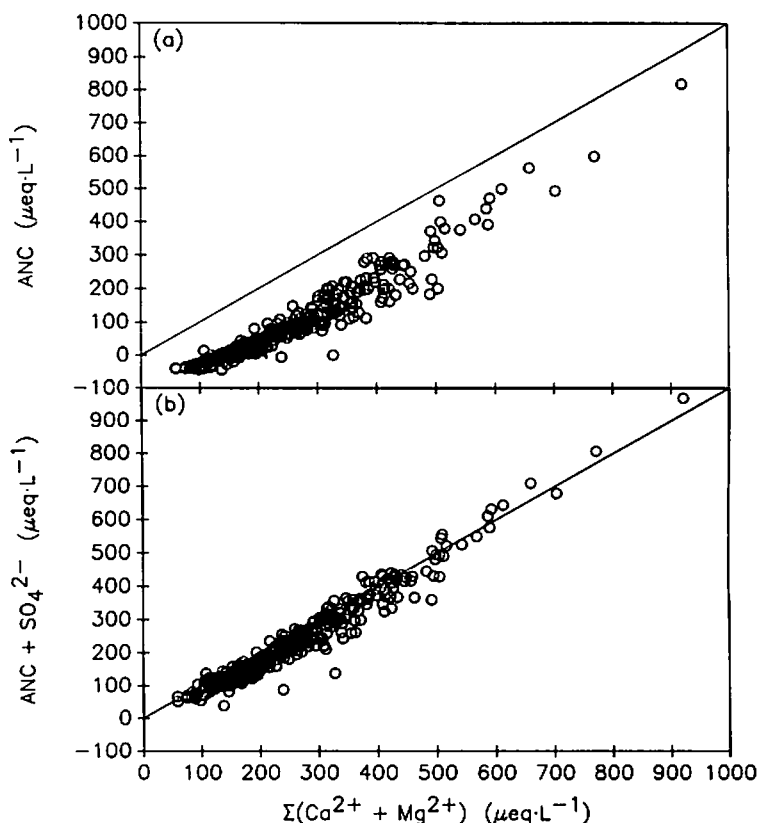
FIGURE 8.9. Plots of (a) ANC versus base cations $[Ca^{2+} + Mg^{2+}]$, and (b) ANC + SO_4^{2-} versus base cations for samples in USGS/NYCDEP stream survey. 1:1 line is plotted to indicate expected relationship.

Calcium and Mg^{2+} are the dominant cations across most of the range of ANC values observed in the Catskills, as would be expected from the weathering of carbonate minerals. Carbonic acid weathering would be expected to produce ANC in concentrations approximately equivalent to the sum of Ca^{2+} and Mg^{2+} concentrations (Chapter 1, Munson and Gherini, this volume). A plot of $[Ca^{2+} + Mg^{2+}]$ against ANC does not indicate a 1:1 relation, however (Murdoch and Barnes in press; Figure 8.9a). Although the scatter clearly indicates a close correlation between ANC and $[Ca^{2+} + Mg^{2+}]$, ANC values fall short of the 1:1 line by a consistent amount across the range of concentrations observed.

When SO_4^{2-} concentration is added to ANC and the relationship with $[Ca^{2+} + Mg^{2+}]$ is re-examined, deviation from the expected relation is decreased dramatically (Figure 8.9b). The difference between ANC and $[Ca^{2+} + Mg^{2+}]$ is closely approximated by SO_4^{2-} concentration, which remains relatively constant at all ionic strengths (Figure 8.7). The differ-

ence between observed ANC and expected ANC, based on $[Ca^{2+} + Mg^{2+}]$, is consistent across the Catskill region, as evidenced by the tight cluster in Figure 8.9a,b, and is relatively unaffected by changes in stream discharge (Murdoch and Barnes press). Figure 8.9 includes samples at both baseflow and high flow. This pattern could result if: (1) sulfuric acid deposition decreased ANC by direct titration of HCO_3^- by H^+, (2) sulfuric acid deposition increased base cation concentrations by increasing weathering and/or cation exchange rates (Chapter 1, Munson and Gherini, this volume), (3) some combination of decreased ANC and increased base cation concentrations occurred, or (4) some geologic source of SO_4^{2-} contributed to a natural difference between expected and observed ANC. Of these possibilities, only the last can be ruled out.

Both the spatial (Table 8.4) and seasonal (Figure 8.5g) uniformity in SO_4^{2-} concentrations in the Catskills are inconsistent with a geologic source. Some gypsum may be present in the westernmost basins (see section entitled Spatial Variability in
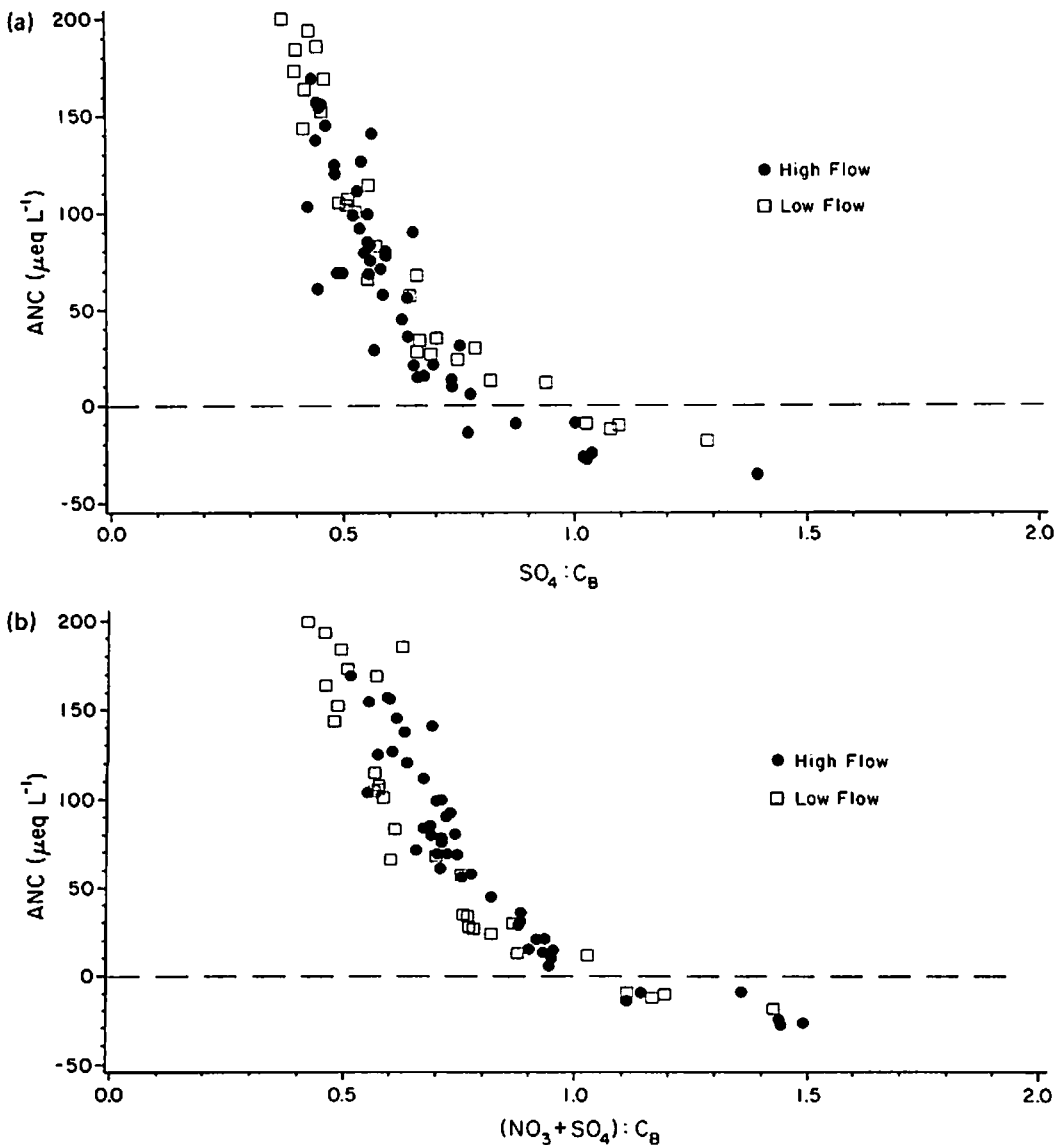
FIGURE 8.10. Plots of (a) ANC versus ion ratio $SO_4^{2-}:[Ca^{2+} + Mg^{2+}]$, and (b) ANC versus ion ratio $[SO_4^{2-} + NO_3^-]:[Ca^{2+} + Mg^{2+}]$ for samples in USGS/NYCDEP stream survey. Nitrate is included in (b) to illustrate its importance as an acid anion in low ANC Catskill streams.

Stream Chemistry), but the difference in SO_4^{2-} concentration between these basins and the remainder of the region is small. If this entire difference were attributed to gypsum dissolution, it would amount to less than 12% of streamwater SO_4^{2-} (i.e., about 15 μeq L^{-1}). Pyrite has been observed in bedrock outcrops to the east and south of the Catskill region (Way 1972), but if it were present within the region boundaries, it would be expected to produce spatially irregular SO_4^{2-} concentrations in streams, reflecting the irregular distribution of pyrite along faults and seams. Perhaps the best evidence against an important geologic source of SO_4^{2-} in the Catskill region comes from input/output budget data from Biscuit Brook (see Comparison of Precipitation and Stream Chemistry), where precipitation inputs of

SO_4^{2-}, adjusted for dry deposition and evapotranspiration, closely match volume-weighted streamwater SO_4^{2-} concentrations (Murdoch 1988).

The preceding discussions imply that a stream's response to acidic deposition depends on rates of base cation release, in addition to the rate of acid anion deposition. Acid neutralizing capacity approaches zero as the ratio of SO_4^{2-} to $[Ca^{2+} + Mg^{2+}]$ approaches 0.8 (Figure 8.10a). Sulfate, although it accounts for a majority of the difference between ANC and $[Ca^{2+} + Mg^{2+}]$, is therefore not the only important acid anion. Nitrate also plays an important role in controlling streamwater ANC. Acid neutralizing capacity approaches zero when the ratio of $NO_3^- + SO_4^{2-}$ to $[Ca^{2+} + Mg^{2+}]$ approaches one (Figure 8.10b). The sum of NO_3^- and SO_4^{2-}, therefore, accounts for nearly 100% of the difference between ANC and $[Ca^{2+} + Mg^{2+}]$ at ANC values above zero.

At ANC values below zero, a deficit in base cation concentrations (relative to anion concentrations) is compensated for by an increase in protolytic cations—H^+ and free aluminum (Driscoll and Newton 1985; Chapter 6, Driscoll et al., this volume). Concentrations of protolytic cations began to increase in several Adirondack lakes when the sum of acid anions ($SO_4^{2-} + NO_3^-$) approached 90% to 100% of the sum of base cations (Driscoll and Newton 1985). A similar pattern is evident in Catskill streams (Figure 8.11), where H^+ and aluminum concentrations increase when the concentration of SO_4^{2-} and NO_3^- exceeds 80% of base cations (defined as $Ca^{2+} + Mg^{2+}$) (Murdoch and Barnes in press). Concentrations of protolytic cations above 60 µeq L^{-1} were found primarily in the Rondout and Neversink basins, where pH and ANC values are lowest (Figure 8.6a,b).

Organic Anions

One of the objectives of this chapter is to assess the relative roles of inorganic acid anions and organic acid anions in controlling Catskill streamwater chemistry. The data necessary to make this assessment are not available for the USGS/NYCDEP dataset, because neither DOC nor aluminum speciation was measured. Data for the LTM sites (a lower ANC subset of the USGS/NYCDEP sample sites; Table 8.1) include DOC measurements, and
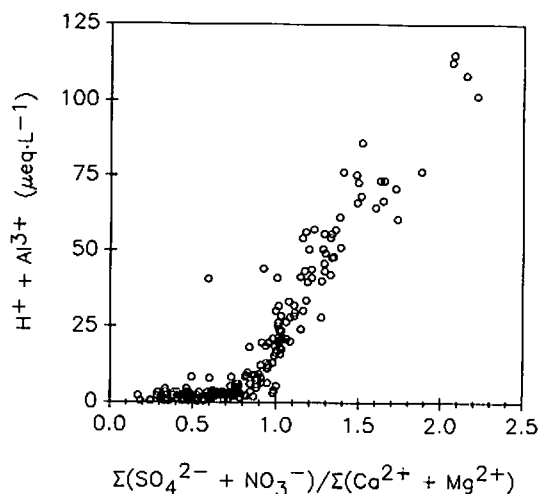

FIGURE 8.11. Plot of $[H^+ + Al^{3+}]$ versus ion ratio $[SO_4^{2-} + NO_3^-]:[Ca^{2+} + Mg^{2+}]$ for USGS/NYCDEP stream survey. Aluminum values are for total dissolved aluminum.

can be used to make rough estimates of the importance of organic anions.

The total organic acid (A_t) concentration can be estimated by calculating the anion deficit, the difference between the sum of measured cations and the sum of measured anions (LaZerte and Dillon 1984; Chapter 13, Cook and Jager, this volume). The anion deficit theoretically should yield a value equal to A_t (the sum of weak and nonprotonated organic anions), but its calculation has a very large uncertainty due to the propagation of analytical errors associated with the analysis of each major ion. In addition, the inclusion of aluminum in the calculation of anion deficit is problematic when measurements of inorganic monomeric aluminum are unavailable, as is the case for Catskill LTM sites. For the purposes of this chapter, anion deficit is calculated as:

$$\begin{aligned} \text{Deficit} = & \, 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] \\ & + 2[Al^{n+}] + 2[Fe^{2+}] + [H^+] \\ & - 2[SO_4^{2-}] - [HCO_3^-] - [NO_3^-] \\ & - [Cl^-] \end{aligned} \tag{8-1}$$

where concentrations are in µmol L^{-1}. Aluminum values are for total dissolved aluminum, and a charge of +2 is assumed, consistent with the results of Sullivan et al. (1989). Calculated anion deficits are likely to be overestimates of A_t whenever aluminum concentrations are high (i.e., at
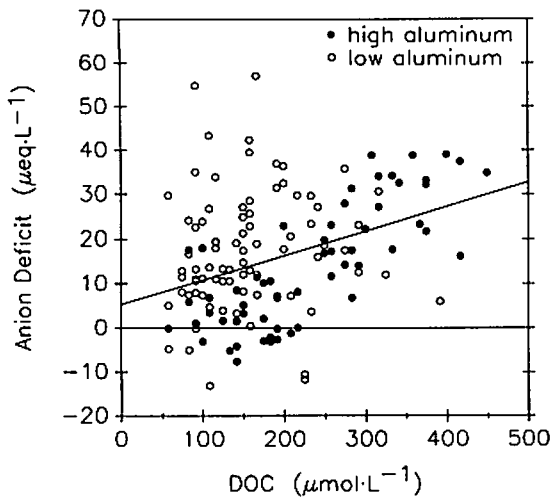
FIGURE 8.12. Plot of anion deficit (sum of measured cations minus sum of measured anions) versus DOC for samples from Catskill Long-Term Monitoring (LTM) sites. Samples with aluminum > 3 μmol L^{-1} are shown as closed circles to illustrate the effect of high aluminum concentrations on anion deficit. Regression line (Anion Deficit $= 5.3 + 0.055 \times$ DOC) is based on all samples assuming valence of aluminum (total dissolved) is $2+$.

ANC < 0), because total dissolved aluminum values are overestimates of inorganic monomeric aluminum.

If anion deficit is a good measure of A_I, rather than simply a measure of combined analytical error, it should correlate closely with DOC (LaZerte and Dillon 1984, Linthurst et al. 1986). For the Catskill LTM sites the correlation between anion deficit and DOC is very significant, but with high variance ($r^2 = 0.12, p < 0.001$), and suggests that 5.5 μeq of organic acid anions exist per 100 μmol DOC (Figure 8.12). For comparative purposes, Oliver et al. (1983) estimated a charge density of 12.6 μeq per 100 μmol DOC for 20 sites in eastern North America, and Linthurst et al. (1986) estimated 10.1 μeq per 100 μmol DOC for the ELS Catskill/Pocono region. The relationship between anion deficit and DOC in the Catskills, however, is not significant ($r^2 = 0.01, p > 0.3$) if samples with high aluminum concentrations (total dissolved aluminum > 3 μmol L^{-1}) are removed (Figure 8.12). If only high aluminum samples are used, the relationship between anion deficit and DOC is strong ($r^2 = 0.38$) and suggests 9.3 μeq L^{-1} of A_I per 100

μmol L^{-1} of DOC. Interpretation of calculated A_I results are very dependent on aluminum concentrations. Because some organically bound aluminum will necessarily be included in total dissolved aluminum measurements, results for calculated A_I based on these values should be regarded with caution.

When compared with concentrations of inorganic acid anions (SO_4^{2-} and NO_3^-), A_I is relatively unimportant. Median A_I, as calculated above, is 14 μeq L^{-1} (interquartile range is 11 to 19 μeq L^{-1}), or roughly 8% of the total acid anion concentration (Table 8.1). The DOC values increase at high flows, however, and it is possible that organic acid anions could play a larger role during high-flow episodes than is indicated by their central tendency.

Processes Influencing Surface Water Chemistry

Comparison of Precipitation and Stream Chemistry

Differences between average volume-weighted concentrations of major constituents in Biscuit Brook and those in precipitation indicate significant chemical interaction between precipitation and watershed materials (Figure 8.13). The total concentration of dissolved constituents in Biscuit Brook during WY85 and WY86 was 2.5 times that in precipitation, which can be attributed to the concentrating effect of evapotranspiration (52% of precipitation in WY85 and 31% in WY86), and an unknown contribution from dry deposition (estimated as 33% of wet deposition in Figure 8.13). The relative proportions of ions in stream water differ substantially from those in precipitation, however, which indicates that chemical reactions within the watershed also affect stream chemistry. Much of the following discussion is covered in detail by Murdoch (1988).

Calcium in Biscuit Brook replaces hydrogen from precipitation as the dominant cation and accounts for more than 60% of the total cations. The average annual hydrogen concentration in stream water is insignificant except in the most acidic of Catskill streams (1% of total cation concentration at Biscuit Brook). Cations at Biscuit Brook show the same pattern of dominance ($Ca^{2+} > Mg^{2+} > Na^+ > K^+$) as streams in the USGS/NYCDEP survey (Figure
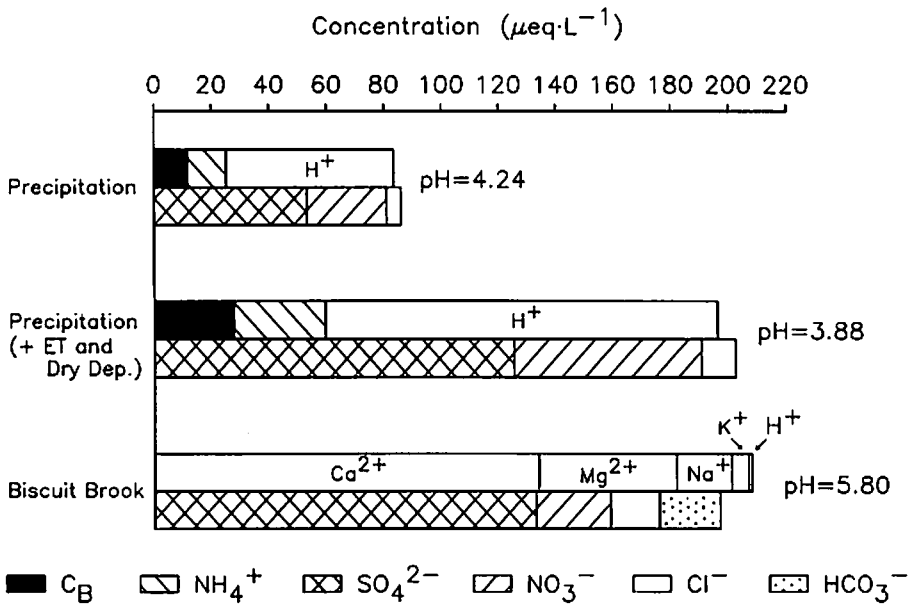
FIGURE 8.13. Ion bar diagrams of precipitation, precipitation modified by dry deposition (assumed to be 33% of wet deposition) and evapotranspiration (ET = 44% of precipitation), and Biscuit Brook stream water for water years 1985 and 1986.

8.7), and their relative concentrations do not change appreciably with increasing discharge. Aluminum and H^+ accounted for as much as 11% and 5%, respectively, of the total cations during peak flows at Biscuit Brook. The general absence of NH_4^+, except at high flows, suggests nearly complete transformation of that ion by biological activity or cation exchange within the watershed.

The dominant anion in both stream water and precipitation is SO_4^{2-}. Sulfate represents 68% of total anion concentrations in Biscuit Brook, and 62% of anionic charge in precipitation (Figure 8.13). Nitrate accounts for approximately one-third of total anion concentrations in precipitation, but only 13% in Biscuit Brook. Chloride makes up a similar proportion of total anions in both stream water and precipitation (8% and 6%, respectively). In Biscuit Brook, HCO_3^- averages approximately 10% of total anion concentrations.

Chemical budgets for Biscuit Brook in WY85 and WY86 suggest a net loss of base cations, SO_4^{2-}, Cl^-, and ANC from the watershed and a net accumulation of NO_3^-, NH_4^+, and H^+ from deposition (Table 8.5; Figure 8.14). Some of the apparent net loss was due to the omission of a dry deposition

contribution in the precipitation calculations. As discussed in the section entitled Chemistry of Atmospheric Deposition, estimates of dry deposition for the northeastern United States are quite variable. Both the SO_4^{2-} and Cl^- budgets for Biscuit Brook can be balanced by assuming that dry deposition is 30% to 40% of wet deposition (Figure 8.13). In the case of Cl^-, estimates of dry deposition made from wet deposition chemistry must be made carefully. The close correspondence of Cl^- concentration to Na^+ concentration (Figure 8.8) in the Catskill region suggests strongly that salt (NaCl) is the predominant source of Cl^- in stream water. Appreciable geochemical sources of Cl^- in the Catskills are unlikely, because bedrock is strongly leached along joint fractures and bedding surfaces where most groundwater in bedrock would flow (Murdoch 1988). Biscuit Brook's distance from the ocean makes significant contributions from marine salts unlikely. Road salt is therefore the most likely source of NaCl, and because there are no roads in the Biscuit Brook watershed, redeposition of road salt dust (in both wet and dry deposition) is the only plausible source of salt for the stream. Chloride in dry deposition is therefore

TABLE 8.5. Annual chemical inputs in wet deposition, chemical outputs in streamwater, and input/output ratios for Biscuit Brook, WY85 and WY86.[a]

	$C_B{}^b$	Ca^{2+}	Mg^{2+}	Na^+	K^+	$NH_4{}^+$	ANC	$SO_4{}^{2-}$	$NO_3{}^-$	Cl^-	H^+	Aluminum
Water Year 1985												
Input	189	82	43	53	11	168	–	592	327	69	588	–
Output	1350	873	317	130	35	0	144	862	191	113	9	1.9
Net difference	1180	791	274	77	24	–168	144	270	–136	44	–580	1.9
Input/output ratio	0.14	0.09	0.14	0.41	0.31	–	–	0.69	1.71	0.61	73.5	–
Water Year 1986												
Input	149	64	29	47	9	212	–	877	432	68	929	–
Output	2255	1435	518	207	28	0	191	1412	234	158	20	4.4
Net difference	2106	1371	489	160	19	–212	191	535	–198	90	–909	4.4
Input/output ratio	0.07	0.04	0.06	0.23	0.32	–	–	0.62	1.85	0.43	46.5	–

[a] Aluminum (total dissolved) values are mol ha^{-1}; all other values are eq ha^{-1}.

[b] $C_B = [Ca^{2+} + Mg^{2+} + Na^+ + K^+]$, and is calculated separately for each weekly interval. The sum of individual inputs and outputs of major cations do not necessarily sum to the C_B inputs and outputs due to rounding differences.

very local in origin, and should not be expected to appear as the same proportion of wet deposition that other ions do.

Sulfate yields in Biscuit Brook exceeded $SO_4{}^{2-}$ deposition in wetfall in both WY85 and WY86 (Table 8.5). Inputs from wetfall accounted for 69% of the stream's $SO_4{}^{2-}$ yield in WY85 and 62% in WY86. These input-output ratios are similar to those at Hubbard Brook (71%), Panther Lake in the Adirondacks (77%), and Birkenes in Norway (63%), all of which have similar stream $SO_4{}^{2-}$ concentrations and have had weathering discounted as a significant $SO_4{}^{2-}$ source (Hemond and Eshleman 1984).

Unlike the Cl^- and $SO_4{}^{2-}$ budgets, the $NO_3{}^-$ budget indicates a net retention during both years. The mean annual wetfall input-output ratio for WY85 and WY86 was 1.78, which indicates significant retention and is similar to the ratio calculated for two pristine lake outlets in the Adirondacks during 1978–80 (Galloway et al. 1983b). Also, the input-output ratio for $NO_3{}^-$ probably represents a minimum estimate because it excludes contributions from dryfall, gaseous nitrogen, or $NH_4{}^+$. Most of the $NH_4{}^+$ received from atmospheric loading in the Biscuit Brook watershed is retained, as it is in other watersheds studied in the Northeast (e.g., Hemond and Eshleman 1984). If $NH_4{}^+$ is included in the total nitrogen input load, the input-output ratio increases to 2.59 for WY85 and 2.75 for WY86. A precise estimate of the

nitrogen input-output ratio for the Biscuit Brook watershed is very difficult to make, because dry deposition, nitrification, and denitrification in forest soils, and an unknown export of organic nitrogen, all contribute significant uncertainty to its calculation. Based on budgets of inorganic nitrogen, however, it is clear that substantial nitrogen is retained by the Biscuit Brook watershed (Table 8.5). Both $NO_3{}^-$ and $NH_4{}^+$ are retained, and because their retention has opposite effects on ANC ($NH_4{}^+$ retention is an acidifying process, $NO_3{}^-$ retention produces ANC), the net effect of nitrogen retention on Biscuit Brook ANC is small (+7.6 µeq L^{-1}; Figure 8.14).

A large net loss of base cations occurred in the Biscuit Brook watershed in both WY85 and WY86 (Table 8.5). Weathering and/or cation exchange of C_B in the watershed is the primary mechanism for producing ANC in Biscuit Brook (Figure 8.14). Base cation concentrations and yields are the primary factors that distinguish Biscuit Brook from other Catskill streams, as well as from the Adirondack lake outlets and Hubbard Brook (Murdoch and Barnes in press). Because anion concentrations are similar among all these streams, the differences in their buffering capacities are probably related to the differences in base cation export rates from their watersheds. In the case of Biscuit Brook, the H^+ budget indicates that C_B export is sufficient nearly to balance H^+ inputs (Table 8.5; Figure 8.14).
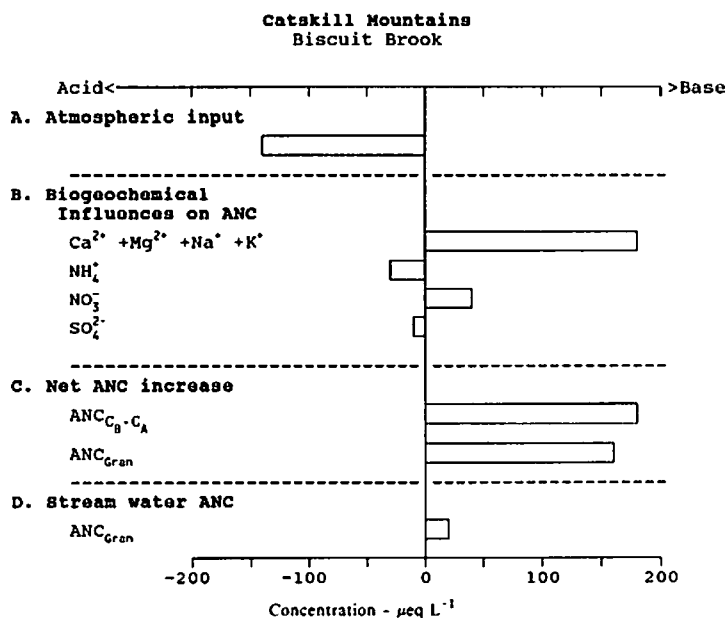
Catskill Mountains
Biscuit Brook

FIGURE 8.14. Modification of atmospheric deposition by watershed and stream biogeochemical processes at Biscuit Brook, WY85 and WY86. A. Precipitation |H$^+$| adjusted for estimated dry deposition and ET, as in Figure 8.13. Equivalent to expected stream water ANC$_{C_B·C_A}$ in the absence of any process other than ET. B. Reactions influencing ANC. Bars to the right indicate ANC production; those to the left show ANC consumption. C. Net ANC production. ANC$_{C_B·C_A}$ is the sum of ANC production terms for measured anions and cations including those shown in B.; ANC$_{Gran}$ is determined by the difference between input ANC (A.) and stream water ANC (D.). D. Stream water ANC represents the net reaction of atmospheric inputs with stream/watershed system. All data are calculated from volume-weighted concentrations in Figure 8.13. For a further explanation of calculation procedures and figure interpretation, see Appendix A. Volume-weighted mean DOC for Biscuit Brook is 303 μmol L^{-1}. Mean A_t = 17 μeq L^{-1}.

Relation Between Stream Ion Concentrations and Discharge

Results of the USGS/NYCDEP survey of Catskill stream chemistry indicated significant changes in concentrations with changes in discharge (Figure 8.5). In order to investigate this pattern further, stream discharge and chemistry were monitored during 14 storms and snowmelt periods between April 1983 and May 1986 at Biscuit Brook (Murdoch 1988). Peak flows ranged from 0.17 to 22.7 m^3 s^{-1} (Table 8.6). Maximum stream acidity occurred at or near peak flows, and peak flow pH ranged from 6.18 to 4.89. The maximum observed change in pH was 1.71 units during Hurricane Gloria on September 27, 1985. Minimum ANC during the 14 high flows ranged from 34 to −16 μeq L^{-1} (net acidity). A maximum observed change in ANC of 60 μeq L^{-1} occurred during Hurricane Gloria.

Stream pH values at Biscuit Brook decrease and approach those of precipitation during very high flow events, but significant buffering occurs in the watershed during most high flows (Table 8.6). Precipitation pH and minimum stream pH were similar only during the large storm of April 3–6, 1984. Minimum stream pH during Hurricane Gloria (September 27–28, 1985) was actually lower than precipitation pH, which indicates a net acidification of the rain water by materials already in the watershed. The minimum stream pH during all other storms exceeded precipitation pH, which indicates a net buffering of rain water acidity.

The relation between stream discharge and precipitation volume during the storms improved with increasing volume but was poorly defined at low volumes because (1) snowmelt contributed to discharge during the spring when precipitation volume was low and discharge was high, and (2)

TABLE 8.6. Characteristics of precipitation, stream hydrology, and stream chemistry during 14 high-flow periods at Biscuit Brook, 1983–86.

Date	Precipitation Volume (cm)	pH	Antecedent precipitation[a] (cm)	Peak discharge ($m^3 s^{-1}$)	Maximum change[b]	pH minimum	Maximum change[b]	ANC minimum (μeq L^{-1})	Maximum change[b]	Maximum aluminum[c] (μmol L^{-1})
Apr 10–11, 1983	3.04	4.7	6.83	2.92	2.35	5.18	−0.62	1.0	−25.0	8.5
Nov 10–11, 1983	3.96	4.5	0.15	0.19	0.16	6.18	−0.22	34.0	−2.0	1.5
Mar 21, 1984	1.04	4.5	7.80	0.79	0.42	5.89	−0.32	14.0	−4.0	1.9
Apr 3–6, 1984	12.98	4.9	6.02	18.61	18.20	4.89	−1.28	−12.0	−32.0	11.1
Nov 5, 1984	2.08	4.0	4.64	0.17	0.14	6.10	−0.14	31.8	−25.0	1.9
Feb 23–26, 1985	0.46	4.1	4.80	2.32	2.19	5.40	−1.00	6.8	−29.2	5.2
Mar 11–13, 1985	3.83	4.1	2.74	2.38	2.20	5.45	−0.83	4.0	−32.0	5.6
May 17–21, 1985	3.91	4.3	6.85	0.60	0.53	6.02	−0.38	20.0	−22.0	3.7
Jul 31, 1985	4.39	3.9	5.46	1.08	0.79	6.06	−0.84	24.0	−14.0	4.8
Sep 27–28, 1985	12.62	5.3	1.16	22.70	22.60	4.90	−1.71	−10.0	−60.0	11.9
Jan 19–21, 1986	2.94	4.7	0.48	5.04	4.94	5.51	−0.72	8.0	−22.0	5.6
Mar 13–16, 1986	8.99	4.6	0.71	13.90	13.73	4.94	−1.69	−16.0	−38.0	10.0
Mar 18–20, 1986	3.40	4.0	9.70	14.36	13.54	4.92	−0.78	−16.0	−20.0	8.5
May 20–22, 1986	9.01	4.4	2.00	6.95	6.81	5.19	−1.22	−8.0	−36.0	8.5

[a] Precipitation volume during 14 days preceding a storm or snowmelt period.
[b] Difference between initial values and values at peak flow.
[c] Total dissolved aluminum.

antecedent soil-moisture conditions, which affect the amount of precipitation reaching the stream, differed from storm to storm. Adding a surrogate variable for antecedent soil-moisture conditions (precipitation in the 14 days preceding a storm) to the comparison of storm precipitation volume with streamflow volume did not significantly improve the correlation between precipitation and flow (Murdoch 1988). Lynch et al. (1986) have used the hydrologic response of a small stream in central Pennsylvania to precipitation volume as an index of stream sensitivity to acidic deposition. The sensitivity of Biscuit Brook may also be viewed as a function of hydrologic response to precipitation volume.

In general, results of high-flow analyses show dilution of C_B, SO_4^{2-}, and ANC during individual flow peaks, and increased concentrations of H^+ and NO_3^- (Figure 8.15). Concentrations of minor constituents also changed during high flows. Potassium, a minor constituent, showed small increases with increased flow. Hydrogen and aluminum concentrations showed rapid increases with increased flow. Silica decreased with increased flow, which indicates dilution of dissolved weathering products. Values of DOC increased with flow, which suggests flow through the organic soil layer to the stream or bank erosion; seepage from the organic soil layer may provide organic acids to the stream
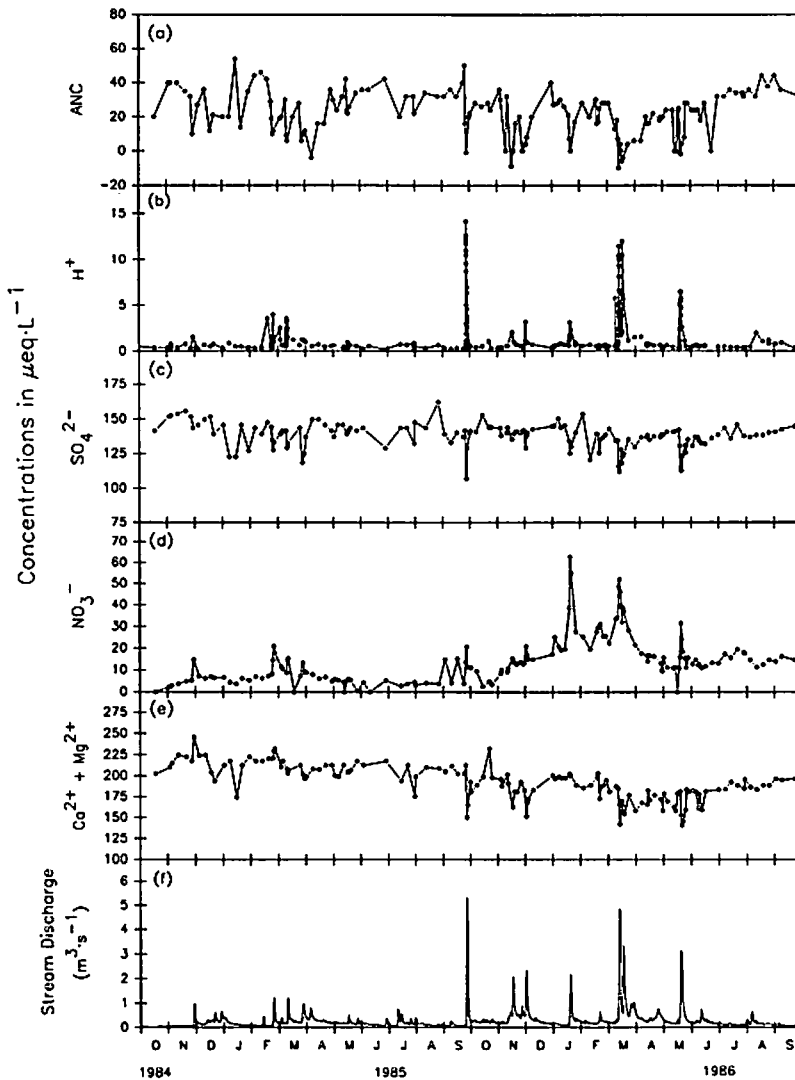
FIGURE 8.15. Temporal patterns in Biscuit Brook stream water chemistry and mean daily stream discharge, WY85 and WY86.

and account for some of the pH decrease observed during storms.

Data from seven LTM streams that together represent a wide range of baseflow ANC values support the concentration-discharge relations observed at Biscuit Brook (Murdoch and Barnes in press). Sulfate concentrations observed in these streams decreased with increased flow and were similar to each other at flows ranging through three orders of magnitude (Figure 8.16). Base cation concentrations, by contrast, differed widely among

the streams, and the dilution with increased flow was greatest in the streams with highest concentrations (Figure 8.17). Base cation concentrations in the LTM streams undergo more dilution at high flows than SO_4^{2-} concentrations. This differential dilution causes the $SO_4^{2-}:C_B$ ratio to become higher at high flows, and contributes to low ANC values observed during storm and snowmelt events (Murdoch 1988). Aluminum and H^+ concentrations increased with flow, and NO_3^- increased with flow to values similar to those observed at Biscuit
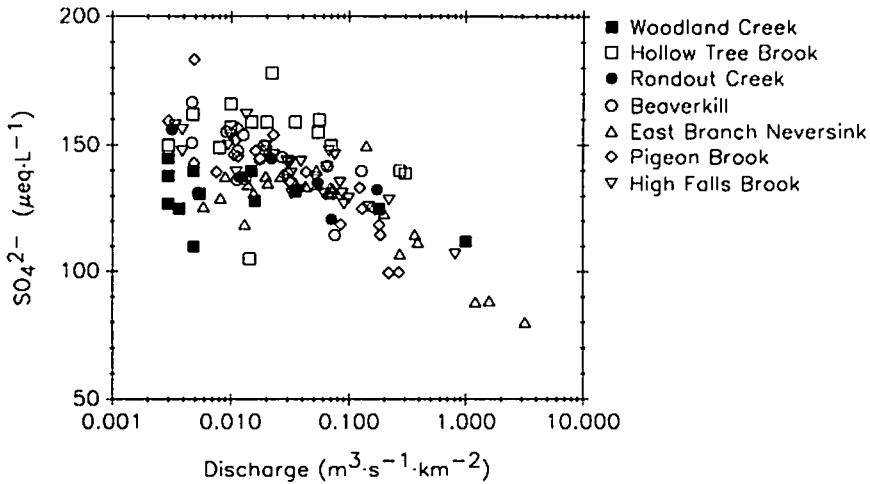
FIGURE 8.16. Plot of SO_4^{2-} concentration versus stream discharge (normalized for drainage area) for Catskill LTM streams.

Brook during peak runoff (Figure 8.15c). Differences in base cation concentrations, rather than SO_4^{2-} or NO_3^- concentrations, are therefore associated with differences in ANC among streams, especially at baseflow. Changes in SO_4^{2-} and NO_3^-, in addition to dilution of C_B, are associated with ANC changes during high-flow events in individual streams (Figures 8.14, 8.15, 8.16).

A model developed by Johnson et al. (1969) that relates the chemistry of stream water to the stream's discharge was applied to the Biscuit Brook data. The method has been successfully applied to Hubbard Brook data (Johnson et al. 1969) and to Adirondack Mountain lake outlet data (Peters et al. 1982) and is considered more accurate than graphical methods of calculating stream yields, if the r^2 values for the concentration-discharge regressions are significant. The resulting concentration-discharge relations for Biscuit Brook suggest that concentrations of C_B, H^+, Al, SO_4^{2-}, Cl^-, and ANC can be predicted from discharge values with reasonable confidence (Murdoch 1988). The r^2 value
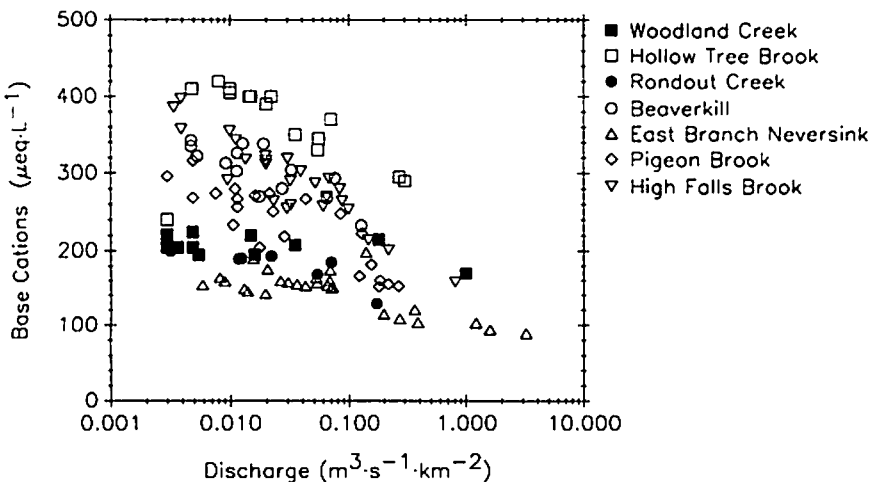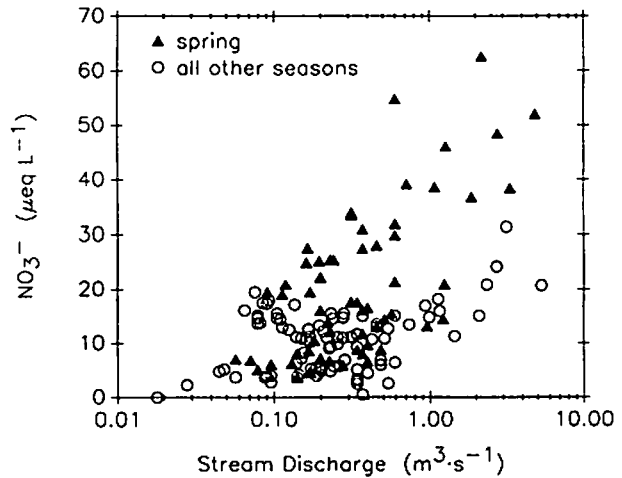

FIGURE 8.17. Plot of C_B ($Ca^{2+} + Mg^{2+} + Na^+ + K^+$) versus stream discharge (normalized for drainage area) for Catskill LTM streams. Stream symbols are as in Figure 8.16.

FIGURE 8.18. Plot of NO_3^- concentration versus stream discharge for Biscuit Brook, WY85 and WY86. Spring (March-May) data are plotted separately to illustrate the effect of season on NO_3^- retention by watershed.

for the C_B-discharge relation suggests that 63% of the variability in concentrations can be attributed to changes in discharge. The H^+ and aluminum r^2 values were 0.90 and 0.77, respectively. Sulfate concentration also was strongly correlated with discharge ($r^2 = 0.76$).

Nitrate concentrations were poorly correlated with flow ($r^2 = 0.17$) when data for all seasons were combined (Figure 8.18). The relation was stronger ($r^2 = 0.38$), however, when spring data (March through May) were analyzed separately. Biological uptake of NO_3^- is likely to alter the concentration-discharge relation during the growing season (late spring to early fall), and undoubtedly contributes to the poor relation observed between concentration

and discharge on an annual basis. Cessation or slowing of biological activity during the winter months probably causes NO_3^- to be more available to stream runoff during winter and spring, which leads to a steeper increase in NO_3^- concentration at high discharges (Murdoch 1988; Figure 8.18).

Effect of Storm Runoff and Snowmelt on Catskill Stream Chemistry

The data collected at Biscuit Brook during WY84 and WY85 indicate that storm runoff and snowmelt contribute substantially to annual stream acidity in the Catskill Mountains. Plots of daily stream discharge for those years (Figure 8.19)
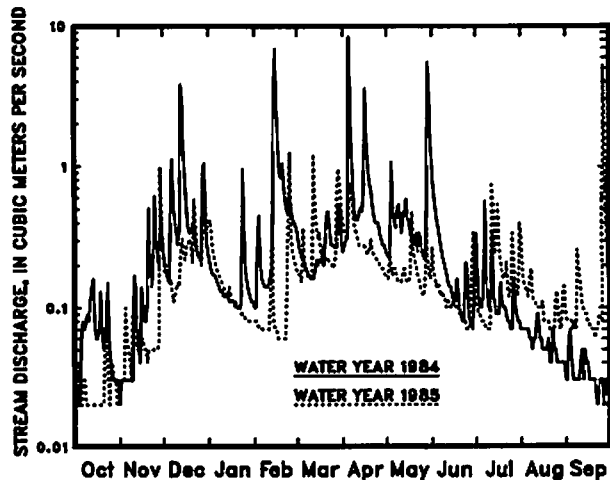

FIGURE 8.19. Hydrographs for Biscuit Brook, WY84 and WY85.

TABLE 8.7. Percent of total annual yield of water and major ions in baseflow at Biscuit Brook, WY84 and WY85.

	Flow (cm)		% in baseflow					
	Total	Base	Water	SO_4^{2-}	NO_3^-	Ca^{2+}	H^+	ANC
WY84	111.0	63.2	57.1	61.9	52.5	63.1	19.0	96.7
WY85	62.0	42.2	69.1	72.4	65.8	72.4	28.5	88.0

indicate that peak flows during the drought period from June 1984 to June 1985 were smaller and less frequent than before and after the drought period. The daily baseflows for the two years were similar, however. The main hydrologic difference between the two years, therefore, was the magnitude and frequency of discharges that exceeded seasonal baseflow values (Murdoch 1988).

The cumulative yields of H^+ and aluminum from Biscuit Brook in WY84 were substantially greater than in WY85 (Murdoch 1988). If chemical yields for each year are divided by graphic flow separation techniques into baseflow and high-flow components, results indicate that the vast majority of the H^+ yield is derived from high flows (Table 8.7). These data suggest that storm runoff and snowmelt provide most of the annual stream acidity and that this acidity develops in the stream during several short episodes over the course of each year.

Another effect of snowmelt and storm runoff is the large increase in stream NO_3^- during the spring (Figure 8.15d). This spring pulse is consistent with results from the Adirondacks and Hubbard Brook, but is contrary to the results at Bickford Reservoir in Massachusetts, where stream NO_3^- concentrations remained low (1 μeq L^{-1}) through the spring (Hemond and Eshleman 1984). The annual wet deposition of NO_3^- at Biscuit Brook (438 eq ha^{-1}) appears slightly greater than at the other watersheds (Bickford Reservoir, 295 eq ha^{-1}; Hubbard Brook, 317 eq ha^{-1}).

Nitrate concentration not only showed large increases during the spring storms of WY84, WY85, and WY86, but also during the storms of all other seasons except late summer, and showed substantial increases during Hurricane Gloria in September 1985 (Figure 8.15d). Analysis of annual average and stormflow NO_3^- concentrations at Biscuit Brook, and of average NO_3^- concentrations at other Catskill streams, suggests that the biological demand for NO_3^- in the Biscuit Brook watershed exceeds the supply of NO_3^- only during late sum-

mer. The WY85 net yield of nitrogen showed a seasonal pattern similar to that observed in Adirondack lake outlets (Galloway et al. 1983b), with net accumulation during the summer and fall, net loss during snowmelt periods, and balanced inputs and outputs during winter (Murdoch 1988). This seasonal pattern provides clear evidence of the importance of biological processes in regulating the dynamics of NO_3^- in the watershed.

Evidence of Historical Trends

Evidence of trends in major ion chemistry of Catskill streams comes primarily from historical water quality data gathered by the NYCDEP as part of their routine monitoring network. Because most of New York City's drinking water originates in the Catskill region, laboratories of the NYCDEP have monitored ANC, NO_3^-, water hardness, and other relevant variables since before the construction of the Catskill reservoirs. Data collection in the Schoharie and Ashokan basins began about 1920; data collection in the southern basins began in the 1950s. A second, less extensive, long-term data base has been developed at the USGS hydrologic benchmark station on Esopus Creek in Shandaken, New York (Figure 8.1) where data have been collected since 1964. The following discussion focuses primarily on one site, Schoharie Creek, at Prattsville (Figure 8.1), which has the most complete data record of any of the historical sites. Trends at Schoharie Creek are consistent with trends in about 20 other Catskill streams (Stoddard in review). The USGS has monitored stream discharge at Schoharie Creek since 1907.

One common problem in interpreting historical records of surface water chemistry is that methods of analysis have changed substantially over several decades, and results may be biased as a result of differences between these methods' ability to determine major ion concentrations accurately (Kramer

FIGURE 8.20. Plot of estimated SO_4^{2-} vs. measured SO_4^{2-} used as a test of SO_4^{2-} estimation method employed for historical reconstruction of SO_4^{2-} trends. Data for estimated SO_4^{2-} (see text for explanation of estimation method) and measured SO_4^{2-} (by ion chromatography) are for samples in USGS/NYCDEP survey. 1:1 line is included to indicate expected relationship.
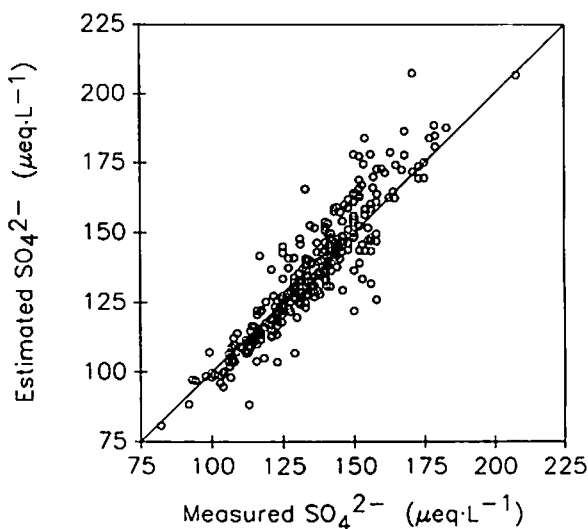
and Tessier 1982, Kramer 1985). Acid neutralizing capacity is particularly prone to this problem, and many attempts have been made to determine what effect changes in methods have had on ANC estimates (Kramer and Tessier 1982, Kramer 1985, Pfeiffer and Festa 1980, Kramer et al. 1986). For this chapter, all ANC values were corrected for biases caused by the titration methods used. Correction factors were based on the results of replicated titrations conducted with all of the historical methods, and comparison to Gran titration results. Details on ANC corrections and on outlier tests applied to all chemical data are given in Stoddard (in review). [Ca^{2+} + Mg^{2+}] values are calculated from water hardness measurements; analytical methods for determining hardness were consistent throughout the period of data collection. Nitrate concentrations were determined by two methods; comparisons indicate that accuracy and precision of the two methods were similar.

Sulfate concentrations were not measured directly by NYCDEP laboratories until 1979, and then only infrequently. Sulfate is therefore estimated using the method of Ceraso et al. (1986), modified to utilize the chemical variables available in the NYCDEP dataset. This estimation method is based on the formula for calculated conductivity, which is simplified to remove unmeasured variables (i.e., the major cations), and solved for SO_4^{2-} concentration. For the NYCDEP data, Ca^{2+} and Mg^{2+} concentrations are estimated from water hardness, HCO_3^-

is set equal to ANC, and Na^+ is set equal to Cl^-, based on data in Figure 8.8. Potassium, a minor cation in Catskill streams (Figure 8.7) is set equal to 9 μeq L^{-1}, a typical value for the Schoharie basin (Table 8.4). Sulfate is assumed in this method to account for all of the difference between measured and calculated conductivity (i.e., organic acids and minor inorganic ions are assumed to be absent).

The SO_4^{2-} estimation method was tested using data from the USGS/NYCDEP stream survey (Figure 8.20). The results indicate reasonable agreement between estimated and measured values, although estimated values appear to overestimate measured SO_4^{2-} at high values. Estimated SO_4^{2-} concentrations are therefore expected to show greater variability than measured concentrations.

Strong seasonality, which produces the marked scatter among the points in Figure 8.21, complicates the statistical identification of trends in streamwater chemistry. Trends in Schoharie Creek chemical composition were therefore tested using analysis of covariance (ANCOVA) on rank-transformed data (Loftis and Taylor 1989). This method allows the fitting of regression parameters to serially correlated time series data; it has an effect similar to that of deseasonalizing the data through a nonparametric test (e.g., Hirsch et al. 1982, van Belle and Hughes 1984), and has the advantage of detecting nonlinear trends.

Acid neutralizing capacity at Schoharie Creek exhibits a highly significant ($p < 0.0001$) curvi-
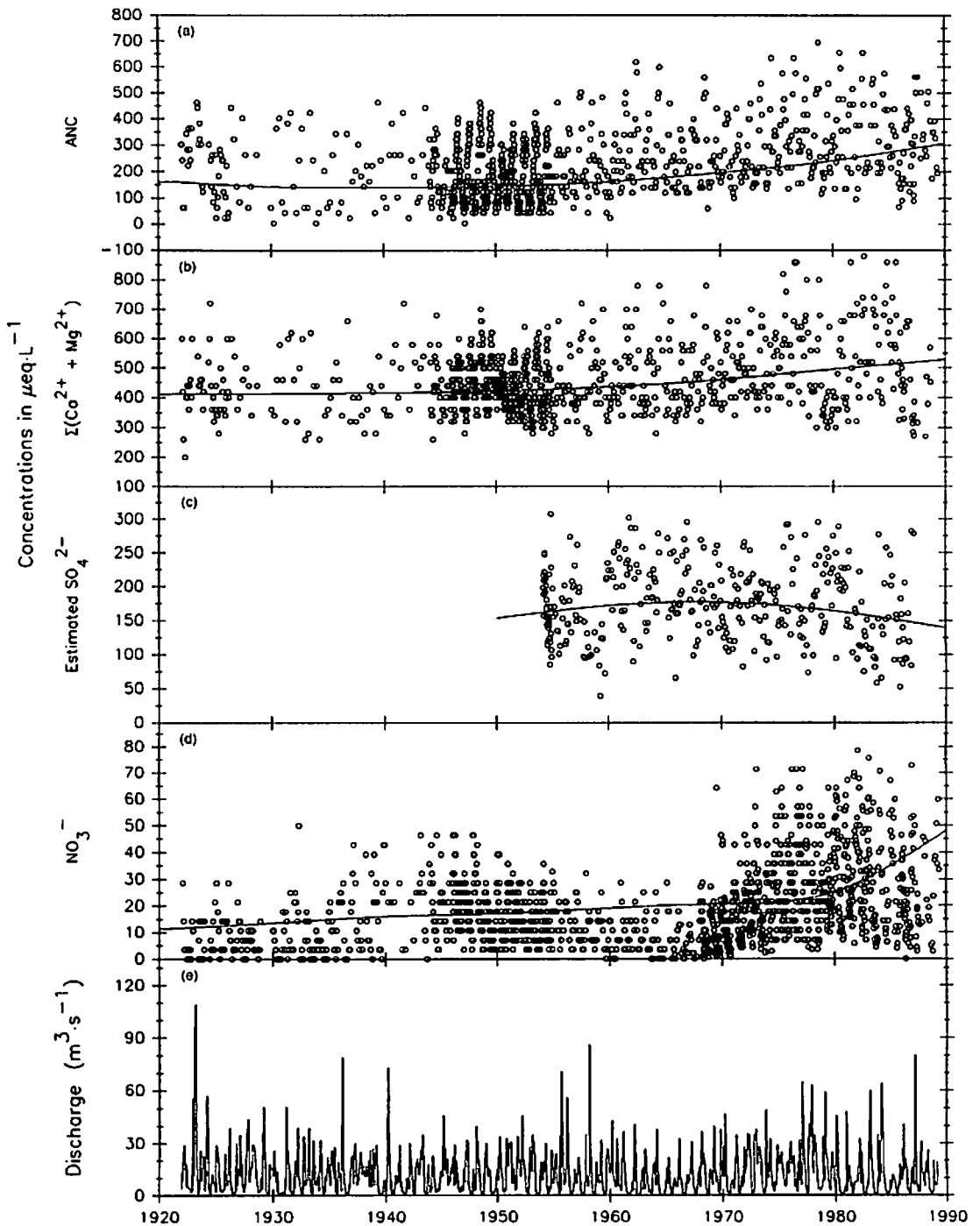
FIGURE 8.21. Temporal trends in streamwater chemistry and stream discharge for Schoharie Creek at Prattsville, 1922–89: (a) ANC values corrected for methods bias; (b) Ca^{2+} + Mg^{2+} concentrations, calculated from water hardness measurements; (c) estimated SO_4^{2-} concentrations (see text for explanation of estimation method); (d) NO_3^- concentrations; and (e) discharge measurements from USGS gauge at site. All concentrations are in $\mu eq\ L^{-1}$. Lines in each box are the results of best-fit regressions, using analysis of covariance (ANCOVA) on rank-transformed data.

linear trend with time (Figure 8.21a); ANC decreased from a value around 160 μeq L^{-1} to a minimum of 140 μeq L^{-1} in the 1940s. After 1950, ANC increased dramatically to a value of approximately 300 μeq L^{-1} in 1989.

The concentration of [Ca^{2+} + Mg^{2+}] at Schoharie Creek also shows a highly significant ($p < 0.01$) curvilinear trend (Figure 8.21b), which increases throughout the period of record. Concentrations have risen from a minimum of 415 μeq L^{-1} to a maximum of almost 500 μeq L^{-1} in 1989, with most of the increase occurring after 1950.

Estimated SO$_4^{2-}$ concentrations (Figure 8.21c) also show a significantly curvilinear trend ($p < 0.001$) and appear to have reached maximum values during the late 1960s. Estimated SO$_4^{2-}$ decreased from 175 μeq L^{-1} in 1965 to 140 μeq L^{-1} in 1989. A decreasing trend in the SO$_4^{2-}$ concentrations of surface waters since 1970 in the Northeast has been verified by several investigators (Peters et al. 1982, Smith and Alexander 1983) and is consistent with the observed decreases in sulfate deposition recorded in this region since the 1960s (Smith and Alexander 1986, Hedin et al. 1987).

Nitrate concentrations in Schoharie Creek were consistently low (ca. 10 μeq L^{-1}) until approximately 1960 (Figure 8.21d). After 1965, NO$_3^-$ concentrations increased dramatically to levels near 50 μeq L^{-1}. The recent upward trend in NO$_3^-$ concentration in Schoharie Creek is consistent with trends in other surface waters in the Northeast (Smith et al. 1987, Kramer et al. 1986), but not with trends in NO$_x$ emissions. Estimates of NO$_x$ emissions suggest that they have increased monotonically throughout most of the 20th century until about 1970, and have remained more or less constant since then (Husar 1986; Chapter 3, Husar et al., this volume); they certainly do not show any evidence of a precipitous increase beginning around 1965.

Stream discharge has a profound effect on major ion concentrations in Catskill streams (see section entitled Seasonal Variability in Ion Composition of Streams); it is therefore important to determine whether any of the trends shown in Figure 8.21 are attributable to trends in stream discharge. No significant trend ($p > 0.5$) in stream discharge is observable at Schoharie Creek for the period of record (Figure 8.21e).

When combined, the trends illustrated in Figure 8.21 suggest that ANC in Schoharie Creek has increased since 1950, primarily as a result of increasing base cation concentrations. Hypothesized decreases in streamwater SO$_4^{2-}$ (about -35 μeq L^{-1} since 1965), based on estimated concentrations, are nearly offset by increases in NO$_3^-$ concentrations (about $+30$ μeq L^{-1} since 1965). The mechanisms responsible for the trends in [Ca^{2+} + Mg^{2+}], SO$_4^{2-}$, and NO$_3^-$ are not obvious and cannot all result from the effects of acidic deposition. Decreasing SO$_4^{2-}$ concentrations are almost certainly the result of decreasing sulfur dioxide emissions in the area upwind of the Catskill region. Increasing [Ca^{2+} + Mg^{2+}] concentrations, on the other hand, cannot be attributed to acidic deposition, because they are accompanied by increases in ANC and they continue during the period when rates of sulfuric acidic deposition are known to be decreasing (i.e., 1970 to the present). The most likely cause of the trend in [Ca^{2+} + Mg^{2+}] is changing land use. The Schoharie basin has undergone substantial development, starting in the period after World War II, and landscape disturbance is likely to have increased base cation concentrations.

Changes in NO$_3^-$ concentrations cannot be readily attributed either to changes in acidic deposition, or to changes in land use. Agricultural activity is minimal in the Schoharie watershed. Other kinds of land use disturbances that would lead to increased streamwater NO$_3^-$ (i.e., inputs from sewage or septic systems) would all produce highest concentrations during baseflow periods. But Schoharie Creek exhibits the same pattern of low NO$_3^-$ in the summer and high NO$_3^-$ in the winter and spring that Biscuit Brook does (Figure 8.15c). One plausible mechanism for increased streamwater NO$_3^-$ in Schoharie Creek is a change in the same kinds of biological processes (e.g., denitrification or nutrient uptake) that are thought to control the seasonal pattern of nitrogen dynamics in the Biscuit Brook watershed (see section entitled Processes Influencing Surface Water Chemistry), but the nature of that change is unknown. Changes in the ability of forests and soils to retain nitrogen may be due to natural causes, such as forest maturation (Melillo et al. 1983), or possibly to the cumulative effects of chronic deposition of sulfuric and nitric acids (Aber et al. 1989). Henriksen et al. (1988) found that NO$_3^-$ concentrations in Norwegian lakes have doubled since 1974, but rates of nitrogen deposition have increased only 10%. Henriksen and Brakke (1988b) suggest that
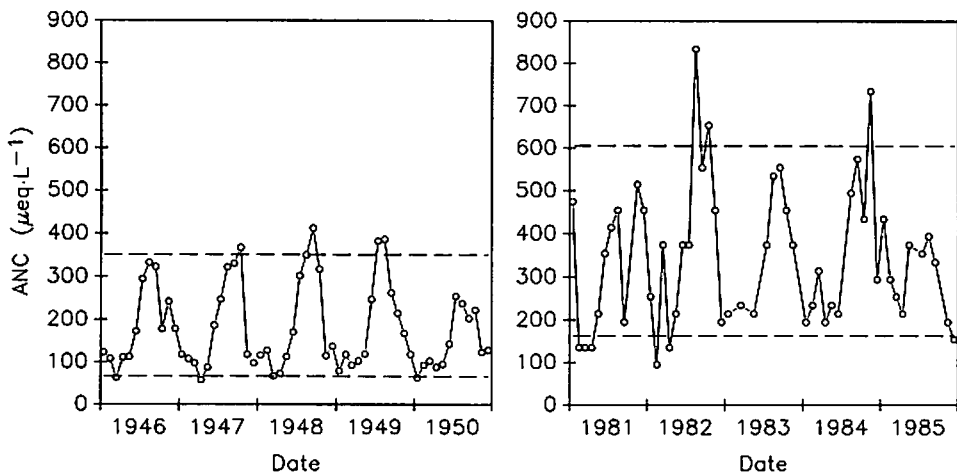
FIGURE 8.22. Short-term temporal patterns in monthly mean ANC during two time periods (1946–50 and 1981–85) in Schoharie Creek at Prattsville. Dashed lines are mean annual maximum (summer) and minimum (spring) values for each 5-year period.

decreases in forest uptake, rather than increases in nitrogen deposition, have caused the increasing trend in NO_3^-. Similar processes may be operating in both the Catskills and in Norway to limit the ability of watersheds to retain nitrogen.

An important pattern in the Schoharie Creek ANC data that warrants further examination is the apparent increase in the annual range of observed values (Figure 8.21a). In the 1940s, yearly ANC minima occurred reliably each spring at around 80 μeq L^{-1} (Figure 8.22), and yearly maxima occurred late each summer at approximately 350 μeq L^{-1}. In the 1980s, the seasonal pattern was still evident, but the minimum and maximum values increased, although to different degrees. Springtime minimum ANC values have increased by approximately 100 μeq L^{-1}, to 180, whereas summer maximum ANC values have increased by more than 250 μeq L^{-1}, to approximately 610 μeq L^{-1}.

The smaller increase in minimum ANC values can be partially explained by the increase in springtime NO_3^- (Figure 8.23). Minimum values for streamwater NO_3^- occur in the late summer, when ANC is maximal, and these minimum NO_3^- concentrations have remained essentially unchanged at approximately 10 μeq L^{-1}. Maximum concentrations of NO_3^- in Schoharie Creek occur in the spring, when stream discharge is high and ANC values are minimal. These maximum NO_3^- concentrations have increased from approximately 30 μeq L^{-1} in the 1940s to near 80 μeq L^{-1} in the 1980s. The increase in springtime NO_3^- is therefore partially responsible for maintaining springtime ANC values at low levels. Nitrate concentrations exert relatively little effect on ANC values in the summer, because NO_3^- levels remain more or less unchanged at this season. Springtime NO_3^- concentrations, however, have increased by as much as 50 μeq L^{-1}, and may control the extent to which springtime ANC values are able to respond to increases in base cations and decreases in SO_4^{2-}.

The only other historical information on Catskill stream chemistry comes from the USGS hydrologic benchmark station on Esopus Creek at Shandaken, where data have been collected since 1964. An increasing trend in ANC (reported increases for the period beginning in 1964 range from $+24$ to 33 μeq L^{-1}, for a mean change of $+1.2$ μeq L^{-1} yr^{-1}) and a decrease in SO_4^{2-} concentration (estimated range from -34 to -48 μeq L^{-1} in the same period, or -2.1 μeq L^{-1} yr^{-1}) have been reported for this site (Peters et al. 1982, Smith and Alexander 1983, Kramer et al. 1986). The SO_4^{2-} trend is very similar to the trend in estimated SO_4^{2-} reported for Schoharie Creek (-35 μeq L^{-1} from 1970 to 1989, or -1.9 μeq L^{-1} yr^{-1}), and lends support to the method of SO_4^{2-} calculation used for the NYCDEP data. The ANC trend at Esopus Creek is much smaller than that reported for Schoharie Creek ($+140$ μeq L^{-1} from 1965 to 1988), but Kramer et al.
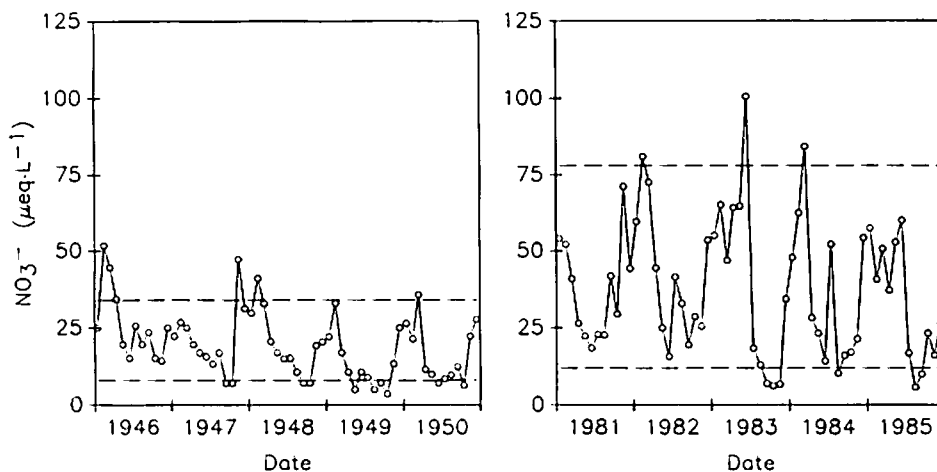
FIGURE 8.23. Short-term temporal patterns in monthly mean NO_3^- during two time periods (1946–50 and 1981–85) in Schoharie Creek at Prattsville. Dashed lines are mean annual maximum (spring) and minimum (summer) concentrations for each 5-year period.

(1986) report no significant trend in Ca^{2+} or Mg^{2+} for the Esopus Creek site, and this is likely to have a strong effect on the ANC trend. In addition, Kramer et al. (1986) have reported a marked increase in NO_3^- concentration at Esopus Creek. In a study of benchmark stations throughout the eastern United States, Smith and Alexander (1986) report that the Esopus Creek at Shandaken site is consistent with sites throughout the Northeast in showing decreasing SO_4^{2-} concentrations at the same time that monitoring stations are reporting decreases in sulfur dioxide emissions densities.

Future Considerations

Analysis of historical streamwater data for the Catskill region suggests that, in the absence of increases in base cation concentrations, ANC values would have remained at their current levels for at least the last 20 years. Rates of SO_4^{2-} deposition are believed to have decreased throughout this time period (Chapter 3, Husar et al., this volume), and conceptual models suggest that this decrease in acid loading should lead to an increase in ANC (Galloway et al. 1983a). In the Catskill region, however, decreases in streamwater SO_4^{2-} concentrations are matched stoichiometrically by increases in streamwater NO_3^-, at least for the time period since 1970.

Predictions of how ANC values will respond to the replacement of SO_4^{2-} by NO_3^- will depend strongly on estimates of the rates of decrease in streamwater SO_4^{2-} and increase in streamwater NO_3^-. Estimation of these rates is complicated by the strong seasonality of streamwater chemistry, and in particular by the association of minimum ANC and maximum NO_3^- during high-flow events in the spring. Seasonal excursions in ANC are much more closely correlated with changes in NO_3^- concentration than with changes in SO_4^{2-} concentration (Figure 8.15) and as a result, an increasing trend in NO_3^- has a greater potential to lower springtime ANC values than a decreasing trend in SO_4^{2-} has to raise them. At our current level of understanding, we cannot make quantitative estimates of future trends in Catskill streamwater ANC. We can say, however, that a continuation of the observed increase in streamwater NO_3^- has the potential to induce a declining trend in springtime ANC values, and to increase the proportion of streams that exhibit negative ANC values during high-flow events.

Biological Status

The Catskill region has long been recognized for its high-quality trout fishing (Kelly 1973, Senectutus 1943). The combination of groundwater inseepage

and shading from the forest overstory results in clear, cold waters. Streamwater temperatures rarely exceed 18 to 20°C, even in summer, providing favorable conditions for trout survival and growth.

The following discussions focus on the fish communities in five key headwater streams: the Beaverkill, Willowemoc Creek, Esopus Creek, Rondout Creek, and the Neversink River (Figure 8.1). The Beaverkill, Willowemoc Creek, and Esopus Creek, in particular, are considered among the finest trout streams in the area (Kelly and Gann 1979). Streams in the Neversink and Rondout basins had the lowest levels of ANC, pH, and C_B among these streams (Table 8.4; Figure 8.6a,b).

Brook trout (*Salvelinus fontinalis*) and brown trout (*Salmo trutta*) are the two most important game species in Catskill streams, with brook trout relatively more important in the upstream reaches that may be most sensitive to potential effects from acidic deposition. Brown trout are generally more tolerant of warmer waters and habitat disruption, and thus often dominate in downstream reaches. Brown trout are also more sensitive to acidic conditions; Baker and Christensen (Chapter 4, this volume) report approximate critical pH thresholds of 4.8 to 5.4 and 4.7 to 5.1 for brown trout and brook trout, respectively. Most Catskill headwater streams provide excellent spawning and nursery areas for brown trout and brook trout; the upper reaches of all five stream systems are classified as natural spawning adequate (NSA) by the New York State Department of Environmental Conservation (NYSDEC, unpublished data). In downstream reaches, however, natural trout production is generally supplemented by stocking. Rainbow trout (*Salmo gairdneri*) also occur in some streams, but in general must be maintained by stocking.

Comprehensive surveys of fish communities in the Beaverkill, Willowemoc, Esopus, Rondout, and Neversink systems conducted by Heacox (NYSDEC, unpublished data) in the 1950s provide an index of the relative importance of other fish species in Catskill streams. Minnows, most commonly the blacknose dace (*Rhinichthys atratulus*), and sculpins (*Cottus bairdi* and *C. cognatus*) occur in large numbers; the white sucker (*Catostomus commersoni*) and other nongame species were caught much less frequently and generally only at lower elevations.

The fewest numbers of fish were caught in the Neversink River, although both the Neversink and the Willowemoc had low estimates of trout per stream km (118 to 122 trout km⁻¹, as opposed to 272 to 1,244 trout km⁻¹ in the other three stream systems; NYSDEC, unpublished data), and low numbers of legal-sized trout per km (22 to 24 legal trout km⁻¹ compared to 41 to 136 legal trout km⁻¹). Heacox (NYSDEC, unpublished data) noted that the relatively low numbers of trout per km in the Willowemoc and Neversink were associated with a scarcity of suitable forage, especially benthic insects, based on qualitative observations of the stream benthic community.

The Willowemoc system, although exhibiting low fish densities, supported a relatively diverse fish fauna. Excluding the Beaverkill, for which individual minnow species were not recorded, the Willowemoc had the highest number of taxa collected: 18, relative to 17 in the Esopus, 13 in the Rondout, and 8 in the Neversink. The relatively low species richness for the Neversink could result from many factors, including lower habitat diversity; numerous investigators, however, have reported lower species richness in waters with lower pH and ANC (e.g., Harvey 1975, Rago and Wiener 1986).

In 1981, Kelly (NYSDEC, unpublished data) duplicated these surveys of fish communities, using similar techniques, at a select group of sites studied in the 1950s by Heacox. For some streams, additional historical data on fish species composition are available for the 1935 and 1936 biological surveys conducted by the NYSDEC (1936, 1937); sampling methods were different for these surveys, however.

Results from the 1950–55 and 1981 surveys are summarized in Table 8.8. No striking pattern of change in the numbers or types of fish caught between the two time periods is evident. Other than brook trout, only sculpins were collected in significant numbers, reflecting the focus in the 1981 surveys on moderate-to-high elevation (335 to 670 m) stream sites that are potentially more sensitive to acidic deposition. In all streams but the East Branch of the Neversink, young-of-the-year trout were collected in 1981, indicating successful natural reproduction and recruitment.

The East Branch of the Neversink had by far the fewest number of fish caught both in 1981 and in

TABLE 8.8. Numbers of fish caught (by species) in 1981 and 1950–55 at selected high-elevation sites in five Catskill stream systems.[a]

Stream	Beaverkill		Willowemoc		Esopus Creek			Rondout Creek		West Branch Neversink		East Branch Neversink			
Elevation (m)	<675	675	590		580			335		395		595		640	
Date	8/9/53	9/81	9/55	9/81	9/50	8/9/51[b]	9/81	8/5	9/81	8/50	9/81	8/51[b]	9/81	8/51[c]	9/81
Temperature (°C)															
Air	26	16	18	14	16	21	19	23	16	17	17	23	17	20	18
Water	18	15	13	13	11	12	12	14	13	12	12	11	11	16	14
Physical characteristics															
Length (m)	90	90	90	107	107	75	112	909	90	90	90	90	150	90	90
Width (m)	7.6	7.0	–	6.1	1.5–4.5	0.6–1.8	2.7	6.1	8.5	6.1	8.2	4.6	4.6	3.6	10.1
Flow (m³ s⁻¹)	–	0.33	–	0.14	0.14	0.85	0.55	–	0.4	–	0.38	–	0.13	–	0.22
Chemical characteristics[d]															
pH	5.9		–		6.5			6.1		5.8		4.8		4.8	
ANC (µeq L⁻¹)	31		–		107			50		49		−18		−20	
Fish species															
Brook trout															
Young-of-year	0	8	13	2	32	0	15	15	0	18	15	0	2	0	0
Age > 1 year	14	52	15	22	10	5	22	26	1	42	12	4	6	5	1
Brown trout															
Young-of-year	1	0	3	2	12	0	0	1	1	0	0	0	1	0	0
Age > 1 year	15	0	13	7	15	5	0	1	10	0	3	10	4	0	0
Sculpins	63	28	50	11	0	0	0	80	14	110	28	0	41	0	0
Longnose dace	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
White sucker	0	0	4	0	0	0	0	0	1	0	0	0	1	0	0

[a] Based on NYSDEC unpublished data.

[b] Stream resurveyed in 1951 to evaluate effects from major floods in November 1950 and spring 1951.

[c] Samples collected following major floods in late 1950/early 1951. No pre-flood data available. Refer to the data for Esopus Creek. Comparison of pre- and post-flood data at a relatively high-elevation site in Esopus Creek suggests potential loss of the trout year-class and adverse effects on sculpins (NYSDEC unpublished data).

[d] Streamwater chemistry data are mean values from USGS/NYCDEP survey, 1985–87.

the 1950s—only one adult brook trout in 1981 and five adult brook trout in 1951. Major floods in late 1950 and early 1951 may be responsible, in part, for the low fish abundance in 1951.

Only limited data are available on nonfish biota in Catskill streams. Qualitative observations of the abundance and types of benthic invertebrates present were recorded as part of both historical and present-day surveys of fish community status. However, these general records (e.g., "aquatic insect life sparse: mayflies and caddis") are not suitable for assessment of potential trends through time. Culp (1980) sampled benthic communities in selected streams in the Schoharie and Ashokan basins during 1975–78. In Esopus Creek, 142 taxa of aquatic macroinvertebrates were collected in total. Aquatic insects, primarily Diptera, Ephemeroptera, and Tricoptera, constituted at least 90%, numerically and gravimetrically, of the total organisms collected. At the uppermost sites in the creek, numerical density ranged between 956 and 6,928 m^{-2} (mean = 1,513 m^{-2}) during 1976–78.

There is no direct evidence from the limited data available that the biological status of Catskill streams has been adversely affected by acidic deposition. Many streams in the Neversink and Rondout basins experience pH < 5.0 on at least an episodic basis during high-flow events (Figure 8.5d); this is within the range of estimated critical pH levels for both brook and brown trout (Chapter 4, Baker and Christensen, this volume), and recruitment failure is likely to occur if early life stages experience these episodic low pH values. The near absence of trout in both the 1951 and 1981 surveys of the East Branch of the Neversink River may indicate the severe effects of poor habitat and flooding, or of acidic conditions that existed at this site during both sampling periods. Data from Schoharie Creek (see Evidence of Historical Trends), a higher ANC stream than the Neversink River, suggest that acidic conditions were as severe, or more severe, in 1951 than they were in 1981. Comparisons of fish data from these time periods are therefore problematic. The lack of difference between fish communities in the 1950s and in 1981 should not be over-interpreted, given the lack of precise information on streamwater chemistry for the earlier sampling period.

Conclusions

1. High rates of acidic deposition in the Catskill region result from concentrations of acid anions and H$^+$ that are comparable to other regions of the northeastern United States, and volumes that are greater than other regions. Sulfate (605 eq ha^{-1} yr^{-1}), NO$_3^-$ (404 eq ha^{-1} yr^{-1}), and H$^+$ (663 eq ha^{-1} yr^{-1}) wet deposition rates are higher than in any other Regional Case Studies region.

2. Streamwater chemistry in the Catskill region is strongly affected by stream discharge. A nonrandom sample of 51 streams collected during high-flow and baseflow periods indicates that many streams (16%) are acidic (ANC ≤ 0) during high-flow events. A few (8%) are acidic at baseflow. Base cation concentrations vary with stream discharge in a manner analogous to ANC. Sulfate concentrations are relatively unaffected by discharge, whereas NO$_3^-$ increases from a median of 14 µeq L^{-1} at baseflow to 42 µeq L^{-1} during high-flow events.

3. Spatial variability in streamwater ANC is associated with variability in base cations, rather than variability in acid anion concentrations. Spatial variability in base cation concentrations can be explained by patterns of glacial movement during the last ice age. Till deposition varied with local topography and location, and may have led to spatial variability in the depth, permeability, and carbonate mineral content of surficial materials, which are hypothesized to be controlling factors in streamwater C_B and ANC.

4. ANC values in all Catskill streams at all seasons of the year are lower than expected, based on measured [Ca^{2+} + Mg^{2+}] values and assuming carbonate weathering. The ANC deficit is consistently in the 120 to 140 µeq L^{-1} range, and is closely approximated by streamwater SO$_4^{2-}$ concentrations. The spatial and seasonal uniformity observed in SO$_4^{2-}$ concentrations in the region strongly suggests that atmospheric deposition of SO$_4^{2-}$ is largely responsible for the observed discrepancy between ANC and [Ca^{2+} + Mg^{2+}].

5. Organic acid anions appear to have less potential for affecting ANC than either SO$_4^{2-}$ or

NO_3^- in Catskill streams. The median A_c concentration (12 μeq L^{-1}) represents approximately 8% of total acid anions.

6. Base cation production in stream watersheds is the major process modifying atmospheric deposition and controlling Catskill streamwater ANC. Sulfate is conservative, whereas nitrogen (both NH_4^+ and NO_3^-) is strongly retained.

7. Low or negative ANC values are episodic and associated with high-flow events such as snowmelt or major storms. ANC declines during high-flow events are associated with three processes: (1) dilution of base cations, (2) more or less consistent SO_4^{2-} concentrations (relative to base cations) that increase the SO_4^{2-}:[Ca^{2+} + Mg^{2+}] ratio, and (3) increased NO_3^- concentrations. ANC values drop below zero when the ion ratio (NO_3^- + SO_4^{2-}):[Ca^{2+} + Mg^{2+}] reaches a value of 1.0.

8. Analysis of historical streamwater data for approximately 20 sites in the Catskill region indicates that ANC values in many streams were declining prior to about 1950, while base cation concentrations were rising. After 1950, both ANC and [Ca^{2+} + Mg^{2+}] began to increase and were probably driven by changes in land use. Estimated SO_4^{2-} concentrations are consistent with trends in SO_2 emissions, and have declined approximately 35 μeq L^{-1} since the late 1960s. Nitrate concentrations show a rapidly increasing trend (+30 μeq L^{-1}) since 1965. Because annual peaks in NO_3^- concentration coincide with annual minima in ANC, the increasing trend in NO_3^- has a greater potential to lower springtime ANC than the increases in [Ca^{2+} + Mg^{2+}] and decreases in SO_4^{2-} have to raise springtime ANC.

9. The limited data available for Catskill stream biota show no direct evidence that fish communities have been adversely affected by acidic deposition. This conclusion is based on comparisons of fish survey data collected in the 1950s and in 1981. Historical data on streamwater chemistry, however, suggest that acidic conditions may have been as severe in 1950 as they were in 1981. The lack of difference between 1950s data and 1981 data for fish is therefore not unexpected.