

NITROGEN SATURATION AND RETENTION IN FORESTED WATERSHEDS OF THE CATSKILL MOUNTAINS, NEW YORK

GARY M. LOVETT,¹ KATHLEEN C. WEATHERS, AND WILLIAM V. SOBCHAK

Institute of Ecosystem Studies, Millbrook, New York 12545 USA

Abstract. The Catskill Mountains of southeastern New York receive relatively high rates of atmospheric N deposition, and NO_3^- concentrations in some streams have increased dramatically since the late 1960s. We measured the chemistry of 39 first- and second-order streams with forested watersheds to determine the variability of nitrogen concentrations within the Catskill Mountain area. We found that some streams have low NO_3^- concentrations throughout the year, some have seasonal cycles of varying amplitude, and some have relatively high concentrations year round. If the concentration and seasonality of NO_3^- in stream water are used as indices of nitrogen saturation, then most stages of nitrogen saturation are evident in our survey of Catskill watersheds. Organic nitrogen was a small portion of the total nitrogen for streams with high NO_3^- concentration, but organic N was the dominant form of N (up to 73% of the total) in the streams with lowest nitrate. Estimated retention of N in these watersheds (based on total N in stream water) ranged from 49% to 90% of the atmospheric input. The variation in stream water NO_3^- concentration and the amplitude of the seasonal fluctuations did not appear to be attributable to differences among watersheds in atmospheric deposition, watershed topography, or groundwater influx to the stream. We hypothesize that differences among watersheds in forest species composition and forest history, which are interrelated, produce most of the variation in NO_3^- concentration that we observed.

Key words: *Catskill Mountains; dissolved organic nitrogen; nitrate; nitrogen retention; nitrogen saturation; nitrogen; streams; watershed.*

INTRODUCTION

In industrialized regions of the world, combustion of fossil fuels has drastically increased the concentration of nitrogen oxides in the atmosphere, and the resulting increase in atmospheric deposition of nitrogen (N) may have serious effects on the N cycle in receiving ecosystems (Aber et al. 1989, Howarth 1996, Vitousek et al. 1997, Aber et al. 1998). As N accumulates in forest ecosystems, N supply may approach or exceed the biotic demand; this process of N accumulation has been termed “nitrogen saturation” (Agren and Bosatta 1988, Aber et al. 1989). One of the key symptoms of nitrogen saturation is increased concentration of nitrate (NO_3^-) in stream water (Stoddard 1994), which can cause acidification of headwater streams and contribute to eutrophication of estuaries and coastal waters (Hinga et al. 1991, Murdoch and Stoddard 1992).

Because of their proximity to midwestern industrial facilities and east-coast urban centers, the Catskill Mountains of southeastern New York State receive among the highest rates of atmospheric deposition of nitrogen oxides in the northeastern U.S. (Ollinger et al. 1993). Nitrate concentrations have been increasing over the last 25 yr in some Catskill streams (Stoddard

and Murdoch 1991, Driscoll and Van Dreaseon 1993), leading some researchers to speculate that nitrogen saturation is underway in Catskill forests (Murdoch and Stoddard 1992, Stoddard 1994). In contrast, no long-term increase in surface water NO_3^- is evident in northern New England (NAPAP 1992, Likens and Bormann 1995), where N deposition rates are lower (Ollinger et al. 1993). This fact has strengthened the argument that recent increases in stream water NO_3^- concentrations in the Catskills are the direct result of air pollution (Newell 1993), as opposed to some change in watershed processing of N. However, the recent increases in NO_3^- concentration in Catskill streams have occurred despite little or no change in the emissions of nitrogen oxides in the eastern U.S. (Stoddard and Murdoch 1991, NAPAP 1992). This indicates that if the stream NO_3^- trend is caused by atmospheric deposition, it is not a direct response to current deposition levels, but a longer-term response to accumulation of N in the ecosystem. Other possible causes of the recent increases in NO_3^- include reductions in forest growth rates and changes in forest species composition, perhaps acting in concert with high levels of atmospheric deposition. These possibilities have not been well studied. Forest growth rates could be declining if the forests are maturing after being heavily harvested in the late 1800s and early 1900s, as forest history studies indicate (e.g., Kudish 1985). Decreases in forest growth would be expected to permit increased leakage of N from the

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¹ E-mail: lovettg@ecostudies.org

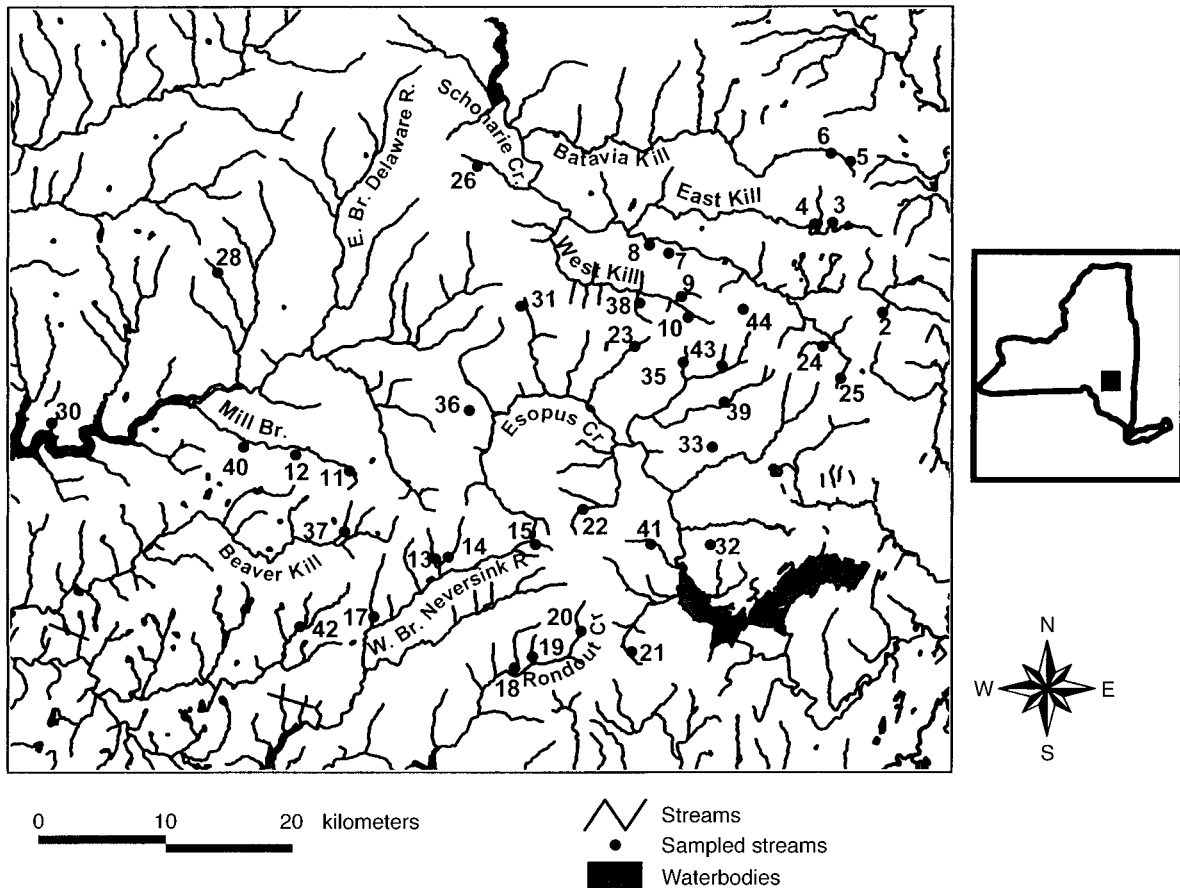


FIG. 1. Map of major streams in the central Catskills, showing stream sampling locations used in this study. Stream numbers refer to Table 1. The inset shows the location of the study area in New York State.

ecosystem (Vitousek and Reiners 1975). In contrast, however, stream water NO_3^- concentrations at Hubbard Brook, New Hampshire are near their lowest levels in the 35-yr record at that site, despite the near-cessation of aboveground biomass accumulation in the watershed forests (Likens et al. 1996). Possible changes in tree species composition in Catskill forests could also play a role, because species respond differently to enhanced N deposition (Lovett and Rueth 1999).

The increase in NO_3^- in Catskill streams is of concern for several reasons. The waters from the Catskills drain to the New York, Delaware, and Chesapeake Bays, all of which have had recent problems with eutrophication from excess nitrogen (Fisher and Oppenheimer 1991, Hinga et al. 1991). Nitrate plays an important role in the acidification of Catskill streams (Murdoch and Stoddard 1992), threatening a world-famous trout fishery. At least one Catskill river supports populations of endangered mussels (Strayer et al. 1996). In addition, high concentrations of NO_3^- in drinking water can be a health threat to humans, and Catskill watersheds supply 90% of the drinking water to the $\sim 9 \times 10^6$ residents of New York City (Iwan 1987).

While most research on nitrogen saturation has focused on a few, well-studied watersheds, our purpose in this study was to take a broader view of the problem within the Catskill region by sampling 39 Catskill headwater streams with forested watersheds. Our goals were to investigate spatial and temporal patterns of stream water chemistry, quantify the variation in chemistry among streams, and to the extent possible, evaluate likely sources of this variation.

STUDY AREA

The Catskill Mountains are an area of flat-topped mountains and deeply incised valleys encompassing $\sim 5000 \text{ km}^2$ in southeastern New York State (Fig. 1). There are 35 peaks over 1067 m, the highest being Slide Mountain at 1274 m. The bedrock in the higher elevations ($>500 \text{ m}$) is relatively homogeneous, consisting primarily of flat-lying sandstones, shales, and conglomerates of Devonian age (Stoddard and Murdoch 1991), and is overlain by glacial till of variable depth (Rich 1934). Soils of the region are primarily thin Inceptisols of moderate to high acidity (Stoddard and Murdoch 1991). The climate of the area is characterized by cool summers and cold winters. The Slide

Mountain weather station at 808 m in the central Catskills has a mean annual temperature of 4.3°C (January mean = -8.5°C, July mean = 16.7°C), and a mean annual precipitation of 153 cm, ~20% of which falls as snow.

The area is primarily forested, with elevations below ~500 m dominated by mixed oak forests, of which the dominant species is usually northern red oak (*Quercus rubra* L.). The vegetation of the zone between ~500 and 1100 m elevation is typical of northern hardwood forests throughout the northeastern U.S., with the dominant tree species being sugar maple (*Acer saccharum* Marsh), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula alleghaniensis* Britton), with eastern hemlock (*Tsuga canadensis* (L.) Carr) occurring primarily in ravines and on cool, north-facing slopes (McIntosh 1972). Black cherry (*Prunus serotina* Ehrh.), white ash (*Fraxinus americana* L.), and red oak also occasionally achieve local dominance in this zone. At elevations >1100 m, some of the mountains have forests dominated by balsam fir (*Abies balsamea* (L.) Miller) and/or red spruce (*Picea rubens* Sarg.), with some paper birch (*Betula papyrifera* var. *cordifolia*), although the extent of this spruce-fir vegetation is quite limited in the Catskill area as a whole.

Currently, much of the forest >1000 m elevation is in the Catskill Forest Preserve, which was established by New York State in 1885 and has been incremented with additional parcels ever since. Forest Preserve lands have not been cut or actively managed since acquisition by the State. First-growth forest covers >200 km² in the Catskills, almost exclusively in areas 1000 m elevation (Kudish 1985). The forests of the lower elevations have a long history of use by European settlers, including selective harvest of the forest for lumber, firewood, charcoal, and tanbark (McIntosh 1972, Kudish 1979). Large-scale clearcutting of the forest was rare, except in areas immediately surrounding settlements. Occasional fires burned limited areas of forest (Kudish 1985).

METHODS

Choice of streams

We chose a set of headwater streams distributed throughout the Catskills matching as closely as possible the following watershed criteria: (1) first or second-order streams, (2) watersheds entirely forested, and (3) lack of obvious lakes or wetlands in watershed, based on topographic maps. While some streams have been added to or dropped from the survey over time, we present here the data from a core set of 39 streams that were sampled from September 1994 to July 1997. All of the streams are fast flowing and the streambeds are composed of boulders and large cobbles with little accumulation of gravel or fine sediment. In general, the forest canopy covers or nearly covers the streams, and there is no obvious zone of riparian vegetation, i.e., the

streamside forest appears similar to the surrounding forest. All the watersheds we sampled are within the area defined by longitude range 74°13' to 74°53' west and latitude range 41°53' to 42°20' north.

Samples were taken during this 3-yr period on 12 dates distributed through the seasons. Samples were not taken immediately after significant rain events to avoid stormflow conditions. All streams were sampled on the same day. Samples were collected in clean polyethylene bottles that were rinsed with the stream water before sampling. Samples were returned to the laboratory and pH was measured potentiometrically on a subsample as soon as it had come to room temperature. A second subsample was preserved with ~200 µL of chloroform per 100 mL of sample, and stored in the dark at 4°C for analysis of NO₃⁻, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, and total nitrogen (TN). No turbidity was visible in the samples, and these subsamples were not filtered. On 4 of the 12 sampling dates, a third subsample was filtered (0.6µm Gelman filter, Gelman Sciences, Ann Arbor, Michigan) and stored at 4°C for dissolved organic carbon (DOC) analysis.

One stream, Winnisook Brook, was sampled more intensively by taking samples roughly weekly in the summer months and every 2–3 wk during the winter and spring (for a total of 58 sampling dates) during the period 1 June 1994 to 31 May 1996. Winnisook Brook is an alternate name for the headwater reach of the West Branch of the Neversink River, and is the same stream discussed by Lovett et al. (1999), Burns (1998), Burns et al. (1998), and Lawrence et al. (1999).

Nitrate, SO₄²⁻ and Cl⁻ were measured with Dionex 2000 or DX500 ion chromatographs, and Ca²⁺ and Mg²⁺ were measured on a Perkin-Elmer P400 inductively coupled plasma emission spectrometer, (Perkin Elmer Corporation, Foster City, California). Ammonium was measured with the indophenol blue method on an Alpkem autoanalyzer (O.I. Analytical, College Station, Texas). Total nitrogen was measured as NO₃⁻ by the cadmium reduction method on the Alpkem autoanalyzer after persulfate digestion (EPA 1987). Dissolved organic carbon was measured with a Shimadzu 5000 carbon analyzer (Shimadzu Scientific Instruments, Incorporated, Columbia, Maryland), which uses high-temperature combustion after acidification and sparging of the sample. Nitrate, SO₄²⁻, Cl⁻, and TN were measured on samples from all 12 sampling dates; pH on 10 dates; Ca²⁺ and Mg²⁺ on eight dates, and DOC on four dates. Ammonium was only measured on two dates (one summer, one winter) and 38% of the measured values were below the analytical method detection limit of 1.1 µmol/L. These values were coded in the data set as one-half the detection limit. Because of the small number of measurements and the analytical uncertainty, we present the mean values for NH₄⁺ below but do not interpret the NH₄⁺ data further in this paper. Total organic N (TON) was calculated as TN minus NO₃⁻-N, ignoring NH₄⁺ because of its low con-

centration. In 10% of the samples, the measured NO_3^- -N equaled or exceeded the measured TN. These values were coded as $\text{TON} = 0$ in the data set.

Watershed characteristics

Watershed boundaries and areas were determined from 1:24 000 scale topographic maps. Watershed topographic variables were defined and calculated as follows:

- a) Total watershed area, in hectares
- b) Area >1000 m elevation, in hectares
- c) Maximum elevation of watershed, in meters
- d) Elevation of stream sampling point, in meters
- e) Total relief ($= c - d$), in meters
- f) Length ($=$ distance from stream sampling point to farthest point in watershed), in meters
- g) Slope index ($=e/f$), unitless
- h) Width index ($=a/f$), in meters.

Atmospheric input and watershed export calculations

We made approximate calculations of atmospheric N inputs and stream water outputs for these watersheds using available data for atmospheric deposition for the region and water discharge data for two of the watersheds, Biscuit Brook and Winnisook Brook.

Atmospheric deposition.—Atmospheric input data were obtained from national monitoring network stations in the vicinity of these watersheds. Wet deposition data for NH_4^+ and NO_3^- (wet only, collected weekly) were obtained from the National Atmospheric Deposition Program/National Trends Network site at Biscuit Brook for the period 1994–1996. This site is in the Biscuit Brook watershed and is ~ 8 km from the Winnisook Brook watershed. Dry deposition data were obtained from the U.S. Environmental Protection Agency Clean Air Status and Trends Network site, which is ~ 2 km from Biscuit Brook and ~ 10 km from Winnisook Brook. The dry deposition is based on measured air concentrations (weekly filter packs) of HNO_3 vapor and fine-particle NH_4^+ and NO_3^- , with deposition fluxes calculated from these concentrations using a model parameterized with measured canopy structure and micrometeorological data (Clarke et al. 1997). The model is theoretically appropriate for flat terrain and homogeneous canopies, and thus is of questionable validity in mountainous terrain such as the Catskills (Lovett 1994). For sulfur, however, the model yields reasonable estimates of dry deposition for midslope sites, based on comparisons with throughfall S measurements in the Winnisook Brook watershed (Lovett et al. 1999). Data were available for this site for the period 20 May 1994 through 30 January 1996.

Discharge and N export.—Of the 39 streams in the data set, only the Biscuit Brook and Winnisook Brook have water discharge measurements available from the U.S. Geological Survey (U.S.G.S.) for the points at which we sample. We obtained the daily discharge data from the U.S.G.S. for these two streams for the period

1 June 1994 through 31 May 1996. To calculate NO_3^- export, we divided the year into flow-regime periods as follows: winter high flow (January, February and March), spring transition (April and May), growing-season baseflow (June–October), and fall transition (November and December). We have at least one NO_3^- concentration measurement for each of these periods for Winnisook and Biscuit Brook from 1 June 1994 to 31 May 1996. If more than one measurement was available for a period, we calculated the mean concentration for the period, weighted by the daily discharge for the sampling day. We then multiplied the discharge-weighted mean concentration by the total discharge for the period to estimate N export flux. The export amounts were summed across the flow-regime periods for a year, and the two years were averaged. This calculation was repeated using total N (TN) concentrations. In our stream survey sampling we specifically avoided stormflow periods, but we did sample high flow periods during snowmelt, when the highest NO_3^- concentrations and export fluxes typically occur (Murdoch and Stoddard 1992). To check the accuracy of our infrequent survey as an estimator of total export, we made the calculation above for Winnisook Brook using the more frequent sampling program in that stream, as well as the survey sampling.

All statistical analysis was done using the SAS statistical package (SAS 1989). We used simple descriptive statistics (mean, coefficient of variation, range) to characterize the mean and variance in the data set. We evaluated correlations between N concentrations in stream water and possible explanatory variables using simple correlation (CORR procedure in SAS [1989]). To identify patterns of seasonal fluctuations of NO_3^- , we performed a cluster analysis using the mean summer and winter NO_3^- concentrations for the streams. For this purpose, winter samples were defined as those taken in December, January, February, and March, while summer samples were those taken in June, July, August, and September. We used a hierarchical, agglomerative clustering method (CLUSTER procedure in SAS [1989], method of average linkage). This procedure initially treats all 39 streams as separate clusters, then groups them into decreasing numbers of clusters based on the average distance between clusters in the summer and winter NO_3^- concentrations. The procedure eventually arrives at a single cluster comprised of all 39 streams. We chose to analyze the grouping at the level of five clusters, which represented a small number of groups with easily interpretable differences.

RESULTS AND DISCUSSION

Mean chemical characteristics

Nitrate dominated the nitrogen chemistry of the 39 sampled streams. On average, NO_3^- contributed 77.5% of the dissolved N in stream water, compared to 16.7% for total organic nitrogen (TON) and 5.8% for NH_4^+

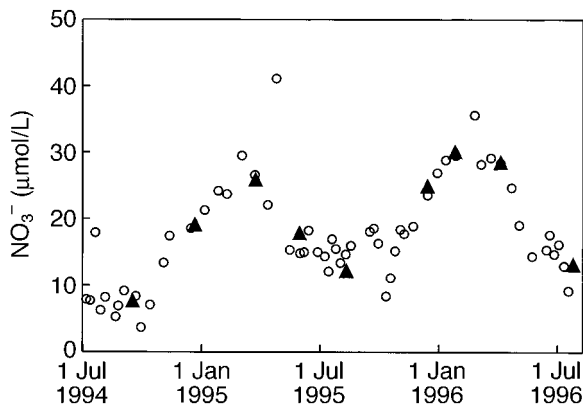


FIG. 2. Nitrate concentrations measured in Winnisook Brook on the stream survey sampling dates (filled triangles) and during the more intensive sampling program (open circles).

(Table 2). Comparison of the NO_3^- concentrations measured on the 12 stream survey dates with those measured in the more intensive sampling of Winnisook Brook indicates that our survey was effective in sampling the mean values and seasonal dynamics of stream water concentration (Fig. 2).

Mean NO_3^- concentration was quite variable among streams, with a coefficient of variation (CV) of 37% and a range from 2.1 to 36.1 $\mu\text{mol/L}$ (Table 1, Fig. 3). Concentrations of Ca^{2+} and Mg^{2+} were somewhat less variable than NO_3^- , and SO_4^{2-} was relatively invariant, with a CV of only 8.5% and a range from 51 to 72 $\mu\text{mol/L}$ (Table 1). The high variability in Cl^- (CV = 54%) probably resulted from road salt influence on two streams in the eastern part of the study region (Tonshi Brook and Grog Kill): without these two streams the data set ($n = 37$ samples) had a mean Cl^- concentration of 20.2 $\mu\text{mol/L}$ with a CV of 23%. Likewise, much of the high variability in H^+ among the streams was attributable to one chronically acidified stream (Winnisook Brook, mean pH 4.70), which also had the highest elevation watershed and the lowest stream water Ca^{2+} concentration, although the SO_4^{2-} and NO_3^- values were near the means for the data set. Without this stream, the data set ($n = 38$) had a mean H^+ of 0.28 $\mu\text{mol/L}$ (pH 6.55) and a range from 0.089 to 1.33 $\mu\text{mol/L}$ (pH 7.05 to 5.88). With or without Winnisook Brook in the data set, there was no significant correlation between NO_3^- and H^+ .

Concentrations of TON were less variable than those of NO_3^- , but because of the variability in NO_3^- , the percentage contribution of TON to the total N concentration ($\text{TON} + \text{NO}_3^-$, ignoring NH_4^+) ranged from 7.4% (Black Brook) to 72.5% (Tonshi Brook) (Fig. 3). Because there was no visible turbidity in the samples, our TON values probably represent primarily dissolved organic nitrogen (DON). The concentration of particulate organic matter at baseflow was too small to be measurable gravimetrically in 1-L samples collected at

a site downstream of our Winnisook sampling station (W. Sobczak, *unpublished data*), suggesting that particulate forms of C and N are probably negligible.

Hedin et al. (1995) found that DON contributed 95% of the N in stream water in an old-growth temperate forest in Chile, and suggested that the widely held view that NO_3^- dominates N export flux is influenced by the ubiquity of N oxide pollution in the north temperate zone, where most of the research has been done. Our data indicate that even in this area of high nitrogen deposition, organic N can dominate stream water nitrogen chemistry in streams having low NO_3^- concentrations.

Nitrogen retention in the watersheds

Calculation of the percentage of atmospherically deposited N that is retained by the watersheds is of interest because the factor is used in models that relate atmospheric N deposition to downstream pollution (e.g., Fisher et al. 1991, Hinga et al. 1991) or to carbon storage in the forest (Townsend et al. 1996). We used atmospheric input and stream export data to calculate N retention for two watersheds, Biscuit Brook and Winnisook Brook. Atmospheric wet deposition at the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) station at Biscuit Brook averaged 511 $\text{mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$, and estimated dry deposition at the CASTNet station near Biscuit Brook averaged 361 $\text{mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$, for a total atmospheric N input of 872 $\text{mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. Nitrogen export per unit area and percentage N retention were quite similar for the two watersheds despite the almost fivefold difference in watershed area (Table 2). Nitrogen retention ($[\text{input} - \text{export}]/\text{input}$) was 72–73% in the two watersheds when calculated using only NO_3^- export, and 67–70% using TN export (Table 2). Both of these watersheds were near the population mean in stream water N concentrations (Fig. 3).

Nitrogen export for the Winnisook watershed based on the more frequent sampling program was 220 $\text{mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for NO_3^- and 263 $\text{mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for TN, which are 7.9% and 1.9% different, respectively, from the values obtained using the less frequent survey sampling (Table 2). This small difference gives us confidence in our calculation of N export using the survey data.

We cannot calculate N export directly for the other streams in the data set for lack of discharge data. However, if among-watershed differences in N export are directly proportional to differences in their N concentration in stream water, then we can approximate the N export from the other watersheds as the product of their stream water TN concentration and an export: concentration ratio (N export/TN concentration) calculated from the Biscuit Brook and Winnisook data (Table 2). Nitrogen export would be proportional to N concentration if differences among watersheds in water discharge per unit watershed area were small compared

TABLE 1. Chemical characteristics of sampled streams and physical characteristics of their watersheds for 39 streams of the Catskill Mountains, New York.

Stream no.	Stream name	Max. elev. (m)	Sample elev. (m)	Length (m)	Area (ha)	NO ₃ ⁻	TON	TN	NH ₄ ⁺	DOC	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	H ⁺
2	Santa Cruz	1006	680	1680	23	24.2	5.6	29.9	0.8	180.4	50.6	15.5	54.7	14.4	0.48
3	Colgate†	1216	628	3912	462	25.4	4.9	30.3	1.4	108.8	55.4	16.4	58.4	17.0	0.24
4	Halsey	1204	625	4032	297	29.7	4.4	33.0	0.8	104.7	56.5	17.1	65.9	19.6	0.47
5	Batavia Kill	1213	663	3072	399	22.1	6.1	28.3	1.4	84.5	57.5	16.8	59.5	19.5	0.23
6	Windham Ridge†	1074	616	2520	207	13.1	5.7	17.6	0.6	82.4	58.3	18.3	54.6	21.9	0.37
7	Silver Spring†	1113	451	3120	348	27.5	3.0	30.8	1.1	86.6	63.0	15.7	68.5	22.4	0.17
8	Little Timber†	1027	463	2064	179	28.1	4.7	32.8	1.4	91.9	66.5	26.9	84.6	26.2	0.14
9	Hunter	1234	634	4416	504	31.2	5.4	37.1	2.5	39.1	64.5	22.0	73.1	25.4	0.14
10	West Kill	1234	658	3600	546	22.6	3.1	26.0	3.1	66.6	63.4	21.3	71.1	21.8	0.16
11	Mill	1137	674	2856	279	35.9	4.9	39.8	1.4	59.3	58.4	29.8	91.2	22.2	0.10
12	Kelly Hollow	1061	533	3960	516	35.9	2.9	40.8	0.6	51.3	70.6	18.4	94.4	28.5	0.11
13	Pigeon	1173	619	4608	706	22.4	5.8	28.0	1.1	93.7	56.9	16.6	59.4	16.0	0.27
14	Biscuit	1125	619	5616	992	22.2	4.0	25.8	0.8	83.5	56.7	16.6	46.7	17.5	0.46
15	Winnisook†	1250	811	2712	230	21.1	3.2	23.7	2.2	107.8	56.0	14.0	20.2	14.9	19.82
17	Fall	1018	530	7176	1263	20.5	3.9	23.3	0.8	70.1	60.4	19.4	70.0	18.2	0.22
18	Bear Hole	1171	363	6960	804	24.9	5.7	30.7	0.8	67.4	67.8	19.9	43.9	25.0	0.50
19	Buttermilk Falls	1076	405	2856	183	33.1	6.2	40.6	1.4	104.4	70.8	20.6	53.3	26.3	0.50
20	Rondout	1171	454	6456	1686	23.4	3.8	26.5	1.1	61.2	58.6	21.5	35.6	19.6	1.33
21	Kanape	939	334	4704	766	10.2	5.9	16.7	2.2	40.2	59.5	25.5	60.3	30.0	0.15
22	Woodland Val.	1277	425	5280	1380	18.6	6.6	25.3	2.5	44.1	55.5	24.5	44.2	24.9	0.35
23	Broadst. Hollow	1180	433	4752	996	19.5	6.8	27.1	3.3	70.8	63.4	22.4	78.4	27.7	0.12
24	Pecoy†	1161	591	2904	290	28.0	4.5	31.9	1.9	84.9	57.8	26.4	56.1	15.5	0.50
25	Prediger†	1030	610	2688	125	21.5	3.9	24.9	3.1	85.1	55.1	20.5	40.8	13.8	1.14
26	Bear Pen†	1076	497	2544	209	22.6	7.7	30.8	1.7	99.5	65.5	13.4	72.5	25.7	0.12
28	Weaver†	1021	786	960	33	17.2	6.7	24.0	1.4	66.1	62.7	13.0	50.3	22.2	0.37
30	BWS6†	754	512	2016	144	3.8	5.7	10.9	1.9	51.3	72.1	18.7	73.4	30.1	0.17
31	Halcott†	1039	555	1584	107	20.9	6.2	27.6	2.2	66.8	63.4	24.6	62.0	27.4	0.17
32	Tonshi†	762	293	2976	267	2.1	5.6	8.3	1.7	82.4	68.5	78.8	54.5	34.7	0.11
33	Grog Kill†	863	271	3384	441	3.0	7.1	10.5	2.2	58.9	65.8	63.6	82.8	31.7	0.09
35	Hollow Tree	1137	457	3096	492	36.1	3.9	40.4	1.9	42.7	69.2	22.3	81.8	26.5	0.10
36	Lost Clove	1091	460	3000	413	22.4	5.8	28.4	2.2	45.4	66.7	18.6	70.4	28.8	0.16
37	Black	1137	683	4416	376	34.4	2.8	36.0	1.4	49.5	59.3	14.9	68.6	18.7	0.13
38	Styles	1186	576	3840	395	31.8	5.5	37.7	0.8	83.3	61.1	17.8	69.4	22.5	0.20
39	Warners	1173	418	8328	1835	21.6	3.6	25.3	1.4	65.4	62.1	34.4	76.8	24.6	0.10
40	Kittle†	957	567	1800	63	32.2	4.4	36.4	2.2	66.2	70.4	24.4	82.5	25.6	0.16
41	Traver Hollow	887	311	3000	604	16.2	4.6	21.3	1.1	57.5	62.1	21.9	67.9	22.8	0.13
42	Willowemoc	983	607	5472	915	19.8	3.2	22.8	1.4	42.7	64.6	16.4	75.5	16.5	0.18
43	Myrtle	1219	475	4320	476	17.4	3.6	22.3	2.5	42.9	61.4	21.0	63.4	19.2	0.14
44	Becker Hollow	1231	588	2664	376	26.9	4.7	30.0	2.5	55.8	56.9	20.9	58.6	18.2	0.16
Mean		1092	535	3727	521	22.8	4.9	27.8	1.7	73.0	61.9	22.8	64.0	22.6	0.78
Standard deviation		129	130	1633	435	8.5	1.3	8.0	0.7	27.1	5.2	12.4	15.5	5.2	3.14

Notes: Stream numbers refer to Fig. 1. All chemical concentrations are means across sampling dates and are expressed in micromoles per liter ($\mu\text{mol/L}$). NH₄⁺ was measured on only two dates, and 38% of the values were less than the method detection limit of 1.1 $\mu\text{mol/L}$. These values were entered in data set as one-half of the detection limit.

† Stream was unnamed on USGS topographic map. We assigned a name from a nearby road or other feature on the map.

to differences in N concentration. This assumption seems reasonable, given that the variation among watersheds in NO₃⁻ concentration is 17-fold (1700%; Table 1), while water discharge per unit area varies by only 11% between the two gauged watersheds despite their substantial difference in size. Assuming atmospheric deposition to all watersheds is equal to that measured at the deposition monitoring sites, and calculating N export as TN concentration in stream water times the mean export: concentration ratio from Winnisook and Biscuit Brook (Table 2), we estimate that N retention varies from 49% at Kelly Hollow to 90% at Tonshi Brook, the streams with highest and lowest TN concentrations in our data set. Basing the calculation on inorganic N only (NO₃⁻ plus NH₄⁺ deposition

and NO₃⁻ export) yields a retention of 54% at Kelly Hollow and 97% at Tonshi Brook.

Seasonal patterns and N saturation

Nitrate concentration in stream water often varies seasonally, and the seasonal variations have been suggested to be indicative of the degree of N saturation in a watershed (Stoddard 1994). Specifically, Stoddard proposed that in stage 0 of N saturation, NO₃⁻ concentrations are low year round with a possible small peak during spring snowmelt. In stage 1, seasonal variations are evident, and the spring peak may be extended. In stage 2, growing-season NO₃⁻ concentrations are elevated, although they are still lower than the dormant-season concentrations. In stage 3, seasonal

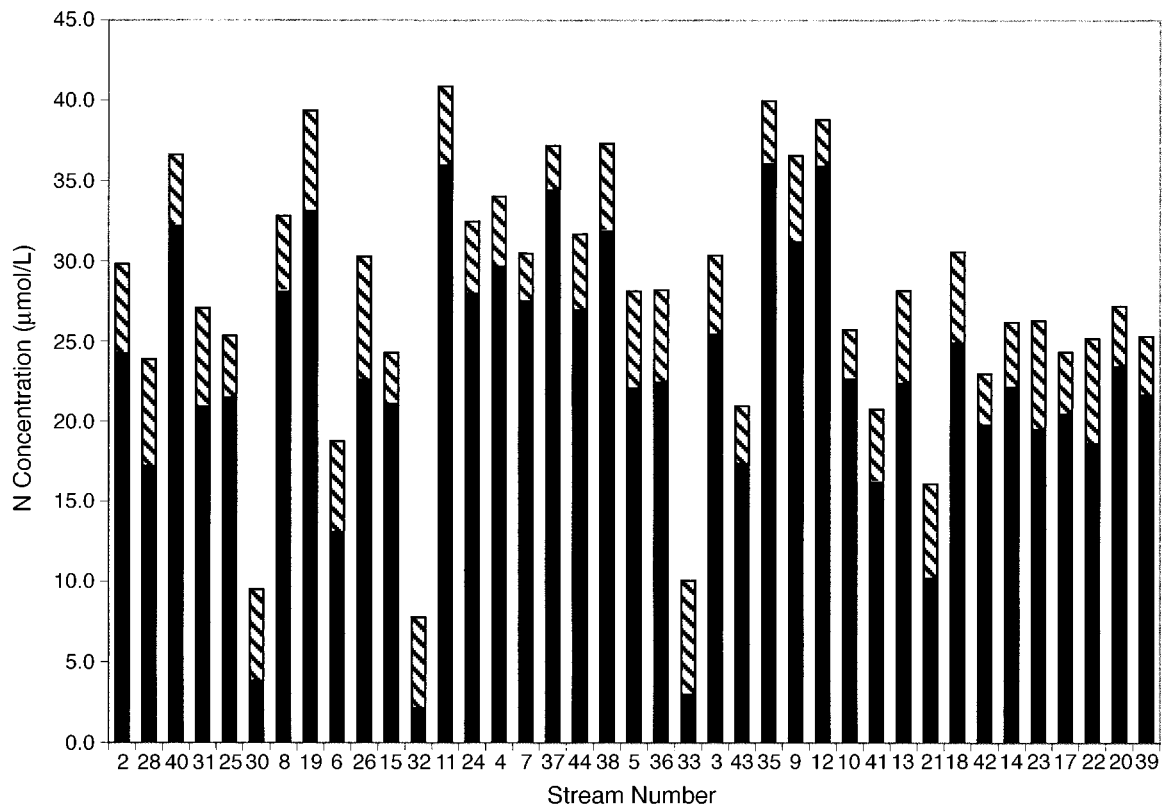


FIG. 3. Mean NO_3^- and organic N concentrations in the 39 sampled streams. Striped portion of the bar represents the mean total organic nitrogen (TON) concentration, and the black portion represents mean NO_3^- concentration. Numbers under bars are stream identification numbers used in Table 1 and Fig. 1. Streams are presented in order of increasing watershed area.

fluctuations diminish as growing-season concentrations increase, and the watershed becomes a net source of NO_3^- .

From the cluster analysis of our stream data set, based on mean summer and winter NO_3^- concentrations

TABLE 2. Parameters used in export and retention calculations in a study of nitrogen in 39 streams of the Catskill Mountains, New York.

Parameter	Winnisook	Biscuit Brook
Mean water discharge (m^3/d)	5915	25,412
Watershed area (ha)	199	963
NO_3^- export ($\text{mol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$)	239	242
TN export ($\text{mol}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$)	258	284
NO_3^- unweighted mean concentration ($\mu\text{mol/L}$)	21.1	22.2
TN unweighted mean concentration ($\mu\text{mol/L}$)	23.8	25.8
NO_3^- export/ NO_3^- concentration (dm/yr)	11.3	10.9
TN export/TN concentration (dm/yr)	10.8	11.0
N retention: NO_3^- (%)	73	72
N retention: TN (%)	70	67

Notes: See Methods: Atmospheric input and export calculations: Discharge and N export for explanation of calculations. Percentage retention based on estimated atmospheric input of $872 \text{ mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$.

for the streams, we identified five clusters as follows, with NO_3^- concentration ranges in micromoles per liter ($\mu\text{mol/L}$):

- 1) winter and summer mean concentrations of NO_3^- both <10 (3 streams)
- 2) winter concentrations 10–20, summer concentrations <10 (2 streams)
- 3) winter concentrations 18–31, summer concentrations 10–18 (19 streams)
- 4) winter concentrations 30–44, summer concentrations 11–20 (9 streams)
- 5) winter concentrations 27–38, summer concentrations 26–35 (6 streams)

(Note that the winter and summer concentrations used here are seasonal means, not peak values, and the ranges represent the variation among streams.) These groups represent a sequence of increasing apparent N saturation, corresponding in some ways to the stages identified by Stoddard (1994). The groups are illustrated by representative streams in Fig. 4. Group 1 has low concentrations year round, while group 2 has slightly elevated concentrations in winter. Group 3 has moderate concentrations in winter and slightly elevated concentrations in summer. Group 4 has high concentrations in winter and moderate concentrations in sum-

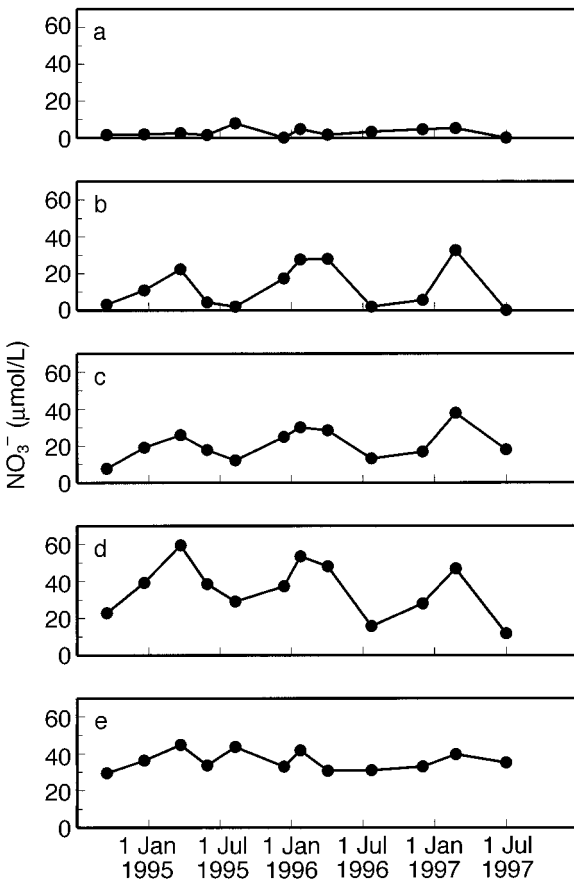


FIG. 4. Temporal patterns of NO_3^- concentration in five streams representing the five groups identified in the cluster analysis (see *Methods: Atmospheric input and export calculations: Discharge and N export*): (a) Grog Kill, (b) Windham Ridge Brook, (c) Winnisook Brook, (d) Mill Brook, and (e) Hollow Tree Brook.

mer. Group 5 has high concentrations year round. Using Stoddard's stages of N saturation, group 1 would be in stage 0, group 2 in stage 1, groups 3 and 4 in stage 2, and group 5 may be in stage 3 based on the lack of seasonality, although none of the watersheds is a net source of N. (The N retention calculations discussed above indicate that even the watersheds with the highest N export retain roughly 50% of the nitrogen deposited on them.)

The majority of streams we sampled have mean winter concentrations in the range 20–40 $\mu\text{mol/L}$ and mean summer concentrations in the range 10–20 $\mu\text{mol/L}$. However, the range of seasonal patterns is large, and Fig. 3 illustrates that most stages of nitrogen saturation are present in the Catskills despite the small size and geological homogeneity of the area. The fact that the watersheds vary in the amount and the timing of NO_3^- loss suggests that the process of nitrogen saturation is not controlled entirely by rates of atmospheric deposition, which are probably quite similar among the watersheds.

Burns et al. (1998) note that the elevation of summer NO_3^- concentrations in Catskill streams may be explained by the presence of a deep groundwater flow path, through which the high- NO_3^- drainage water from the dormant season can be released slowly into streams during the summer. However, differences in groundwater influx, which are most important in the summer, cannot explain the differences we observe in winter NO_3^- concentrations (Fig. 4).

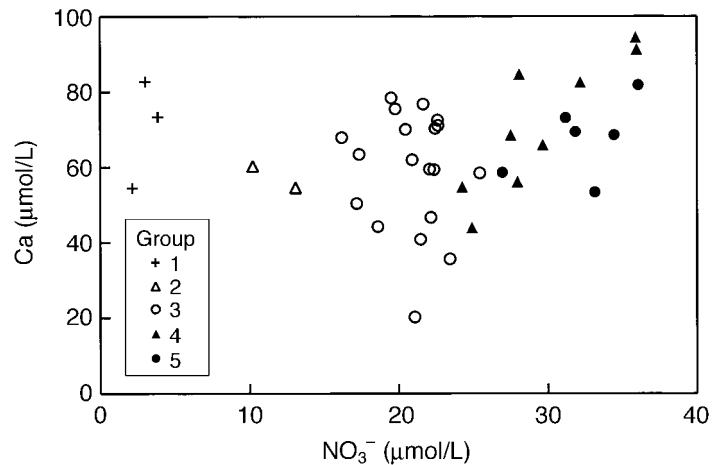
What controls nitrogen concentration in Catskill streams?

Nitrate.—A large number of factors are known to influence NO_3^- concentrations in stream water draining forested watersheds. Much research has been devoted to the role of disturbances such as forest harvest (Likens et al. 1970) and insect defoliation (Swank et al. 1981, Webb et al. 1995) in producing flushes of NO_3^- , and to the various microbial and hydrological variables that control the extent of nitrification and nitrate loss in disturbed systems (Vitousek et al. 1979). After a disturbance, N assimilation by vigorously growing forests has been shown to limit the loss of inorganic N (Vitousek 1977), and Vitousek and Reiners (1975) hypothesized that net ecosystem production controlled the pattern of N losses during succession.

However, it is less clear what controls N losses from intact forest with little disturbance to vegetation, such as the forested watersheds we sampled in the Catskills. Many factors could be responsible for the differences in stream water NO_3^- concentration we observed, including differences in: (1) atmospheric deposition rates; (2) groundwater influx into streams; (3) watershed topography, especially to the extent that topography influences hydrology; (4) net ecosystem production in the watershed, perhaps reflected in growth rates of the forest; (5) forest history and past land use; and (6) tree species composition. Many of these factors interact and may be interrelated. We can evaluate the likelihood of some of these factors using the data we have collected.

We do not think differences in atmospheric deposition of nitrogen are responsible for the variation in NO_3^- we observe in these Catskill streams because SO_4^{2-} concentrations are relatively invariant among streams (Table 1). In ecosystems with little SO_4^{2-} adsorption capacity such as the Catskills (Murdoch and Stoddard 1993), SO_4^{2-} in drainage waters reflects total atmospheric deposition of S (Mitchell et al. 1992). Atmospheric deposition of S and N tend to vary in concert in the northeastern U.S., with similar patterns across the region (Ollinger et al. 1993) and across elevational gradients in the mountainous areas (Miller et al. 1993). Consequently, if atmospheric deposition were very different among watersheds, we might expect to observe a large variation in SO_4^{2-} concentrations of stream water. In fact, we observed very little variation in SO_4^{2-}

FIG. 5. Relationship between mean NO_3^- and Ca^{2+} concentrations for the 39 streams. Different symbols represent the different groups identified in the cluster analysis (see *Methods: Atmospheric input and export calculations: Discharge and N export*).



(Table 1) and SO_4^{2-} and NO_3^- concentrations were not correlated within the data set ($r = -0.03$, $P = 0.84$).

Burns et al. (1998) suggested that deep groundwater in Catskill watersheds has high concentrations of NO_3^- because the groundwater is recharged during late fall and early spring periods when biological uptake of N is not active. Variations among watersheds in the influx of deep groundwater to the streams might then explain variations in NO_3^- concentration of stream water. Because this mechanism produces a lag in NO_3^- export of several months to several years (Burns et al. 1998), it is more likely to affect the seasonal pattern of NO_3^- concentration than the mean annual export. We might expect that the deep groundwater should also have high Ca^{2+} concentrations because of extended contact with bedrock or deep till that has been less highly weathered than surficial material. Murdoch and Stoddard (1993) attributed variations in base cation concentrations among Catskill streams to differences in groundwater influx, based on the observation that among-stream variation in base cation concentration was high in base-flow conditions, when groundwater dominates flow, but variation decreased with increasing discharge. If variations in groundwater sources is an important determinant of the variation in NO_3^- concentration, we would expect to observe a correlation between Ca^{2+} and NO_3^- . However, we find no significant correlation between mean Ca^{2+} and NO_3^- concentrations in the streams of our data set, either in the mean annual values (Fig. 5, $r = 0.23$, $P = 0.16$), in the winter ($r = 0.13$, $P = 0.41$), or even in the summer, when groundwater may be the dominant source of water in some streams ($r = 0.10$, $P = 0.56$). Silicon (Si) concentrations are also frequently used as an indicator of groundwater influence, but West (1999) found negative correlations between concentrations of NO_3^- and Si for these streams.

While NO_3^- and Ca^{2+} are poorly correlated in the overall data set, closer inspection of Fig. 5 reveals a significant correlation between these ions in the streams

with highest NO_3^- , i.e., groups 4 and 5 from the cluster analysis ($n = 15$ streams, $r = 0.70$, $P = 0.004$). We do not believe that this represents a groundwater influence on NO_3^- , however, because the correlation is stronger in the winter ($r = 0.54$) than in the summer ($r = 0.10$). This suggests to us that the correlation between NO_3^- and Ca^{2+} is a result of NO_3^- induced leaching of Ca^{2+} in the streams with highest NO_3^- .

In the overall data set and in the low- NO_3^- subset (groups 1, 2, and 3 from the cluster analysis) the strongest correlate with Ca^{2+} concentration is SO_4^{2-} concentration ($r = 0.51$, $P = 0.001$ for the overall data set and $r = 0.64$, $P = 0.0008$ for the low- NO_3^- subset) and the correlation between Ca^{2+} and NO_3^- is not significant. However, in the high- NO_3^- streams the correlation of Ca^{2+} with SO_4^{2-} is not significant but the correlation with NO_3^- is significant ($r = 0.70$, $P = 0.004$). This occurs despite the fact that mean SO_4^{2-} concentrations are higher than mean NO_3^- concentrations on a charge-equivalent basis in all the streams. This suggests that among-watershed variation in Ca^{2+} leaching is driven by SO_4^{2-} in the low- NO_3^- streams, but control of the variation switches to NO_3^- as concentrations of NO_3^- rise.

Mean NO_3^- concentration was poorly correlated with the physical features of the watersheds that one might expect to influence hydrologic residence time, such as watershed area ($r = -0.08$), length ($r = 0.02$), relief ($r = 0.18$), slope index ($r = 0.13$), and shape index ($r = -0.11$). This leads us to suspect that hydrologic variations are not producing the differences in NO_3^- concentrations we observe. No significant correlation was observed with these topographic variables either for the overall mean NO_3^- concentrations, mean summer concentrations, mean winter concentrations, or the amplitude of the seasonal fluctuation in ([mean winter concentration] - [mean summer concentration]).

In contrast, Dillon and Molot (1992) reported that watershed slope was correlated with NO_3^- export in 32 watersheds in central Ontario. Similarly, Creed and

Band (1998a) reported that topographic characteristics explained much of the variability in NO_3^- export from a cluster of small watersheds in southern Ontario. They suggested that topography controls both the production and flushing rate of NO_3^- from the watersheds (Creed and Band 1998b). The forests of the watersheds studied by Creed and Band are fairly homogeneous and dominated by a single species (sugar maple) (Creed and Band 1998a), which generates soils with high rates of NO_3^- production (Finzi et al. 1998; Lovett and Rueth 1999). Stream water NO_3^- concentrations varied by two- to threefold in the Creed and Band (1998a) data set, compared to 17-fold in our Catskill data set. Uniformly high production of NO_3^- in the watershed soils of the Creed and Band study may permit the expression of topographic and hydrologic controls on NO_3^- loss in stream water. In our data set, we suspect that biological controls on NO_3^- production and retention in the soils produce the broader range of NO_3^- concentrations we observe, and reduce the relative influence of topographic and hydrologic controls.

We do not have sufficient information to evaluate the other possible causal factors mentioned above: net ecosystem production, forest history, and species composition. These factors are probably highly interrelated and may be difficult to separate. Our qualitative reconnaissance of the watershed forests has given us some clues, however, which can guide further research. The three watersheds with lowest NO_3^- concentrations (Grog Kill, Tonshi Brook, and BWS6 Brook) all have forests in which red oak is a major dominant. In contrast, we found no oaks in the high- NO_3^- watersheds we have inspected to date (Hunter Creek, Mill Brook, Kelly Hollow Brook, Hollow Tree Brook, and Black Brook). Red oak has a poor-quality litter with high lignin:N ratio (Pastor and Post 1986) and low rates of nitrification (Finzi et al. 1998). American beech litter has lignin:N ratio and nitrification rates similar to red oak (Melillo et al. 1982, Finzi et al. 1998), and it is possible that variation in abundance of beech may cause differences in stream water NO_3^- concentrations in watersheds in which oak is not present. Lovett and Rueth (1999) showed that potential nitrification is significantly greater in maple stands than in beech stands in the Catskills.

The three watersheds with lowest NO_3^- also have several other characteristics in common. All three are have relatively low maximum elevations (Table 1) and lie on the fringes of the Catskills, nearer to more highly disturbed areas of the Hudson and Delaware River valleys (Fig. 1). As such, these watersheds have probably been subject to more intense disturbance over a longer period of time (dating back to fires set by Native Americans) than watersheds in the central Catskills. In fact, oak stands in the Catskills are thought by some to be indicative of a history of burning or heavy cutting or both (M. Kudish, *personal communication*). Either cutting or burning could reduce the N capital of an eco-

system and create a long-lasting legacy of reduced N availability (Aber and Driscoll 1997). Given the interdependence of forest history, forest growth rate, and species composition, it may be extremely difficult to distinguish their separate roles in controlling N export. Nonetheless, we hypothesize that some combination of these factors controls NO_3^- export from Catskill watersheds.

Organic nitrogen.—Organic N concentrations showed much less variation than NO_3^- , both seasonally (*data not shown*) and among streams (Table 1, Fig. 3). The factors that control TON concentrations in the streams are not evident from these data. There was a low but marginally significant positive correlation ($r = 0.37$, $P = 0.02$) between TON and watershed slope index, and a negative correlation between TON and NO_3^- ($r = -0.37$, $p = 0.02$). We expected, but did not observe, a significant correlation between TON and DOC ($r = 0.13$, $P = 0.43$, using all 145 samples for which DOC and TON were measured) perhaps because of the limited range and low concentrations of both DOC and TON. The mean concentration of DOC we measured in these Catskill streams ($72.9 \mu\text{mol/L}$) was much lower than concentrations measured by Hedin et al. (1995) in Chilean streams, where means ranged from 541 to $674 \mu\text{mol/L}$ in streams draining different forest types. However, the Catskill DOC concentrations are about the same as those in a stream at Coweeta, a hardwood forest site in the southeastern U.S. (mean = $67 \mu\text{mol/L}$, Qualls and Haines [1991]). The range of DOC in the Catskill streams (34 – $180 \mu\text{mol/L}$) also encompasses the range measured at 5 stream sampling points in the valley of the Hubbard Brook, New Hampshire (100 – $146 \mu\text{mol/L}$, McDowell and Likens [1988]). Our mean TON concentration ($4.9 \mu\text{mol/L}$) is lower than DON concentrations reported for streams in Chile (means ranged from 9.5 to $15.5 \mu\text{mol/L}$, Hedin et al. [1995]), but higher than DON concentrations at Coweeta (mean $1.9 \mu\text{mol/L}$, Qualls and Haines [1991]). The site in Chile studied by Hedin et al. (1995), which had relatively high concentrations of DOC and DON and low concentrations of NO_3^- in stream water (range 0.004 – $0.8 \mu\text{mol/L}$), is characterized by very wet conditions and frequently saturated soils. This could produce anaerobic conditions in the soil, which would inhibit complete decomposition and nitrification and enhance denitrification, perhaps leading to higher export of DOC and DON and lower export of NO_3^- in the streams.

Because the dissolved component of the TON must be transported from the watershed in association with DOC, the DOC:TON ratio must vary enough among our Catskill streams to obscure any correlation between the two variables. The DOC:TON ratio, expressed on a mass basis, in the samples averaged 18 ± 32 (mean ± 1 SD, $n = 141$ samples). In comparison, higher DOC:TON ratios were measured in the streams in Chile (means ranged from 39 to 49 , Hedin et al. [1995]) and in Coweeta (mean = 31 , Qualls and Haines [1991]).

Our relatively low DOC:TON ratio may be influenced by the exclusion of NH_4^+ in the calculation of TON or the fact that the samples were not filtered, yielding TON rather than DON measurements.

Conclusions and implications

Forested watersheds in the Catskill Mountains show a wide range of seasonal patterns and mean values of NO_3^- concentrations in stream water, indicating that the region contains watersheds in most stages of nitrogen saturation as it is commonly defined. Concentrations of NO_3^- vary 17-fold among the watersheds despite similar geology and rates of atmospheric deposition. This result implies that predicting nitrogen saturation from rates of N deposition will be complex and subject to a large amount of among-watershed variability. Likewise, attempting to model N export to downstream waters using a single retention coefficient for all forested watersheds is of questionable value unless the mean retention coefficient for the area under study is known accurately. We cannot yet explain the variation in N retention that we observe, but our data suggest that it does not result from variation in atmospheric deposition, watershed topography, or groundwater influx into streams. We hypothesize that between-watershed differences in species composition and forest history may explain much of the variation in N export and retention. Further exploration of the causes of variance in stream water N concentrations will help identify factors controlling N cycling and export in watersheds, and will lead to a better predictive knowledge of N saturation.

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