

An Unexpected Nitrate Decline in New Hampshire Streams

Christine L. Goodale,^{1*} John D. Aber,¹ and Peter M. Vitousek²

¹Complex Systems Research Center, University of New Hampshire, Durham, New Hampshire 03824, USA; and ²Department of Biological Sciences, Stanford University, Stanford, California 94305, USA

ABSTRACT

Theories of forest nitrogen (N) cycling suggest that stream N losses should increase in response to chronic elevated N deposition and as forest nutrient requirements decline with age. The latter theory was supported initially by measurements of stream NO_3^- concentration in old-growth and successional stands on Mount Moosilauke, New Hampshire (Vitousek and Reiners 1975; *Bioscience* 25:376–381). We resampled 28 of these and related streams to evaluate their response to 23 years of forest aggradation and chronic N deposition. Between 1973–74 and 1996–97, mean NO_3^- concentration in quarterly samples from Mount Moosilauke decreased by 71% (25 $\mu\text{mol/L}$), Ca^{2+} decreased by 24% (8 $\mu\text{mol/L}$), and Mg^{2+} decreased by 22% (5 $\mu\text{mol/L}$). Nitrate concentrations decreased in every stream in every season, but spatial patterns among streams persisted: Streams draining old-growth stands

maintained higher NO_3^- concentrations than those draining successional stands. The cause of the NO_3^- decline is not evident. Nitrogen deposition has changed little, and although mechanisms such as insect defoliation and soil frost may contribute to the temporal patterns of nitrate loss, they do not appear to fully explain the NO_3^- decline across the region. Although the role of climate remains uncertain, interannual climate variation and its effects on biotic N retention may be responsible for the synchronous decrease in NO_3^- across all streams, overriding expected increases due to chronic N deposition and forest aging.

Key words: atmospheric deposition; biogeochemical theory; nitrate leaching; nitrogen saturation; nutrient retention; old-growth forests; succession.

INTRODUCTION

Forests in the eastern United States presently receive five to 10 times the amount of nitrogen (N) deposition as during preindustrial times (Holland and others 1999), and deposition rates have been elevated for at least 3 decades (Likens and Bormann 1995). Ecosystem theories suggest that both N deposition and forest succession should lead to increased stream NO_3^- loss over time. The N saturation hypothesis suggests that chronic elevated N deposition should eventually lead to increases in nitrification and NO_3^- loss to drainage waters (Aber

and others 1989, 1998; Stoddard 1994). Nitrate losses are also expected to increase as stands age. Vitousek and Reiners (1975) proposed that ecosystem retention of limiting nutrients should decrease from strong retention in rapidly aggrading stands to essentially no net retention in steady-state old-growth systems. They supported this hypothesis with stream data from Mount Moosilauke, New Hampshire, where they observed that streams draining old-growth stands had higher NO_3^- concentrations than streams draining young successional stands. In 1996–97, we resampled these and other streams on Mount Moosilauke and Mount Washington, New Hampshire, that Vitousek (1975, 1977) sampled throughout 1973–74. We tested whether NO_3^- losses had increased after 23 years of forest maturation and chronic N deposition, and whether spatial patterns of N loss persisted. In re-

Received 4 December 2001; accepted 30 May 2002.

*Corresponding author's current address: Woods Hole Research Center, P.O. Box 296, Woods Hole, Massachusetts 02543, USA; e-mail: cgoodale@whrc.org.

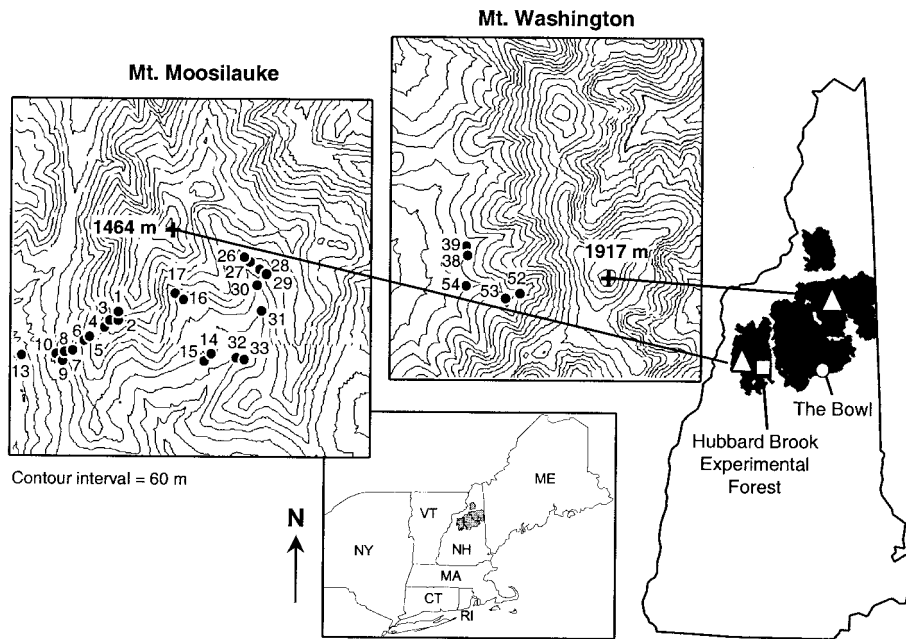


Figure 1. Stream sampling locations on Mount Moosilauke and Mount Washington in the White Mountain National Forest, New Hampshire. Stream numbers are from Vitousek (1975). Stream data from the Hubbard Brook Experimental Forest (Likens and Bormann 1995) and the Bowl Research Natural Area (Martin and others 2000) are included for comparison.

gions with very little inorganic N deposition, chronic losses of dissolved organic nitrogen (DON) or N trace gases may maintain strong ecosystem N limitation and low NO_3^- losses in old-growth forests; nonetheless, NO_3^- losses are expected to increase with time in regions with elevated deposition (Hedin and others 1995; Aber and others 1998; Vitousek and others 1998; Perakis and Hedin 2002).

In the northeastern United States, NO_3^- concentrations in precipitation have not changed significantly over the past several decades, although concentrations of SO_4^{2-} and base cations have declined (Driscoll and others 1989; Hedin and others 1994; Likens and others 1996, 1998; Stoddard and others 1998b). Monitoring networks established in the early 1980s indicate that surface water SO_4^{2-} concentrations have generally declined across the northeastern United States over the last 2 decades, but that acid-neutralizing capacities have not consistently rebounded due to compensating declines in base cations, or in some cases, to increases in stream NO_3^- concentrations (Murdoch and Stoddard 1992; Stoddard and others 1999). There are relatively few sites with stream measurements dating from the 1970s or earlier (but see Martin and others 2000), making the long-term record of stream chemistry (1964 to present) from the Hubbard Brook Experimental Forest (HBEF) particularly valuable (Likens and others 1996; Driscoll and others 2001). However, long-term NO_3^- records from individual sites may be confounded by successional effects or by unique disturbance events (for example, see Aber and others 2002). Resampling

the network of streams on Mount Moosilauke and Mount Washington sampled in 1973–74 provided opportunities to test established ecosystem theories of forest N cycling and to evaluate the regional forest and stream response to the combined effects of attenuated SO_4^{2-} deposition, decreased deposition of base cations, and chronic inputs of N between the mid-1970s and the mid-1990s.

METHODS

Vitousek (1975, 1977) sampled 57 streams throughout 1973–74. Sixteen streams drain high-elevation alpine tundra or fir krummholz and were not sampled in 1996–97. Of the 41 forested watersheds, sampling points for eight could not be located due to trail rerouting, and five watersheds had been harvested between 1974 and 1997 (US Forest Service records, Plymouth, New Hampshire). We sampled the remaining 28 streams; five of them drained the western slope of Mount Washington, and the rest were distributed across the southwestern and eastern slopes of Mount Moosilauke (Figure 1). All streams were sampled along hiking trails at essentially the same locations as in 1973–74.

STUDY SITES

Mount Moosilauke ($44^\circ 1' \text{N}$, $71^\circ 50' \text{W}$) lies on the southwestern edge of the White Mountain National Forest (WMNF), New Hampshire, and Mount

Washington (44°16'N, 71°18'W) rises from the northcentral portion of the WMNF (Figure 1). The bedrock of both mountains was previously classified as Littleton formation mica schist (Billings 1956). Mount Washington retains this designation, but the geology of Mount Moosilauke is now classified as quartz–feldspar–biotite metagraywacke (Hatch and Moench 1984). Ammonoosuc Volcanics occur off Mount Moosilauke's western slope (Hatch and Moench 1984) and contain large amounts of calcium-rich hornblende and plagioclase feldspar relative to the base-poor metamorphic formations (Bailey and Hornbeck 1992). Soils are largely Hap-lorthods, grading to Cryorthods and Cryofolists with elevation (Huntington and others 1990). The climate is cool and humid. At the nearby HBEF, annual precipitation averages 1400 mm and is distributed evenly throughout the year (Federer and others 1990). Monthly mean temperature ranges from -8.7°C in January to 18.8°C in July. Snowpacks accrue during winter, and monthly streamflow generally peaks with April snowmelt. Bulk deposition of inorganic N averages about $7\text{--}8\text{ kg N ha}^{-1}\text{ y}^{-1}$ in the southwestern WMNF (Likens and Bormann 1995; Campbell and others 2000), and deposition generally increases with elevation (Lovett and Kinsman 1990). Lovett and others (1982) measured an additional $35\text{ kg ha}^{-1}\text{ y}^{-1}$ of cloud deposition of inorganic N to high-elevation (1220 m) balsam fir (*Abies balsamea*) forests on Mount Moosilauke.

Vegetation varies with elevation from northern hardwoods below about 750 m to spruce–fir between about 750 and 1200 m, subalpine balsam fir between 1200 and 1400 m, and alpine tundra above 1400 m (Reiners and Lang 1979). Extensive logging occurred in the WMNF in the late 19th and early 20th centuries. On the Mount Washington watersheds, accessible red spruce (*Picea rubens*) stands were cut heavily around 1910, whereas the subalpine forests on the steep upper slopes were left uncut (USDA Forest Service records, Laconia, New Hampshire). On the southwestern flank of Mount Moosilauke, low-elevation forests were cut heavily prior to 1901; however, red spruce was cut selectively from the upper slopes, leaving minimally disturbed northern hardwoods and a patch of uncut spruce (Brown 1958; Cogbill 1989). Seven of the nine old-growth growth watersheds presented in Vitousek and Reiners (1975) are in this area (streams 1–7, Figure 1). On the eastern side of Mount Moosilauke, heavy cutting between 1896 and 1923 stripped timber from all but one ravine. Much of this ravine was salvage-logged after the 1938 hurricane (1943–47), but stands on the upper

rim were not cut (Brown 1958; Cogbill 1989). All five of the logged (streams 25–29) and two of the old-growth (streams 22, 23) watersheds from Vitousek and Reiners (1975) occur in this ravine.

SAMPLE COLLECTION AND ANALYSIS

Vitousek (1977) collected streamwater from Mount Moosilauke every 2–4 weeks from May 1973 to October 1974. During 1996–97, these streams were sampled seasonally: in fall (11 and 14 November 1996), winter (21 and 23 January 1997), snowmelt (8 and 10 April 1997), and during the growing season (21 July 1997). Seasonal sampling is commonly used for synoptic surveys of surface water chemistry (for example, see Stoddard and others 1998b; Lovett and others 2000). To compare chemistry between 1973–74 and 1996–97, we selected the four collections from 1973–74 nearest the sampling dates in 1996–97 (18–20 November 1973 and 21–25 January, 6–10 April, and 20–25 July 1974). Mean concentrations derived from 1973–74 quarterly samples did not differ from mean concentrations derived from the 17 collections comprising the water year of October 1973 to September 1974 (see Results). Streams 1, 2, and 4 froze to the ground in winter and could not be collected; these streams were not included in statistical analyses. The Mount Washington streams are difficult to access in winter and were collected every 2–4 weeks in late fall and from May through September in both 1973–74 (nine collections) and 1996–97 (seven collections). We tested for differences in chemistry between 1973–74 and 1996–97 with two-way analysis of variance (year, month, and year \times month), using quarterly measurements of 20 streams ($n = 20$) on Mount Moosilauke and monthly nonwinter measurements of five streams ($n = 5$) on Mount Washington. This approach allowed for comparison between years while controlling for the expected seasonal cycle of stream NO_3^- concentrations.

Vitousek (1977) details the analytical methods used in 1973–74, and differences are summarized here (Table 1). DON was not measured in 1973–74, although dissolved organic carbon (DOC) was measured once in autumn in 15 streams with a Beckman Model 915 total carbon analyzer after acidification and sparging. The 1973–74 method of most concern was the turbidimetric method used for the SO_4^{2-} analysis (Golterman 1969), which has a high detection limit ($10\text{ }\mu\text{mol/L}$ in Golterman 1969, Greenberg and others 1992; $15\text{ }\mu\text{mol/L}$ in Vitousek 1977) and can be affected by interference with dissolved organic matter. Although observed DOC concentrations were low ($25\text{--}142\text{ }\mu\text{mol/L}$) and the

Table 1. Analytical Methods and Limits of Detection (LOD) ($\mu\text{mol/L}$)

1973–74		1996–97		
Method	LOD ^a	Method	LOD	
NO_3^-	Nitrate reduction & ammonia-specific electrode ^b	N/A	Ion chromatography	0.4
NH_4^+	Ammonia-specific electrode ^b	1	Automated phenate method	1.0
Ca^{2+}	Atomic absorption ^c	0.3	Direct current plasma	0.7
Mg^{2+}	Atomic absorption ^c	0.1	Direct current plasma	0.2

^aAs reported in Vitousek (1977)

^bOrion Research (Anonymous 1972)

^cLanthanum oxide dissolved in 50% HCl added to prevent aluminum and silicate interference (Likens and others 1970)

N/A indicates not available

observed SO_4^{2-} concentrations (30–80 $\mu\text{mol/L}$) should have been within the method's range, we lacked confidence in the 1973–74 SO_4^{2-} values and therefore excluded them from this comparison. During early summer 1974, SO_4^{2-} values on Mount Moosilauke drifted up about 20 $\mu\text{mol/L}$ without a corresponding increase in base cation concentration or a decrease in pH, while SO_4^{2-} concentrations at watershed 6 (W6) at Hubbard Brook remained nearly constant at 60 $\mu\text{mol/L}$ throughout most of 1974. Buso and others (2000) contend that the turbidimetric method is not sufficiently sensitive for SO_4^{2-} concentrations below about 50 $\mu\text{mol/L}$.

The 1996–97 samples were collected in 250-ml high-density polyethylene (HDPE) bottles that had been triple-rinsed with streamwater prior to collection. The samples were then refrigerated until processing the following day. Samples were suction-filtered through combusted (1 h at 425°C), well-rinsed Whatman GF/F glass fiber filters (pore size, 0.7 μm) and frozen in 30-ml HDPE (DOC and DON) or polyethylene (inorganic ions) vials until analysis. After thawing, anion samples were refiltered through 0.2- μm pore size Acrodisk (Gelman Sciences) prior to analysis with a Waters ion chromatograph and a Dionex AS4A column with micromembrane chemical suppression. Ammonium was measured with flow injection analysis using the automated phenate method on a Lachat QuikChem AE. Base cations were measured with direct current plasma emission spectroscopy on a Fisons Spectra-Span III. DOC samples were acidified and sparged prior to analysis. DOC and total dissolved nitrogen (TDN) were measured in separate analyses using high-temperature (680°C) catalytic (platinum) oxidation on a Shimadzu TOC 5000. TDN was measured with an Antek 720C N chemiluminescent detector (Merriam and others 1996), and DON was calculated by difference: $\text{DON} = \text{TDN} - (\text{NO}_3^- - \text{N} + \text{NH}_4^+ - \text{N})$.

COMPARISON WITH HUBBARD BROOK

Observations of stream chemistry over 2 isolated years alone cannot substitute for long-term data; however, they can indicate relative changes across different systems, and comparison with the continuous long-term record at Hubbard Brook allows some general inferences about long-term changes across the region. The HBEF is a long-term ecological research (LTER) site located 12 km east of the summit of Mount Moosilauke (Figure 1). The HBEF maintains long-term records of stream discharge and chemistry (described in Federer and others 1990; Likens and Bormann 1995; Buso and others 2000; and elsewhere) that we use as a reference for comparison between 1973–74 and 1996–97. Daily stream flow through December 1997 and monthly flow-weighted stream chemistry through December 1995 were obtained from the LTER web site (<http://www.hbrook.sr.unh.edu>). We compared changes in stream chemistry between 1973–74 and 1996–97 on Mount Moosilauke and Mount Washington relative to those observed for the HBEF reference watershed (W6) over a similar time period and used the HBEF record to place these 2 years in the context of long-term trends. The long-term record of stream chemistry at W6 has been published through 1992 in Likens and others (1996), Likens and Bormann (1995), and related publications, and through 1994 in Driscoll and others (2001). Hornbeck and others (1997) report W6 stream chemistry for October 1991–September 1994, and Campbell and others (2000) provide N chemistry for June 1995–May 1997.

Stream discharge sometimes affects ion concentrations through dilution or flushing of solutes during conditions of high flow (for example, see Johnson and others 1969; Arheimer and others 1996). Because the streams on Mount Moosilauke and Mount Washington were not gauged, we used daily

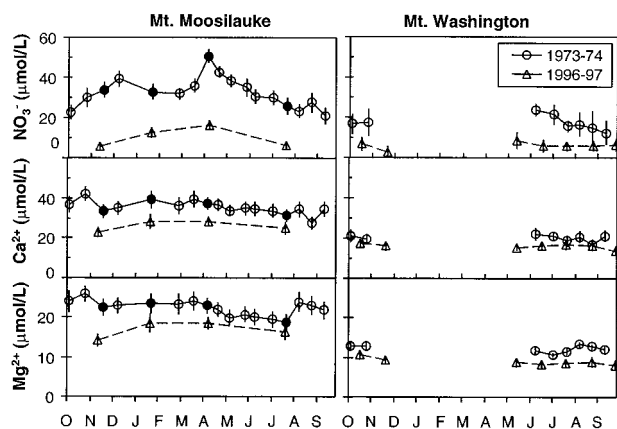


Figure 2. Mean (± 1 SE) NO_3^- , Ca^{2+} , and Mg^{2+} concentrations from Mount Moosilauke (20 streams) and Mount Washington (five streams) for sampling dates in 1973–74 and 1996–97. Filled circles indicate the 1973–74 samples included in statistical analyses of quarterly stream chemistry.

streamflow measurements from W6 on sample collection dates as an index of temporal variation of White Mountain streamflow. Analysis of covariance was used to determine whether relationships between ion concentration and W6 discharge differed between 1973–74 and 1996–97. We present mean results by mountain to summarize the results for multiple streams (20 for Mount Moosilauke, five for Mount Washington) that all display similar patterns relative to W6 streamflow.

RESULTS

Nitrate concentrations were lower at all streams on all sample dates in 1996–97 relative to 1973–74 (Figures 2–6). Decreases occurred in all four seasons. Two-way analysis of variance indicated that NO_3^- , Ca^{2+} , and Mg^{2+} concentrations all differed by year (all $P < 0.01$) and that NO_3^- differed by season (Mount Moosilauke) or month (Mount Washington) ($P < 0.01$), but year \times month interactions were not significant. On Mount Moosilauke, mean NO_3^- concentrations estimated from quarterly sampling decreased by 71% (25 $\mu\text{mol/L}$), Ca^{2+} decreased by 24% (8 $\mu\text{mol/L}$), and Mg^{2+} decreased by 22% (5 $\mu\text{mol/L}$) between 1973–74 and 1996–97 (Figure 3a). On Mount Washington, similar percent decreases occurred in nonwinter mean NO_3^- , Ca^{2+} , and Mg^{2+} concentrations as on Mount Moosilauke, although all ion concentrations were lower (Figure 3b). Higher rainfall and limited evapotranspiration in high-elevation tundra may dilute the Mount Washington streams.

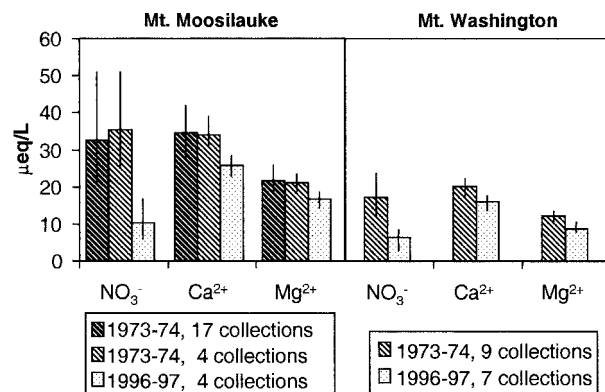


Figure 3. Mean NO_3^- , Ca^{2+} , and Mg^{2+} concentrations of quarterly samples from Mount Moosilauke (20 streams) and nonwinter samples from Mount Washington (five streams) in 1973–74 and 1996–97. Bars represent seasonal maxima and minima averaged across all streams.

Decreases in ion concentrations between years did not appear to be caused by differences in streamflow. All 1996–97 concentrations were lower than all 1973–74 concentrations, regardless of discharge measured at HBEF W6 (Figure 4). Analysis of covariance indicated that mean ion concentrations did not vary significantly with log-transformed W6 discharge on either Mount Moosilauke ($P = 0.12$ for NO_3^- , 0.43 for Ca^{2+} , and 0.90 for Mg^{2+}) or Mount Washington ($P = 0.55$ for NO_3^- , 0.84 for Ca^{2+} , and 0.42 for Mg^{2+}); nor were there significant year \times discharge interactions ($P = 0.10$ for Ca^{2+} on Mount Washington; $P = 0.45$ – 0.97 for the other analyses). After considering streamflow, NO_3^- , Ca^{2+} , and Mg^{2+} concentrations differed by year on both mountains ($P < 0.01$ for all analyses).

Qualitative trends among streams persisted across the years, in that streams with high concentrations in 1973–74 also had the highest concentrations in 1996–97 (Figure 5). Nitrate concentrations decreased across all Mount Moosilauke streams, regardless of forest type or successional stage. During both 1973–74 and 1996–97, NO_3^- concentrations in streams draining old-growth stands exceeded those of successional stands logged in 1943–47 (Figure 6). The NO_3^- decline was not due to compensating increases in other forms of dissolved N loss (NH_4^+ or DON), since TDN concentrations in 1996–97 were lower than NO_3^- concentrations alone in 1973–74 (Figure 6b). Ammonium concentrations were rarely above 1 $\mu\text{mol/L}$ in either 1973–74 or 1996–97 (more detailed 1973–74 NH_4^+ data were not available). DON was not measured in 1973–74, but DOC concentrations were low in autumn sam-

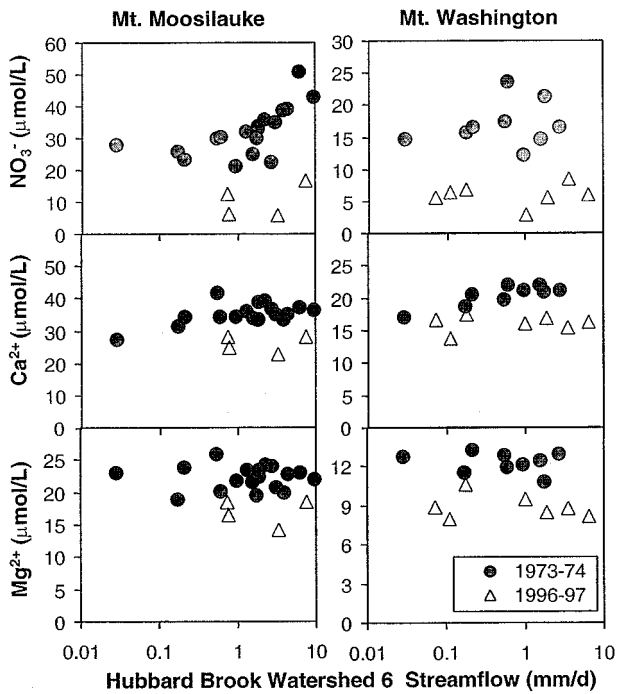


Figure 4. Comparison of concentrations measured on Mount Moosilauke and Mount Washington with discharge measured at Hubbard Brook watershed 6 for both 1973–74 (filled circles) and 1996–97 (open triangles). Each point represents the mean concentration of 20 streams (Mount Moosilauke) or five streams (Mount Washington).

ples of 15 streams (25–142 $\mu\text{mol/L}$). Mean DOC concentrations in 1996–97 ranged from 85 to 322 $\mu\text{mol/L}$ across all 25 streams and averaged 157 $\mu\text{mol/L}$; because these values represent different streams and different collection dates from the 1973–74 measurements, DOC concentrations should not be compared across years. DON concentrations ranged from 3 to 15 $\mu\text{mol/L}$ in 1996–97 and averaged 7 $\mu\text{mol/L}$. DON concentrations varied little between old-growth and logged watersheds; but because of differences in NO_3^- loss, DON constituted 60% of TDN from logged stands but only 30% from old-growth stands (Figure 6b).

Concentrations of all base cations were higher on the western side of Mount Moosilauke than on the eastern side (Figure 5), possibly due to differences in till chemistry across the mountain. Glacial movement from northwest to southeast transported till such that locally derived soils often resemble the bedrock mineralogy up to 32 km “upglacier” (Bailey and Hornbeck 1992; Hornbeck and others 1997). This glacial transport 14,000 years ago may have enriched soils on the western flank of Mount Moosilauke with base cation-rich minerals.

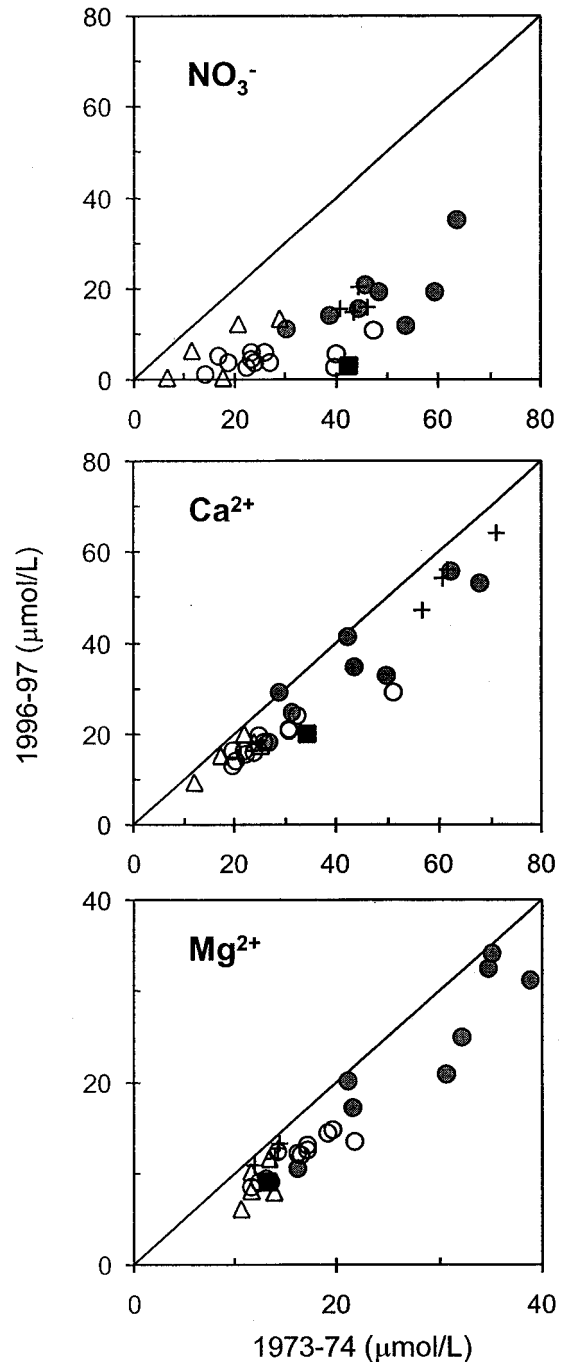


Figure 5. Stream-by-stream comparison of mean ion concentrations in 1996–97 and 1973–74 for nonwinter samples of streams on Mount Washington (open triangles) and quarterly samples of streams on the southwest (filled circles) and southeast (open circles) sides of Mount Moosilauke. Data for 1973–74 and 1993–94 from Hubbard Brook watershed 6 (filled squares) (Likens and Bormann 1995; Hornbeck and others 1997) and for 1973–74 and 1994–97 from the Bowl Research Natural Area (+ symbols) (Martin and others 2000) are included for comparison. Distances below the 1:1 lines indicate decreases from 1973–74 values.

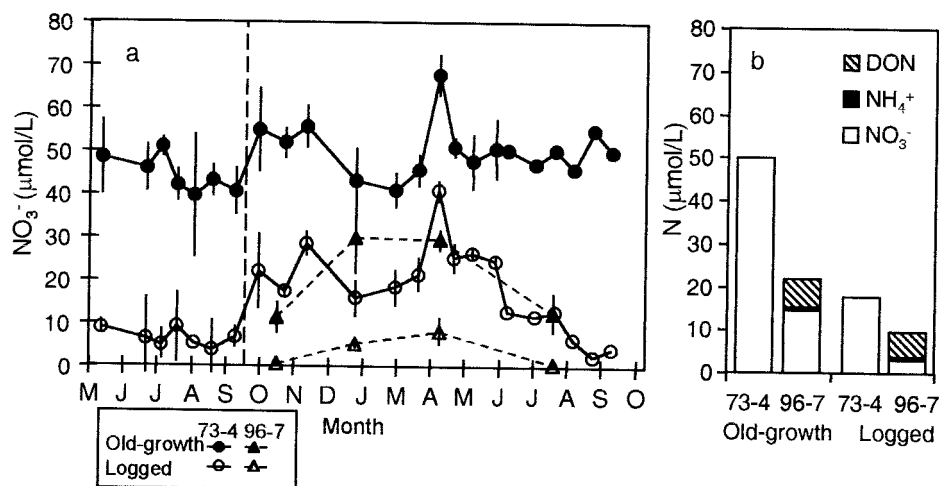


Figure 6. (a) Stream nitrate concentrations in 1973–74 (—) and 1996–97 (---) for old-growth (solid symbols) and successional (open symbols) forests on Mount Moosilauke, New Hampshire. Each point represents the mean (\pm SE) of four streams draining successional forests or seven streams draining old-growth forests. (b) Mean annual NO_3^- , NH_4^+ , and DON concentrations for the seven old-growth and four successional watersheds. DON and NH_4^+ data were not available for 1973–74.

DISCUSSION

The decrease in NO_3^- concentration appears to contradict current theories of both N saturation and successional changes in N retention. Yet before attributing changes in stream chemistry to biogeochemical causes, we address possible effects introduced by differences in analytical methods and streamflow. We then discuss regional trends in stream chemistry and the biogeochemical mechanisms proposed to explain temporal patterns of NO_3^- loss, including changes in atmospheric chemistry, insect defoliation, soil frost, and climate variation.

Real Change or Sampling Artifact?

Some of the analytical methods used in 1996–97 have greater precision and lower detection limits than those used for these streams in 1973–74 (Table 1). However, methodological differences do not easily account for the large decline in stream NO_3^- . In 1973–74, NO_3^- concentrations were measured by reduction to NH_4^+ , conversion to NH_3 with NaOH, and use of an ammonia electrode (Orion Model 404; Anonymous 1972). Nitrate standards were included to confirm complete conversion of NO_3^- to NH_3 . The ammonia electrode can overestimate low NO_3^- concentrations by 3–6 $\mu\text{mol/L}$ (Greenberg and others 1992), but this potential bias does not explain the large (25 $\mu\text{mol/L}$) decrease in NO_3^- concentration between 1973–74 and 1996–97.

Differences in streamflow between 1973–74 and 1996–97 do not appear to explain the observed differences in stream chemistry. However, the Mount Moosilauke and Mount Washington streams were not gauged, so our assessment of streamflow effects depends on the validity of using

measurements from HBEF W6 as an index of temporal patterns of streamflow in the White Mountains. Similar results were obtained by repeating this analysis using streamflow measured by the US Geological Survey (USGS) for the Ammonoosuc River at a point approximately 25 km downstream from the site where the Mount Washington samples were collected (results not shown).

By coincidence, streamflows during 1973–74 (1159 mm) and 1996–97 (1046 mm) are among the highest in the HBEF record, both exceeding the long-term average (896 mm) (Federer and others 1990). Previous work at Hubbard Brook demonstrated that stream Ca^{2+} and Mg^{2+} concentrations varied little with discharge, with slightly increased Ca^{2+} and decreased Mg^{2+} concentrations observed with discharge in some experimental watersheds (Likens and others 1967; Johnson and others 1969). Long-term sampling suggests lower Ca^{2+} concentrations per unit discharge at W6 during the 1980s and 1990s than during the 1960s and 1970s (Likens and others 1998; Buso and others 2000), consistent with our far less frequent observations for 1973–74 and 1996–97 at Mount Moosilauke and Mount Washington (Figure 4). Nitrate concentrations at Hubbard Brook can increase with discharge during the dormant season (Johnson and others 1969), although correlations between NO_3^- concentration and discharge at other temperate forest watersheds are often weak and can vary in sign (for example, see Arheimer and others 1996; McHale and others 2000). Simple consideration of discharge (Figure 4) suggests that differences in stream NO_3^- between 1973–74 and 1996–97 were considerably larger than what might be explained by differences in streamflow, in that all 1996–97

NO_3^- concentrations were below all 1973–74 measurements, regardless of flow.

More complex analyses of relationships between NO_3^- and discharge at other sites suggest that a hysteresis can occur due to flushing of upper soil horizons, with NO_3^- increasing during the rising limb of the hydrograph, followed by a decrease during the receding limb (Creed and Band 1998). The effects of antecedent conditions on NO_3^- concentrations are difficult to estimate for the Mount Moosilauke and Mount Washington streams, and we present only a qualitative assessment. November collections in both 1973 and 1996 occurred 2–4 days after rainstorms, as did the July 1997 collection, such that these samples could have had lower NO_3^- concentrations than expected due to recent flushing. Winter snowpack maintained steady, low flows during the period prior to January sampling in both years, and April sampling in both years occurred during the middle of the rise of flow at snowmelt. Although it remains plausible that antecedent flow conditions may have affected some of the 1996–97 collections, it is unlikely that they affected all four collections to similar degrees. Flow conditions may have had some effect on observed concentrations, but it does not appear that differences in streamflow between years introduced enough bias to have caused the consistent decreases in NO_3^- , Ca^{2+} , and Mg^{2+} concentration.

Regional Comparison of Long-term Trends

Across the northeastern United States, SO_4^{2-} concentrations of surface waters have generally declined over the last 2 decades in response to reduced SO_4^{2-} deposition (Stoddard and others 1998a, 1998b, 1999; Driscoll and others 2001). Surface water base cation concentrations have also declined over the last 2 decades, particularly during the 1990s (Stoddard and others 1999). Surface water NO_3^- concentrations increased throughout the 1980s in the Adirondack and Catskill mountains, of New York, but then declined through the 1990s, while New England surface waters showed few NO_3^- trends (Stoddard 1994; Stoddard and others 1999).

Across the White Mountain region, stream NO_3^- , Ca^{2+} , and Mg^{2+} concentrations appear to have declined since the mid-1970s. In 1994–97, Martin and others (2000) resampled four streams in the Bowl Research Natural Area, an old-growth watershed about 25 km east of the HBEF, and found similar changes in stream chemistry relative to 1973–74 (Martin 1979) as we observed at Mount Moosilauke and Mount Washington (Figure 5). All of these results are consistent with changes between

1973–74 and 1993–94 observed at HBEF W6 (Figure 5). The long-term record at Hubbard Brook (Likens and Bormann 1995; Driscoll and others 2001) confirms that stream chemistry during 1973–74 and 1996–97 was typical for the mid-1970s and the mid-1990s and was consistent with long-term patterns. At HBEF W6, SO_4^{2-} and base cation concentrations declined gradually and relatively consistently since about 1970 (Driscoll and others 1989, 2001; Likens and Bormann 1995; Likens and others 1996), although most of the decline in Ca^{2+} occurred during the first half of this period (Likens and others 1998). Nitrate displayed a much more erratic pattern with high concentrations during 1969–76, low concentrations in the mid-1990s (Hornbeck and others 1997; Campbell and others 2000), and variable concentrations in between (Likens and Bormann 1995; Likens and others 1996). Nitrate loss peaked at $6.9 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in 1973–74 (Likens and Bormann 1995) and dropped to 0.3 and $0.4 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in 1993–94 and 1996–97, respectively (Hornbeck and others 1997; Campbell and others 2000).

Suggested causes for declining base cation concentrations in surface water include reduced leaching by acid anions (Galloway and others 1983; Reuss and Johnson 1986; Likens and others 1996, 1998), reduced deposition of base cations (Driscoll and others 1989; Likens and others 1996, 1998), and depletion of exchangeable base cations in soil due to long-term exposure to acid deposition (Likens and others 1996; Lawrence and others 1999). We cannot discern the relative importance of these three mechanisms in affecting the base cation concentrations in the streams measured here.

Why a Nitrate Decline?

We expected that stream NO_3^- would increase in response to 23 years of chronic N deposition and forest maturation; instead, it decreased dramatically. Seasonal patterns may have shifted as well. In 1973–74, the Mount Moosilauke old-growth watersheds displayed little seasonal variation in NO_3^- concentration, but in 1996–97 the same streams appear to have dormant-season maxima and growing-season minima (Figure 6), although further confirmation of this trend is required because there were few collections during 1996–97. This change in seasonal pattern would correspond with a shift in N saturation status from the high, aseasonal NO_3^- leaching of late stage 2 to a late stage 1 pattern of seasonal trends and slightly elevated base flow (Stoddard 1994). Several mechanisms have been proposed to account for the long-term change in stream NO_3^- at the HBEF, including changes in at-

atmospheric chemistry, insect outbreaks, soil frost, and interannual climate fluctuations. The decline in NO_3^- concentrations across all resampled streams suggests a regional controller, such as climate variation or changes in atmospheric chemistry.

Changes in N deposition do not explain the sharp declines in stream NO_3^- across the region. There are no significant long-term trends (1965–94) in either the concentration or flux of inorganic N in bulk deposition at the HBEF (Likens and Bormann 1995; Driscoll and others 2001), nor have trends in wet N deposition been observed across the northeastern United States in the last 2 decades (Stoddard and others 1998b). Bulk deposition of inorganic N at W6 was $8.2 \text{ kg ha}^{-1} \text{ y}^{-1}$ in 1973–74 (Likens and Bormann 1995) and $8.5 \text{ kg ha}^{-1} \text{ y}^{-1}$ in 1996–97 (Campbell and others 2000).

Between 1973–74 and 1996–97, atmospheric carbon dioxide (CO_2) concentration increased by 10% from 330 to 364 ppm (Keeling and Whorf 2000). Vitousek and others (2000) suggest that this change plausibly could have stimulated vegetation growth and N uptake, reducing stream NO_3^- loss. Model simulations suggest that observed changes in atmospheric CO_2 might lead to reduced stream NO_3^- losses at HBEF W6, but not by enough to explain the very low NO_3^- losses in the 1990s (Aber and others 2002). Furthermore, there is little evidence for stimulation of tree growth at the HBEF. By contrast, Likens and others (1996) report that tree biomass accumulation has decreased in recent decades. Whether this decrease in accumulation is due to natural succession or to external factors remains unclear, but the decline in stream NO_3^- at W6 does not appear to be due to increased N sequestration in tree biomass. Furthermore we observed similar decreases in stream NO_3^- losses from both successional and old-growth watersheds (Figure 6b).

Insect infestation and defoliation can raise stream NO_3^- concentrations (Swank and others 1981; Eshleman and others 1998). Hubbard Brook experienced heavy insect defoliation in 1969–71 (Bormann and Likens 1979), and Eshleman and others (1998) suggest that the high NO_3^- concentrations at W6 in the early 1970s were due to this event. Although defoliation may have contributed to the particularly large change in NO_3^- concentrations at W6 (Figure 5), it is unlikely that this mechanism could explain the NO_3^- decline across both Mount Moosilauke and Mount Washington in watersheds with forest cover ranging from northern hardwood to spruce–fir and subalpine forest.

Soil frost can trigger losses of NO_3^- to streams by disrupting soil structure and causing mortality of

microbes and fine roots (Groffman and others 2001). Mitchell and others (1996) observed synchronous patterns of peak NO_3^- losses in streams across the northeastern United States following unusually cold temperatures in the winter of 1989–90, and Fitzhugh and others (2001) experimentally induced NO_3^- loss at the HBEF by removing snow cover and allowing the underlying soil to freeze. Likens and Bormann (1995) noted that high NO_3^- losses at Hubbard Brook in early 1970 and 1974 coincided with widespread soil frost, and Fahey and Lang (1975) observed frozen soil across Mount Moosilauke during the late fall and winter of 1973–74. Yet even though soil frost may partially explain the high NO_3^- observed in winter 1973–74 or snowmelt in 1974, it is difficult to explain the relatively high NO_3^- in Moosilauke streams prior to the freezing event, in the summer and fall of 1973 (Figure 6a). Soil frost may be one—but not the only—weather-related factor contributing to interannual NO_3^- fluctuations.

Interannual climate variation remains as a plausible mechanism for explaining the temporal pattern of nitrate loss, although the specific climate factor driving these nitrate losses are uncertain. Plant uptake and N mineralization both respond to variation in temperature and moisture conditions, so that subtle differences in the rate or timing of biotic responses may lead to either NO_3^- leaching or N retention. At the Harvard Forest in Massachusetts, plant uptake of N in unfertilized hardwoods can vary from year to year by more than $20 \text{ kg ha}^{-1} \text{ y}^{-1}$, and net N mineralization can vary by more than $30 \text{ kg ha}^{-1} \text{ y}^{-1}$ (Magill and others 2000). This variability in plant N uptake and net soil N release exceeds the variation in stream N loss at HBEF (less than $7 \text{ kg ha}^{-1} \text{ y}^{-1}$, Likens and Bormann 1995). Model simulations (PnET-CN) suggest that including climate-driven variation in growth and mineralization allows the model to reproduce much of the observed variability in NO_3^- leaching at W6 and the Bowl, although the extremely low values of the mid-1990s remain unexplained (Aber and Driscoll 1997; Aber and others 2002). Modeled NO_3^- losses did not correlate with any particular climate variable, such as mean temperature (for example, see Murdoch and others 1998), but resulted from the interplay of many processes. If interannual climate variation does indeed explain the observed change in NO_3^- leaching since 1973–74, then future climate variation could cause NO_3^- losses to match or exceed those observed in the 1970s.

Climate-induced variability in biotic N retention may have masked any recent signal of increased NO_3^- loss from chronic N deposition or forest mat-

uration, but these factors are likely to have important impacts on stream NO_3^- at longer time scales. In regions with elevated N inputs, forest successional status does influence spatial patterns of NO_3^- leaching when compared within the same year (Silsbee and Larson 1982; Flum and Nodvin 1995; Goodale and others 2000) (Figure 6). In a literature review of NO_3^- losses from nine old-growth stands, Hedin and others (1995) demonstrated that NO_3^- losses were far higher in regions receiving chronic anthropogenic N inputs than in unpolluted stands in Chile and the western United States. Nitrate values for two of the nine old-growth stands in this review were from Mount Moosilauke (Vitousek 1977) and the Bowl (Martin 1979) from the early 1970s, yet the basic conclusion would not be altered if the lower, 1990s values (see Figure 5 and Martin and others 2000) were included instead. Sampling of additional old-growth watersheds by Perakis and Hedin (2002) confirms this result. Despite the large decline observed in the White Mountains, NO_3^- concentrations are still more than an order of magnitude greater than those observed in Chile and other unpolluted parts of South America.

ACKNOWLEDGMENTS

The NASA Earth System Science Fellowship Program, EPA grant no. 825865, and a Cooperative Agreement from the USDA Forest Service, Northeastern Station to W. H. McDowell provided funding for this research. Jennifer Pontius and Jeffrey Merriam assisted with sample analyses; and Ruth Bristol, Gary Filgate, Jen Jenkins, Alison Magill, Steve Newman, and Laura Stone assisted with sample collection. Beth Boyer and Neal Scott provided useful advice on streamflow considerations; and Bill McDowell, Jim Hornbeck, Andy Friedland, Tom Lee, Gene Likens, Scott Ollinger, Linda Pardo, Marie-Louise Smith, and John Stoddard provided helpful comments on previous versions of this paper. We are grateful for the long-term record of hydrology and stream chemistry maintained by Jim Hornbeck, Gene Likens, and many others at the Hubbard Brook Experimental Forest. The HBEF is operated and maintained by the Northeastern Research Station, USDA, Newtown Square, Pennsylvania.

REFERENCES

- Aber J, McDowell W, Nadelhoffer K, Magill A, Berntson G, Kamakea M, McNulty S, Currie W, Rustad L, Fernandez I. 1998. Nitrogen saturation in temperate forest ecosystems. *BioScience* 48:921–34.
- Aber JD, Driscoll CT. 1997. Effects of land use, climate variation and N deposition on N cycling and C storage in northern hardwood forests. *Global Biogeochem Cycles* 11:639–48.
- Aber JD, Nadelhoffer KJ, Steudler P, Melillo JM. 1989. Nitrogen saturation in northern forest ecosystems: excess nitrogen from fossil fuel combustion may stress the biosphere. *BioScience* 39:378–86.
- Aber JD, Ollinger SV, Driscoll CT, Likens GE, Holmes RT, Freuder RJ, Goodale CL. 2002. Inorganic N losses from forested ecosystems in response to physical, chemical, biotic and climatic perturbations. *Ecosystems* 5:648–658.
- Anonymous. 1972. Instructional manual, ammonia electrode model 95–10. Cambridge (MA): Orion Research. 24 p.
- Arheimer B, Andersson L, Lepisto A. 1996. Variation of nitrogen concentration in forest streams—influences of flow, seasonality and catchment characteristics. *J Hydrol* 179:281–304.
- Bailey SW, Hornbeck JW. 1992. Lithologic composition and rock weathering potential of forested, glacial-till soils. Research Paper NE-662. Radnor (PA): USDA Forest Service, Northeastern Forest Experiment Station.
- Billings MP. 1956. The geology of New Hampshire. Part II. Bedrock geology. Concord (NH): New Hampshire Department of Resources and Econ Development.
- Bormann FH, Likens GE. 1979. Pattern and process in a forested ecosystem. New York: Springer-Verlag.
- Brown JW. 1958. Forest history of Mount Moosilauke. Part II. Big logging days and their aftermath (1890–1940). *Appalachia* 24:221–33.
- Buso DC, Likens GE, Eaton JS. 2000. Chemistry of precipitation, streamwater, and lakewater from the Hubbard Brook Ecosystem Study: a record of sampling protocols and analytical procedures. General Technical Report NE-275. Newtown Square (PA): USDA Forest Service, Northeastern Research Station.
- Campbell JL, Hornbeck JW, McDowell WH, Buso DC, Shanley JB, Likens GE. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. *Biogeochemistry* 49:123–42.
- Cogbill CV. 1989. Assessment of disturbance in the forest history of Mt. Moosilauke, New Hampshire. Miscellaneous Technical Report. Broomall (PA): USDA Forest Service, Forest Response Program, Northeast Forest Experiment Station.
- Creed IF, Band LE. 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resour Res* 34(11):3105–20.
- Driscoll CT, Lawrence GB, Bulger AJ, Butler TJ, Cronan CS, Eagar C, Lambert KF, Likens GE, Stoddard JL, Weathers KC. 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* 51:180–98.
- Driscoll CT, Likens GE, Hedin LO, Eaton JS, Bormann FH. 1989. Changes in the chemistry of surface waters: 25 year results at the Hubbard Brook Experimental Forest, NH. *Environ Sci Technol* 23:137–43.
- Eshleman KN, Morgan RP II, Webb JR, Deviney FA, Galloway JN. 1998. Temporal patterns of nitrogen leakage from mid-Appalachian forested watersheds: role of insect defoliation. *Water Resour Res* 34:2005–116.
- Fahey TJ, Lang GE. 1975. Concrete frost along an elevational gradient in New Hampshire. *Can J For Res* 5:700–5.
- Federer CA, Flynn LD, Martin CW, Hornbeck JW, Pierce RS. 1990. Thirty years of hydrometeorologic data at the Hubbard

- Brook Experimental Forest. Radnor (PA): USDA Forest Service, Northeastern Forest Experiment Station.
- Fitzhugh RD, Driscoll CT, Groffman PM, Tierney GL, Fahey TJ, Hardy JP. 2001. Effects of soil freezing disturbance on soil solution nitrogen, phosphorus, and carbon chemistry in a northern hardwood ecosystem. *Biogeochemistry* 56:215–38.
- Flum T, Nodvin SC. 1995. Factors affecting streamwater chemistry in the Great Smoky Mountains, USA. *Water Air Soil Pollut* 85:1707–12.
- Galloway JN, Norton SA, Church MR. 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model. *Environ Sci Technol* 17:541A–5A.
- Golterman HL. 1969. *Methods for analysis of fresh waters*. London: Blackwell.
- Goodale CL, Aber JD, McDowell WH. 2000. The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. *Ecosystems* 3:433–50.
- Greenberg AE, Clesceri LS, Eaton AD. 1992. *Standard methods for the examination of water and wastewater*. Washington (DC): American Public Health Association.
- Groffman PM, Driscoll CT, Fahey TJ, Hardy JP, Fitzhugh RD, Tierney GL. 2001. Colder soils in a warmer world: a snow manipulation study in a northern hardwood forest ecosystem. *Biogeochemistry* 56:135–50.
- Hatch NL Jr, Moench RH. 1984. Bedrock geologic map of the wildernesses and roadless areas of the White Mountain National Forest, Coos, Carroll, and Grafton Counties, New Hampshire. *Miscellaneous Field Studies. Map MF-1594-A*. Scale 1:125,000. Reston (VA): US Geologic Survey.
- Hedin LO, Armesto JJ, Johnson AH. 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. *Ecology* 76:493–509.
- Hedin LO, Granat L, Likens GE, Bulshand TA, Galloway JN, Butler TJ, Rodhe H. 1994. Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* 367:351–54.
- Holland EA, Dentener FJ, Braswell BH, Sulzman JM. 1999. Contemporary and pre-industrial global reactive nitrogen budgets. *Biogeochemistry* 46:7–43.
- Hornbeck JW, Bailey SW, Buso DC, Shanley JB. 1997. Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications. *For Ecol Manage* 93:73–89.
- Huntington TG, Peart DR, Hornig J, Ryan DF, Russo-Savege S. 1990. Relationships between soil chemistry, foliar chemistry, and condition of red spruce at Mount Moosilauke, New Hampshire. *Can J For Res* 20:1219–27.
- Johnson NM, Likens GE, Bormann FH, Fisher DW, Pierce RS. 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resour Res* 5:1353–63.
- Keeling CD, Whorf TP. 2000. Atmospheric CO₂ records from sites in the SIO air sampling network. In: *Trends: a compendium of data on global change*. Oak Ridge (TN): Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge National Laboratory, US Department of Energy.
- Lawrence GB, David MB, Lovett GM, Murdoch PS, Burns DA, Stoddard JL, Baldigo BP, Porter JH, Thompson AW. 1999. Soil calcium status and the response of stream chemistry to changing acidic deposition rates. *Ecol Appl* 9:1059–72.
- Likens GE, Bormann FH. 1995. *Biogeochemistry of a forested ecosystem*. New York: Springer-Verlag.
- Likens GE, Bormann FH, Johnson NM, Fisher DW, Pierce RS. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecol Monogr* 40:23–47.
- Likens GE, Bormann FH, Johnson NM, Pierce RS. 1967. The calcium, magnesium, potassium and sodium budgets for a small forested ecosystem. *Ecology* 48:772–785.
- Likens GE, Driscoll CT, Buso DC. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272:244–6.
- Likens GE, Driscoll CT, Buso DC, Siccama TG, Johnson CE, Lovett GM, Fahey TJ, Reiners WA, Ryan DF, Martin CW, and others. 1998. The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry* 41:89–173.
- Lovett GM, Kinsman JD. 1990. Atmospheric pollutant deposition to high-elevation ecosystems. *Atmos Environ* 24A:2767–86.
- Lovett GM, Reiners WA, Olson RK. 1982. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical inputs. *Science* 218:1303–4.
- Lovett GM, Weathers KC, Sobczak WV. 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. *Ecol Appl* 10:73–84.
- Magill AH, Aber JD, Berntson GM, McDowell WH, Nadelhoffer KJ, Melillo JM, Steudler P. 2000. Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems* 3:238–53.
- McHale MR, Mitchell MJ, McDonnell JJ, Cirimo CP. 2000. Nitrogen solutes in an Adirondack forested watershed: importance of dissolved organic nitrogen. *Biogeochemistry* 48:165–84.
- Martin CW. 1979. Precipitation and streamwater chemistry in an undisturbed forested watershed in New Hampshire. *Ecology* 60:36–42.
- Martin CW, Driscoll CT, Fahey TJ. 2000. Changes in streamwater chemistry after 20 years from forested watersheds in New Hampshire, USA. *Can J For Res* 30:1206–13.
- Merriam J, McDowell WH, Currie WS. 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. *Soil Sci Soc Am J* 60:1050–55.
- Mitchell MJ, Driscoll CT, Kahl JS, Likens GE, Murdoch PS, Pardo LH. 1996. Climatic control of nitrate loss from forested watersheds in the northeast United States. *Environ Sci Technol* 30:2609–12.
- Murdoch PS, Burns DA, Lawrence GB. 1998. Relation of climate change to the acidification of surface waters by nitrogen deposition. *Environ Sci Technol* 32:1642–7.
- Murdoch PS, Stoddard JL. 1992. The role of nitrate in the acidification of streams in the Catskill Mountains of New York. *Water Resour Res* 28:2707–20.
- Perakis SS, Hedin LO. 2002. Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. *Nature* 415:416–19.
- Reiners WA, Lang GE. 1979. Vegetational patterns and processes in the balsam fir zone, White Mountains, New Hampshire. *Ecology* 60:403–17.
- Reuss JO, Johnson DW. 1986. *Acid deposition and the acidification of soils and waters*. New York: Springer-Verlag.
- Silsbee DG, Larson GL. 1982. Water quality of streams in the Great Smoky Mountains National Park. *Hydrobiologia* 89:97–115.

- Stoddard JL. 1994. Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences. In: Baker LA, editor. *Environmental chemistry of lakes and reservoirs*. ACS Advances in Chemistry Series no. 237. Washington (DC): American Chemical Society. p 223–82.
- Stoddard JL, Driscoll CT, Kahl JS, Kellogg JH. 1998a. Can site-specific trends be extrapolated to a region? An acidification example for the northeast. *Ecol Appl* 8:288–99.
- Stoddard JL, Driscoll CT, Kahl JS, Kellogg JH. 1998b. A regional analysis of lake acidification trends for the northeastern U.S., 1982–1994. *Environ Monit Assess* 51:399–413.
- Stoddard JL, Jeffries DS, Lukewille A, Clair TA, Dillon PJ, Driscoll CT, Forsius M, Johannessen M, Kahl JS, Kellogg JH, Kemp A, and others. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* 401: 575–78.
- Swank WT, Waide JB, Crossley DAJ, Todd RL. 1981. Insect defoliation enhances nitrate export from forest ecosystems. *Oecologia* 51:297–99.
- Vitousek PM. 1975. The regulation of element concentrations in mountain streams in the northeastern United States [dissertation]. Hanover (NH): Dartmouth College.
- Vitousek PM. 1977. The regulation of element concentrations in mountain streams in the northeastern United States. *Ecol Monogr* 47:65–87.
- Vitousek PM, Aber JD, Goodale CL, Aplet GH. 2000. Global change and wilderness science. In: Cole DN, McCool SF, Freimund WA, O'Loughlin J, editors. *Wilderness science in a time of change conference*. RMRS-P-15-VOL-1 1. Ogden (UT): USDA Forest Service, Rocky Mountain Research Station. p 5–9.
- Vitousek PM, Hedin LO, Matson PA, Fownes JH, Neff J. 1998. Within-system element cycles, input-output budgets, and nutrient limitation. In: Pace ML, Groffman PM, editors. *Successes, limitations, and frontiers in ecosystem science*. New York: Springer-Verlag. p 432–51.
- Vitousek PM, Reiners WA. 1975. Ecosystem succession and nutrient retention: a hypothesis. *BioScience* 25:376–81.