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Controls on nitrogen flux in alpine/subalpine watersheds of Colorado

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Abstract. High-altitude watersheds in the Front Range of Colorado show symptoms of advanced stages of nitrogen excess, despite having less nitrogen in atmospheric deposition than other regions where watersheds retain nitrogen. In two alpine/subalpine subbasins of the Loch Vale watershed, atmospheric deposition of NO_3^- plus NH_4^+ was 3.2–5.5 kg N ha^{-1}, and watershed export was 1.8–3.9 kg N ha^{-1} for water years 1992–1997. Annual N export increased in years with greater input of N, but most of the additional N was retained in the watershed, indicating that parts of the ecosystem are nitrogen-limited. Dissolved inorganic nitrogen (DIN) concentrations were greatest in subsurface water of talus landscapes, where mineralization and nitrification augment high rates of atmospheric deposition of N. Tundra landscapes had moderately high DIN concentrations, whereas forest and wetland landscapes had low concentrations, indicating little export of nitrogen from these landscapes. Between the two subbasins the catchment of Icy Brook had greater retention of nitrogen than that of Andrews Creek because of landscape and hydrologic characteristics that favor greater N assimilation in both the terrestrial and aquatic ecosystems. These results suggest that export of N from alpine/subalpine watersheds is caused by a combination of direct flushing of N from atmospheric deposition and release of N from ecosystem biogeochemical processes (N cycling). Sensitivity of alpine ecosystems in the western United States to atmospheric deposition of N is a function of landscape heterogeneity, hydrologic flow paths, and climatic extremes that limit primary productivity and microbial activity, which, in turn, control retention and release of nitrogen. Conceptual and mechanistic models of N excess that have been developed for forested ecosystems need to be modified in order to predict the response of alpine ecosystems to future changes in climate and atmospheric deposition of N.

1. Introduction

National parks, wilderness areas, and wildlife refuges are intended to be protected from air pollution damage under provisions of the Clean Air Act Amendments of 1977. The Federal land managers (National Park Service, U.S. Department of Agriculture Forest Service, and U.S. Fish and Wildlife Service) have a responsibility to protect air-quality-related values (AQRVs) in these class 1 areas. AQRVs include native vegetation, surface-water quality, ecosystem processes, and visibility. To carry out this responsibility, there is a need to characterize air pollution stressors and associated ecological responses, with a focus on the most sensitive resources in protected areas. Because many of the class 1 areas in the western United States are located at considerable distance from large point sources of air pollution, there is particular concern with regional pollutants that can be transported long distances. Regional pollutants include ozone, visibility-reducing particles, and sulfur and nitrogen compounds that are deposited in rain, snow, and dry deposition. Nitrogen oxide (NO_x) emissions from power plants, industries, and vehicles contribute to all three of these categories of air pollution. Expanded research and monitoring are needed to characterize the deposition of these nitrogen compounds and the effects of this added nitrogen on terrestrial and aquatic ecosystems, especially in the western United States.

Release of nitrogen from undisturbed watersheds occurs when atmospheric deposition of nitrogen exceeds assimilation capacity. This excess or "saturation" of nitrogen is symptomatic of a change in ecosystem nutrient-cycling processes [*Aber et al.*, 1989, 1998]. Degradation of terrestrial and aquatic components of the ecosystem from nitrogen deposition can occur directly as a result of changes in nutrient limitations that may increase primary productivity or alter species composition. Release of nitrate to surface waters also may contribute to episodic or chronic acidification in aquatic ecosystems. Anthropogenic emissions of nitrogen resulting in elevated deposition and release from ecosystems is documented in many parts of the world [*Stoddard*, 1994; *Dise and Wright*, 1995; *Tietema et al.*, 1998; *Fenn et al.*, 1998].

Symptoms of nitrogen excess occur in stages as increasing levels of nitrogen deposition disrupt ecosystem function [*Stoddard*, 1994]. Early stages are characterized by seasonal release of nitrogen; later stages show progressively more intense and longer duration episodes of nitrogen release. Some alpine and subalpine watersheds located in class 1 areas along the Front

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Range of Colorado release nitrogen in a pattern characteristic of advanced stages of nitrogen excess [*Williams et al.*, 1996; *Fenn et al.*, 1998]. Most previous studies of nitrogen excess in undisturbed watersheds have been in forested ecosystems, with very high rates of nitrogen deposition. In the Front Range, deposition rates are elevated compared to other areas in the Rocky Mountains but are moderate compared to other parts of the world that show symptoms of watershed N saturation. Front Range watersheds are a mix of subalpine areas that are primarily forested and alpine areas that contain only small areas of poorly developed soil and lack a deep groundwater-flow system. These alpine and subalpine ecosystems seem to be more sensitive to nitrogen deposition than the forested catchments that have been studied in other parts of the world.

Understanding of nitrogen cycling processes in alpine and subalpine watersheds has evolved considerably during the last decade. When nitrogen excess was first identified in these systems, it was believed that the alpine portions of these watersheds were "Teflon" basins, and the rapid release of water and solutes in snowmelt simply bypassed opportunities for uptake in soil and vegetation. Thus the spring nitrate pulse measured in the streams would be strictly the product of the ionic pulse of nitrate in snowmelt [*Williams and Melack*, 1991]. Alpine watersheds are now understood to be far more complex, with soil and shallow groundwater flow path systems hosting many biogeochemical processes previously associated with well-developed soils [*Williams et al.*, 1995; *Campbell et al.*, 1995a; *Kendall et al.*, 1995].

Biogeochemical processes in the alpine tundra environment have been studied intensively at the Niwot Ridge/Green Lakes Valley long-term ecological research (LTER) site. Air emissions in the Front Range urban corridor have been suggested as a source of elevated N deposition there [*Grant and Lewis*, 1982], and studies indicate that increased N inputs may cause changes in terrestrial plant species composition [*Bowman et al.*, 1993]. Export of nitrogen in surface water from Green Lakes Valley watershed has increased over the last 15 years [*Williams et al.*, 1996].

In the Loch Vale watershed in Rocky Mountain National Park, Colorado, alpine areas are a net source of nitrogen export year-round, whereas subalpine areas are a net source of nitrogen during spring and a sink for nitrogen during the other seasons [*Baron and Campbell*, 1997]. In this paper we examine atmospheric deposition, ecosystem retention, and watershed export of inorganic nitrogen in two alpine subbasins of the Loch Vale watershed for water years 1992–1997 in order to infer the role of various physical and biogeochemical processes in controlling watershed nitrogen budgets. Results from this spatially integrated watershed budget approach are compared to published measurements of nitrogen-cycling processes done at the plot scale in order to evaluate the relative importance of those processes in a heterogeneous environment. Spatial variability of dissolved inorganic nitrogen in surface water and groundwater in various landscapes is also examined.

2. Site Description

The Loch Vale watershed is located in Rocky Mountain National Park in the northern Front Range of Colorado and has been the focus of ecosystem research since 1981. A detailed description of physical setting and biogeochemistry of the Loch Vale ecosystem is given by *Baron* [1992]. Elevation of the Loch Vale watershed ranges from 3050 to 4026 m. The entire watershed consists of 83% bare rock, boulder fields, snow, and ice; 11% alpine ridge (tundra); 5% forest; and 1% subalpine meadow [*Baron*, 1992].

Hydrologic and inorganic nitrogen budgets for two subbasins of Loch Vale, Andrews Creek (183 ha) and Icy Brook (326 ha), are presented in this paper. Basin physical characteristics were quantified using digital topographic, vegetation, and geologic map coverages obtained from the National Park Service (R. Thomas, hydrologist, National Park Service, digital communication, 1999). Average slope in the basins is 32°–34°, with more than half of the basin area greater than 30°. These basins are primarily alpine; less than 1% of their areas are forested, and less than 20% of their areas are covered by vegetated soil (Figure 1). The area shown as rock consists of both bedrock and unconsolidated talus deposits. Differences between the basins include a more developed lake system in Icy Brook and a small glacier in Andrews Creek. Processes controlling major-ion chemistry in the two subbasins are discussed by *Campbell et al.* [1995b].

Climate is typical of midcontinent high-elevation zones, with an annual average of 110 cm of precipitation, of which 65–80% falls as snow [*Baron and Denning*, 1993]. Strong westerly winds redistribute the low-density snow during the winter months, removing snow from ridge top tundra and depositing it on slopes near the valley floor.

3. Methods

3.1. Data Collection

Snowpack chemical-composition samples were collected during a survey of the watershed that was conducted at the time of maximum snow accumulation in mid-April. Samples were depth-integrated snow cores collected in an aluminum Mount Rose sampler and transferred to zip-lock plastic bags. The sampler was rinsed by taking at least three snow cores before sample collection, and care was taken to exclude any soil and vegetation from the snow samples. The bags, bottles, and jars used for all chemical samples were rinsed 3 times with deionized water prior to use. Snow samples were transferred to polyethylene jars in the laboratory and allowed to melt at room temperature overnight. Snowmelt samples were collected daily or more frequently by automatic sampler from a snowmelt lysimeter, 6 m^2 in area, located in a forest clearing during 1994 and 1995.

National Atmospheric Deposition Program (NADP) data were collected for the Rocky Mountain National Park-Loch Vale site near the Icy Brook stream gauge (elevation 3159 m). Precipitation was measured in a weighing bucket, and weekly samples of wet fall were collected (National Atmospheric Deposition Program/National Trends Network (NADP/NTN), Illinois State Water Survey, Urbana, 1999, http://nadp.sws.uiuc.edu/) (hereinafter referred to as NADP/NTN, 1999).

Stream water samples were collected by manual and by automated methods; sampling frequency was intermittent during winter and was weekly or more frequent during spring, summer, and fall. Although sampling frequency was greater during water years 1992–1994 than in the last 3 years of the study, flux calculations were not substantially affected by this change because short-term changes in stream water concentrations were small except during a few days of early snowmelt when discharge was relatively low. Stream stage was recorded at 15-min intervals at the stream sampling sites during the

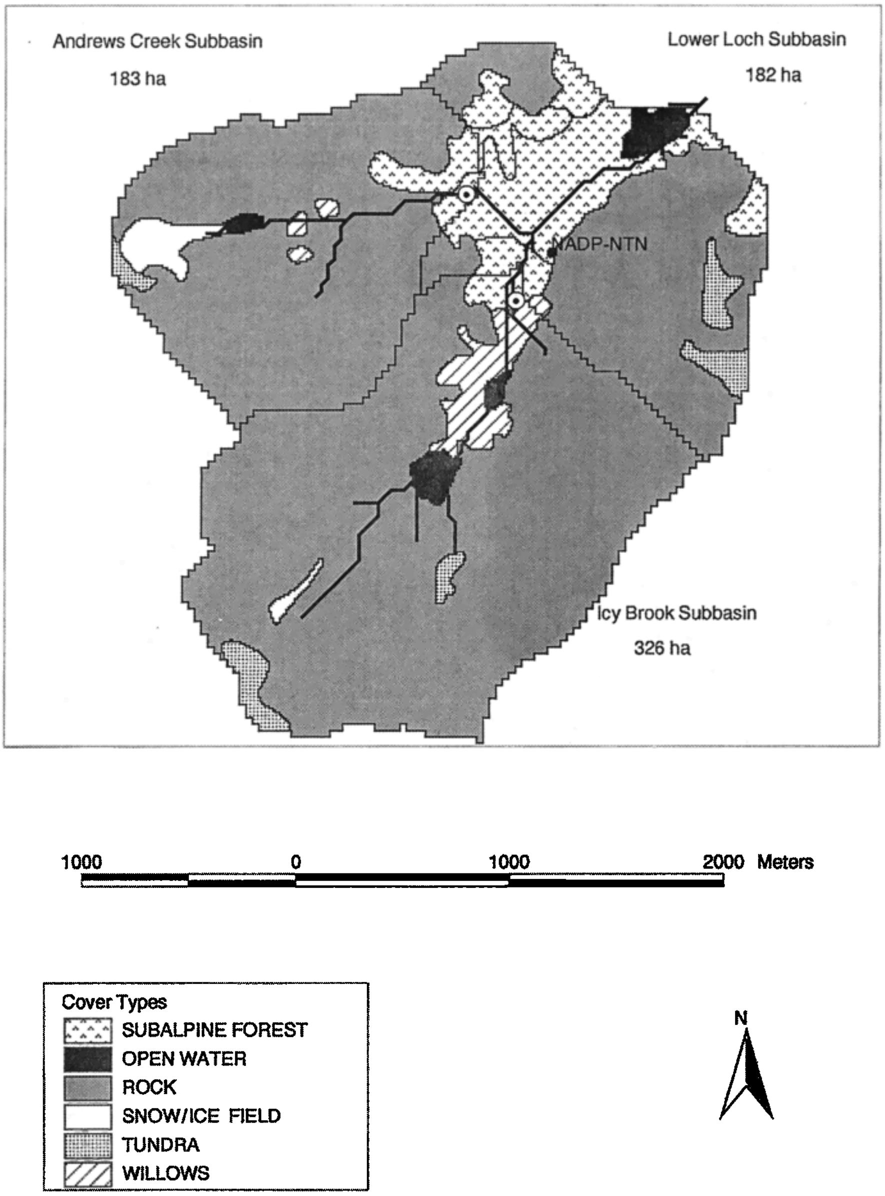

Figure 1. Landscape cover-type map for Loch Vale watershed, showing subbasin boundaries. Stream sampling locations are shown as a solid circle within an open circle, located on subbasin boundaries.

open-water season, and discharge was calculated from rating curves.

Tension lysimeters were used to collect soil water samples from a depth of approximately 0.5 m in forest soils from June to September in 1994 and 1995. Grab samples from seeps located at the base of talus and soil water from tension lysimeters located in a small forested area at the base of a talus field both reflected the composition of subsurface water from talus deposits. Data are presented for synoptic surveys and time series of a subset of springs and lysimeters (June–September in 1994 and 1995). Shallow groundwater from wetlands was sampled from a series of water table wells located in three separate wetland areas (June–September in 1994 and 1995). Grab samples of seeps and springs found in and just below tundra areas were sampled as part of a synoptic survey during June 1996.

Filtered (0.45 μm), unpreserved, refrigerated aliquots were used to analyze NO_3^- by ion chromatography (detection limit was 0.5 μeq L^{-1}). For NH_4^+, filtered aliquots preserved with mercuric chloride were analyzed colorimetrically (detection limit was 1 μeq L^{-1}) during 1992–1994; unpreserved, refrigerated, filtered aliquots were analyzed by ion chromatography (detection limit was 0.7 μeq L^{-1}) during 1995–1997. Experiments showed that samples analyzed within 2 weeks of collection had no detectable loss of NH_4^+.

3.2. Estimation of Inputs

The NADP/NTN site provides the most consistent, long-term record of precipitation amounts and chemical concentrations for the watershed. However, weighing-bucket rain gauges are prone to large measurement errors in windy alpine environments [*Williams et al.*, 1998], and spatial variability of snow accumulation confounds extrapolation of point measurement of precipitation. On the basis of water-budget calculations discussed in section 4.1, October–March precipitation amounts

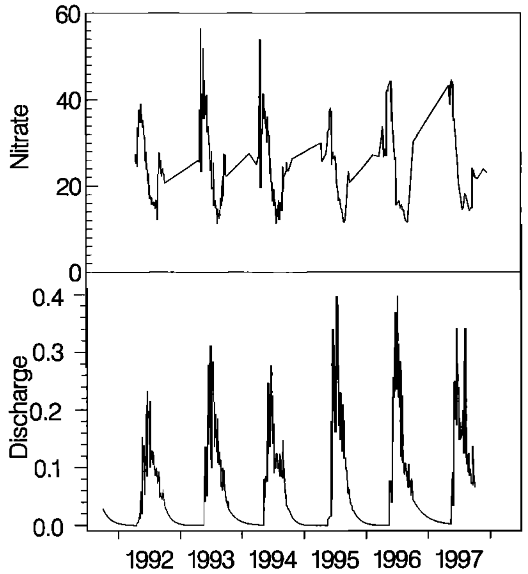

Figure 2. Time series plot of mean daily discharge (m^3 s^{-1}) and nitrate concentration (μeq L^{-1}) for Andrews Creek for water years 1992–1997.

from the NADP/NTN site were adjusted by +20% and −20% for the Andrews Creek and Icy Brook subbasins, respectively. The NADP/NTN precipitation amounts were used without modification for the remainder of the year, because wet spring snows and summer rains are less subject to redistribution by wind.

Dry deposition for the winter months was included in input calculations by combining snowpack chemical concentrations with the adjusted NADP/NTN October–March precipitation amounts to produce total (wet plus dry) deposition for the period. Wet deposition for spring and summer was calculated from NADP/NTN volume-weighted mean (VWM) concentrations. Dry deposition for spring and summer months was estimated from a dry-deposition monitoring site near Long's Peak, approximately 10 km SE at an elevation of 2850 m (Clean Air Status and Trends Network (CASTNet, U.S. Environmental Protection Agency, Washington, D. C., 1999, http://www.epa.gov/acidrain/castnet/). At this site, ambient air concentrations of HNO_3, NO_3^-, and NH_4^+ are measured weekly, and fluxes are calculated using deposition velocities. Nearly complete records were available for April–September of water years 1995–1997; weekly values were averaged for each year and multiplied by the number of weeks during the period. Because the seasonal totals were roughly equal for the 3 years (range = 0.86–0.92 kg ha^{-1}), the mean value of 0.88 kg ha^{-1} was used for all years of this study.

3.3. Estimation of Outputs

The discharge record was extended through the winter months by using a logarithmic extrapolation of streamflow recession. Total estimated winter discharge was only 3–15% of total annual discharge, so errors from the extrapolation were not likely significant in annual budgets. Daily stream water export of N was calculated as the product of measured or extrapolated daily discharge values and the most recent measured concentration of NO_3^-. This method works well because stream water NO_3^- concentrations follow a seasonal pattern rather than responding rapidly to changes in discharge [*Campbell et al.*, 1995b].

4. Results

4.1. Water Budget

The spatial variability in snow accumulation caused by wind redistribution of snow [*Hartmann et al.*, 1999; *Balk and Elder*, this issue] combined with inaccessibility of large areas in the watershed [*Balk and Elder*, this issue] makes actual measurement of snowpack water content difficult in the Loch Vale watershed. In catchments with small net annual change in the groundwater storage, subtraction of runoff from precipitation roughly equals annual loss due to sublimation and evapotranspiration (ET). Comparison of annual ET loss to precipitation amount provides a check on errors in the estimation of precipitation inputs because errors in estimating precipitation are much greater than errors in measuring surface-water discharge. Using unadjusted NADP/NTN data, losses due to ET average 22% of annual precipitation for Andrews subbasin and 37% for Icy Brook, suggesting underestimation and overestimation of precipitation, respectively. In this paper, NADP/NTN winter precipitation (October–March only) is adjusted by +20% for Andrews Creek and −20% for Icy Brook. This adjustment yields losses that average 30% of annual precipitation for Andrews Creek and 32% for Icy Brook.

The adjustment to winter precipitation is supported by the results of *Hartmann et al.* [1999], using the regional hydroecological simulation system (RHESSys) model to simulate snow redistribution, elevation partitioning, and wind-driven sublimation in the Loch Vale watershed. Total estimated precipitation inputs to the Loch Vale watershed averaged 114.2 cm for 6 years of record, during which NADP precipitation averaged 100.7 cm. Model results indicated less snow deposition and more sublimation in Andrews Creek than in Icy Brook (M. Hartmann, Colorado State University, personal communication, 1999); however, it was noted that the model did not account for transport across watershed boundaries, particularly in tundra areas on the east side of the Icy Brook subbasin where snow does not accumulate because of wind scour. Losses due to ET averaged 36% of adjusted precipitation inputs for the entire Loch Vale watershed, which includes more forested area than the upper subbasins examined in this study. *Balk and Elder* [this issue] combined a binary decision tree and geostatistical techniques to model the spatial distribution of snow in the Loch Vale watershed. Their results showed relatively high snow water equivalence (SWE) accumulations in the Andrews Creek subcatchment from deposition of blowing snow and relatively low SWE accumulations in the Icy Brook subcatchment due to wind scour, also supporting the adjustments to precipitation used in this investigation.

The timing, peak discharge, and duration of high flows associated with snowmelt varied somewhat between years depending on climatic conditions. The shape of the hydrograph, in turn, largely determined the variance in the seasonal pattern of NO_3^- concentrations in the streams (Figure 2).

4.2. Inorganic Nitrogen Inputs

Concentrations of NH_4^+ and NO_3^- were similar in NADP October–March precipitation and in snowpack samples collected in early April (Table 1), usually differing by 2 μeq L^{-1} or less. There was no bias for higher concentrations in either type of sample, indicating that dry deposition was not substantial during the winter months. Concentrations of NH_4^+ and NO_3^- were lower in October–March than in other seasons in all years; NO_3^- concentration was always highest in July–

Table 1. Water Amount and Volume-Weighted Mean Inorganic Nitrogen Concentrations in Precipitation and Runoff, Seasonally and by Water Year

	1992	1993	1994	1995	1996	1997
Water Amount, cm						
NADP precipitation, October–March	47	58	66	64	73	76
NADP precipitation, April–June	24	35	23	58	25	43
NADP precipitation, July–September	20	21	29	20	27	29
NADP precipitation, water year total	91	114	118	142	125	148
Adjusted annual precipitation, Andrews subbasin	100	126	131	155	140	163
Annual runoff, Andrews subbasin	76	92	87	103	104	112
Adjusted annual precipitation, Icy subbasin	82	102	105	129	110	133
Annual runoff, Icy subbasin	60	79	69	78	71	93
Ammonium Concentration, μeq/L						
Snowpack mean, April	6.2	3.3	7.3	5.0	4.4	7.2
NADP precipitation, October–March	3.1	4.2	9.6	3.4	5.9	3.3
NADP precipitation, April–June	11.4	7.1	15.1	6.3	10.4	7.9
NADP precipitation, July–September	9.9	13.7	11.7	11.3	11.0	7.2
NADP precipitation, water year VWM	6.8	6.8	11.2	5.7	7.9	5.4
Andrews Creek, water year VWM	<1	1	<1	<1	<1	<1
Icy Brook, water year VWM	1	<1	<1	<1	<1	<1
Nitrate Concentration, μeq/L						
Snowpack mean, April	9.6	9.0	14.4	10.6	7.6	12.3
NADP precipitation, October–March	7.9	10.3	13.0	9.7	9.0	8.7
NADP precipitation, April–June	13.7	12.1	16.6	8.2	14.1	11.3
NADP precipitation, July–September	14.0	17.7	18.4	16.3	12.6	11.4
NADP precipitation, water year VWM	10.8	12.2	15.1	10.0	10.8	10.0
Andrews Creek, water year VWM	23	23	23	22	22	25
Icy Brook, water year VWM	22	21	19	18	18	20

VWM, volume-weighted mean; NADP, National Atmospheric Deposition Program.

September, and NH_4^+ was highest either in April–June or in July–September.

Highest concentrations of inorganic N in precipitation occurred in 1994. Both NH_4^+ and NO_3^- were high in all seasons that year. Other NADP sites in the region also had high concentrations of NH_4^+ and NO_3^- in 1994 relative to other years, indicating that high deposition of N was widespread (NADP/NTN, 1999). Loch Vale snowpack concentrations of both species were also highest in 1994, making sampling or analytical bias unlikely.

April–September dry deposition of 0.88 kg N ha^{-1} was 47% of the 6-year mean April–September wet deposition. Ambient air concentrations and deposition velocities have been used to estimate dry deposition values for Niwot Ridge that were equal to or greater than wet deposition during May–September but were much less during the winter [*Sievering et al.*, 1992, 1996]. Estimates of dry deposition can also be calculated by comparing bulk deposition to wet deposition; *Arthur and Fahey* [1993] measured concentrations in bulk deposition that were 40% greater than wet fall for NH_4^+ and were 36% greater than wet fall for NO_3^- in Loch Vale during May–October of 1986 and 1987. Similar measurements by *Ranalli et al.* [1997] showed ratios of 30–45% for NH_4^+ and 10–30% for NO_3^- for data from two sites in western Colorado that were monitored from May to September in the years 1984–1990. The estimate of April–September dry deposition used in this study from the CASTNet site falls roughly in the middle of these estimates using various techniques.

4.3. Watershed Retention and Export of Inorganic N

Annual VWM concentrations of NO_3^- in Andrews Creek and Icy Brook ranged from 22 to 25 μeq L^{-1} and 18 to 22 μeq L^{-1}, respectively (Table 1). Concentrations of NO_3^- in Andrews Creek were around 25–30 μeq L^{-1} during baseflow preceding snowmelt (Figure 2). During early snowmelt, concentrations increased to 40 μeq L^{-1}, occasionally spiking above 50 μeq L^{-1}. During peak snowmelt runoff, concentrations began to decrease, reaching a minimum of 12 μeq L^{-1} in late summer. In late August or early September, concentrations began to increase and were above 20 μeq L^{-1} by the end of September. Seasonal patterns of concentrations of NO_3^- in Icy Brook were similar to those in Andrews Creek, except during the early part of snowmelt runoff and during late summer and early autumn when they were significantly lower [*Campbell et al.*, 1995b]. There was little or no NH_4^+ in either of the streams throughout the year.

Annual export of inorganic N in the streams was 1.8–3.9 kg ha^{-1} and was consistently greater in the Andrews Creek subbasin (Table 2 and Figure 3). Annual retention was 0.7–2.8 kg ha^{-1} and was consistently higher in the Icy Brook subbasin (Table 2 and Figure 3).

4.4. Dissolved Inorganic N From Different Landscapes

Concentration distributions of NO_3^- from surface water and groundwater in different landscapes for 1994–1995 are compared to snowpack and snowmelt (Figure 4). Median concentrations of NO_3^- in snowpack and snowmelt lysimeter samples were around 10–13 μeq L^{-1}; early during the ionic pulse, snowmelt concentrations reached 40–60 μeq L^{-1}, but levels decreased rapidly to near the VWM in the snowpack during the period when most of the melt occurred. Snowpack and rainfall had moderate concentrations of NH_4^+ with a small range; snowmelt concentrations were of similar magnitude but with a greater range because of the early-season ionic pulse.

In the tundra, water sampled from small seeps, springs, and streams had NO_3^- concentrations ranging from 3 to greater than 60 μeq L^{-1}. Groundwater emerging from talus deposits contained high concentrations of NO_3^-, with large temporal

Table 2. Input (Wet Fall Plus Dry Fall), Export, and Retention of Dissolved Inorganic Nitrogen by Water Year

	Andrews Creek				Icy Brook			
Water Year	Input DIN, kg ha^{-1}	Export DIN, kg ha^{-1}	Net Retention DIN, kg ha^{-1}	Percent Retention DIN*	Input DIN, kg ha^{-1}	Export DIN, kg ha^{-1}	Net Retention DIN, kg ha^{-1}	Percent Retention DIN*
1992	3.6	2.5	1.1	31	3.2	1.9	1.3	41
1993	3.9	3.2	0.7	19	3.5	2.4	1.1	32
1994	5.5	2.9	2.6	48	4.7	1.9	2.8	60
1995	4.5	3.2	1.3	29	4.0	2.0	2.0	49
1996	4.1	3.2	0.9	22	3.6	1.8	1.8	50
1997	5.3	3.9	1.4	26	4.5	2.7	1.8	39
6-year mean	4.5	3.2	1.4	29	3.9	2.1	1.8	45

DIN, dissolved inorganic nitrogen.
*Percent of input.

and spatial variance. Forest soil waters and shallow groundwater from water table wells located in wetlands had little or no NO_3^- throughout the growing season. Some of the wetland groundwater samples contained small but measurable concentrations of NH_4^+, whereas most surface water and groundwater from other landscapes had none.

5. Discussion

5.1. Nitrogen Export and Retention

The relations between deposition, retention, and export of N are used here to infer nitrogen-cycling processes at the watershed scale. Whereas actual measurements of nitrogen-cycling processes are generally done at the plot scale, the relative importance of those processes in a heterogeneous environment can be validated using watershed budgets. Export of inorganic N averaged 71% of total inputs in the Andrews Creek subbasin and 54% in the Icy Brook subbasin (Table 2), indicating that these watersheds are more sensitive to N deposition than other watersheds studied in North America, where N export was less than 50% of wet fall N inputs for comparable amounts of N in wet fall [*Stoddard*, 1994].

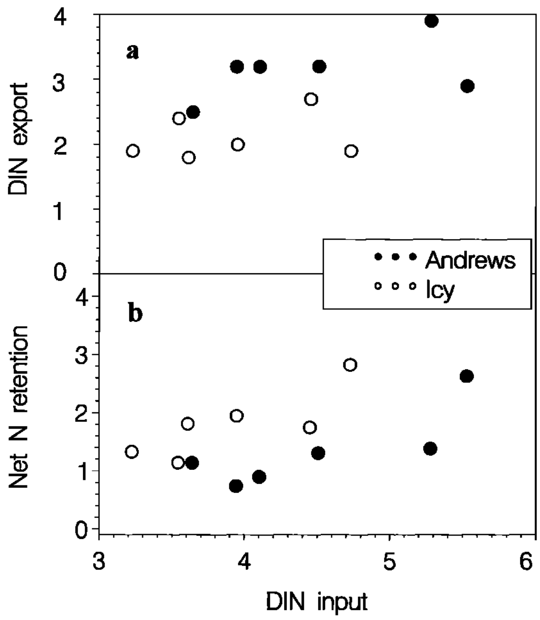

Figure 3. Dissolved inorganic nitrogen fluxes (kg ha^{-1}): (a) annual export and (b) net retention versus input for Andrews Creek and Icy Brook subbasins for water years 1992–1997 is shown.

These calculations of N export do not include particulate organic nitrogen (PON) or dissolved organic nitrogen (DON); additional study of both PON and DON is needed to better understand organic nitrogen fluxes and nitrogen cycling in alpine and subalpine ecosystems. *Baron and Campbell* [1997] estimated that organic N amounted to less than 20% of total watershed N export in Loch Vale, almost entirely in particulate form. *McKnight et al.* [1997] did a detailed characterization of particulate, colloidal, and dissolved organic material during late-summer base flow conditions in Loch Vale, but seasonal patterns of organic material fluxes and nitrogen content have not been quantified.

5.1.1. Interannual variability. If release of N from alpine watersheds is caused by direct flushing of atmospherically deposited N during snowmelt [*Baron et al.*, 1995; *Campbell et al.*, 1995a; *Williams et al.*, 1995], then greater N inputs should cause greater N export. However, there was only a weak relation between annual export of DIN and annual deposition (r^2 = 0.31, p = 0.06, and n = 12 for both subbasins

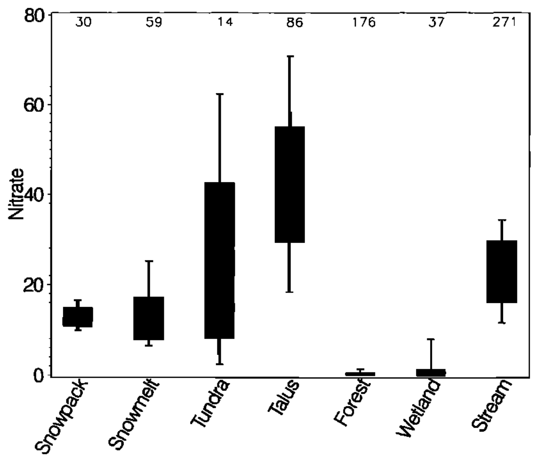

Figure 4. Box and whisker diagram showing distribution of nitrate concentrations (μeq L^{-1}) in atmospheric deposition (snow and snowmelt), surface water (tundra rivulets and subbasin streams), and groundwater (talus, forest, and wetlands). Boxes represent 25th, 50th (median), and 75th percentiles of population; whiskers represent 10th and 90th percentiles. Number of samples for each category is presented above boxes.

combined; the relation was not significant for either subbasin independently) (Figure 3a), suggesting that N cycling processes may control the release of N from the subbasins.

There was a strong positive relation between N retention and N inputs (Figure 3b). N inputs explained 64% of the interannual variance in N retention in the Andrews Creek subbasin (slope = 0.71, $p = 0.06$, and $n = 6$) and 66% in the Icy Brook subbasin (slope = 0.83, $p = 0.05$, and $n = 6$). These results were leveraged by high inputs and retention in 1994. N retention was not related to annual precipitation or runoff amount, indicating that the relation between retention and input was driven by nitrogen concentrations rather than amounts of water. The relation between retention and input of nitrogen in these subbasins is consistent with stage 2 of watershed nitrogen saturation [*Aber et al.*, 1989; *Stoddard*, 1994], characterized by at least partial nitrogen limitation during the growing season and nitrogen saturation during other seasons. We hypothesize that the response of these alpine subbasins to elevated nitrogen deposition can be explained not only by the seasonality of N-cycling processes that has been documented in forest watersheds but also by the heterogeneity of land-cover types, discussed in section 5.2.

5.1.2. Differences between the subbasins. Retention of nitrogen in the Icy Brook subbasin was consistently greater than retention in the Andrews Creek subbasin; the mean difference in nitrogen retention between the subbasins was 0.55 kg ha^{-1}. The most obvious difference between the two subbasins is the effect of algal uptake in Sky Pond and Glass Lake in the Icy Brook drainage, whereas in Andrews Tarn in the Andrews Creek drainage algal uptake has little effect because of its small area and shallow depth [*Campbell et al.*, 1995b]. Total annual PON export in algal biomass was estimated between 14 and 22% of DIN export for the Loch Vale watershed [*Baron and Campbell*, 1997], based on algal biomass calculated from measurement of chlorophyll a [*McKnight et al.*, 1986, 1988]. That percentage is likely similar for the Icy Brook subbasin, but the percentage is much less for the Andrews Creek subbasin. Late-summer concentrations of particulate matter in Icy Brook were about 3 times greater than those in Andrews Creek [*McKnight et al.*, 1997]. Most of this difference was attributed to algal biomass, based on characterization of organic compounds and $\delta^{13}C$. These results suggest that at least some of the DIN "retention" calculated in this study for the Icy Brook subbasin is actually organic nitrogen that is exported in stream water.

An alternate explanation for the difference between the subbasins is the effect of watershed characteristics on terrestrial nitrogen-cycling processes. *Creed and Band* [1998] hypothesized that catchment topography determines source-area dynamics that control flushing of nitrate from catchments. The importance of watershed characteristics such as slope, cover type, and surficial geology in controlling stream water chemistry was identified in comparisons of solute budgets between Andrews Creek, Icy Brook, and other watersheds in Rocky Mountain National Park [*Clow and Sueker*, this issue]. Both the Andrews Creek and Icy Brook subbasins have less than 20% of total area covered by vegetation. However, application of the alpine hydrochemical model to Andrews Creek and Green Lakes Valley watersheds indicated that the relative position of soil and talus deposits along hydrologic flow paths affected biogeochemical processes controlling N fluxes [*Meixner et al.*, this issue]. Analysis of cover type in the riparian zone (defined as a 100-m-wide buffer strip surrounding the stream channels) indicated that 36% of the riparian zone for Icy Brook was covered by vegetation, compared to 19% for Andrews Creek. Similar analysis of the surficial geology indicated that 19% of this Icy Brook riparian zone is covered by talus, compared to 61% for Andrews Creek. These differences suggest that more vegetation and less talus in the riparian zone may contribute to greater N retention in the Icy Brook subbasin (discussed in section 5.2).

5.2. Hydrology and Biogeochemical Processes in Different Landscapes

Both interannual variability within subbasins and differences between the subbasins in N retention emphasize the importance of landscape heterogeneity in controlling nitrogen fluxes in alpine and subalpine watersheds. Hydrology and biogeochemical processes in different landscapes are discussed in sections 5.2.1–5.2.4 and summarized in Table 3.

5.2.1. Forested landscapes. Concentrations of NO_3^- in soil and groundwater from forested areas generally were low compared to alpine tundra and talus deposits (Figure 4). There was little NO_3^- or NH_4^+ present in forest soil water throughout most of the growing season, although concentrations of NO_3^- were as high as 10 μeq L^{-1} during early spring. This seasonal pattern is consistent with fluxes calculated for subbasins of the Loch Vale watershed that showed net release of N from the subalpine zone during snowmelt and net retention of N during other seasons [*Baron and Campbell*, 1997]. Seasonal release of N is characteristic of early stages of nitrogen excess and has been observed in other forest ecosystems with moderate to high deposition [*Stoddard*, 1994]. Some seasonal release of N from forested ecosystems in the Rocky Mountains is likely driven by physical limitations that limit demand and opportunity for biological uptake of N. These limitations include hydrologic flow paths that bypass biologically active systems, the large pulse of N-rich water that occurs over a short time period, and cold air, soil, and water temperatures that prevail for most of the year [*Baron*, 1992]. At this time (1999), subalpine forests are not large sources of the NO_3^- exported in streamflow.

5.2.2. Wetland landscapes. Wetlands make up less than 1% of the Loch Vale watershed area; however, they are typically located along riparian corridors, where direct hydraulic linkages maximize their opportunity to affect stream water export of N [*Clow and Sueker*, this issue]. Much of the substrate in the wetlands has low hydraulic conductivity, and most of the water passing through the wetlands flows over them as surface runoff with short residence time and minimal contact with soil and vegetation [*Bachman*, 1994]. Previous studies concluded that wetlands have little effect on nitrogen loading in the streams [*Huang et al.*, 1996]. In this study, samples collected from shallow water table wells in wetlands had no NO_3^-, indicating that wetlands are not a net source of NO_3^- for the streams. Some wetland groundwater samples in this study contained small concentrations of NH_4^+ (0–6 μeq L^{-1}), indicating that nitrogen transformations associated with anoxic conditions may occur in portions of the wetlands. However, the wetlands are small and denitrification is not believed to be significant to overall watershed N budgets [*Baron and Campbell*, 1997].

5.2.3. Tundra landscapes. Water collected in many of the samples from alpine tundra areas in this study contained moderately high concentrations of NO_3^-. All of these samples were collected in early June of 1996, when snowmelt runoff was increasing in high-elevation parts of the watershed; how-

Table 3. Hydrologic Characteristics and Biogeochemical Processes in Different Landscapes

Landscape	Hydrologic Characteristics	Biogeochemical Processes
Snowpack and direct snowmelt	NH_4^+ and NO_3^- accumulation in snowpack throughout winter and release in spring and early summer; variation in timing of melt within basin	NH_4^+ and NO_3^- conservative in snowpack and snowmelt during winter and spring ionic pulse resulting in high concentrations during early melt contribution from dry deposition
Forest	relatively uniform, average snow accumulation; mature spruce-fir vegetation; relatively well-developed soils; covers much of the lower basin	little to no inorganic N in soil solutions microbial cycling in soils assimilation by vegetation seasonally important source of water, not a source of N to surface waters
Wetlands	1% or less of total watershed area; often in riparian zone; much of the water flows over, rather than through, the peat soils suggested by recent work	vegetation assimilation of some N in waters coming from talus loss of N by denitrification not important not an important source of subsurface water or N to surface waters
Tundra	little snow accumulation; poorly developed soil with alpine vegetation; mostly subsurface water; drainage to cliffs and talus via fractures and small streams	microbial cycling in soils assimilation by vegetation not a large source of water to surface waters seasonally moderate concentrations of N
Talus	snow accumulation range from small to large; substrate range from house- to clay-sized particles; large groundwater storage reservoir with seasonally variable hydrologic residence time	microbially mediated mineralization and nitrification in talus substrate resulting in little NH_4^+ but very high NO_3^- in groundwater sparse vegetation unable to assimilate large amounts of N large source of water and N to surface waters
Lakes and streams	hydrograph dominated by snowmelt; short hydrologic residence time during peak flows; long residence time during fall, winter, and spring	more than half of catchment inorganic N inputs released in surface waters phytoplankton assimilation of N important seasonally some export of particulate and dissolved organic N

ever, the springs, seeps, and small rivulets in the tundra areas had very low discharge, and snowcover was patchy or absent. Much of the tundra is wind-scoured all winter, and little snow accumulates. Some of the rivulets that flowed through the tundra emerged from snowdrifts or scree fields and dried up before reaching the cliffs above the valley floor, indicating that water from the snowdrifts and scree was recharging tundra soils rather than directly contributing to streamflow, even during peak snowmelt. Nitrogen in this recharge water may be assimilated by alpine vegetation and soil microbes; as organic nitrogen, it could be permanently immobilized in the soils, exported in organic form, or mineralized and exported. The recharge water may also reach deeper subsurface flow paths that contribute to streamflow with little opportunity for nitrogen cycling.

At Niwot Ridge/Green Lakes Valley LTER site (40 km south of Loch Vale), extensive nutrient-cycling studies have been conducted in the tundra ecosystem. During the growing season, fertilization experiments [*Bowman et al.*, 1993] and comparison of net N mineralization versus vegetative N demand [*Fisk and Schmidt*, 1995] indicate that this system is N-limited. The greatest amounts of soil inorganic N are typically available during the spring snowmelt season [*Brooks et al.*, 1996]. During this period, tundra soils may serve as net sources or net sinks of N to the watershed, depending on the timing and depth of snowcover during the previous winter [*Brooks et al.*, 1998]. Biologically mediated N retention in the relatively well-developed Green Lakes Valley soils probably accounts for the observation that watershed N excess is less advanced in Green Lakes Valley than in the Loch Vale watershed [*Williams et al.*, 1996].

5.2.4. Bedrock and talus landscapes. Landscapes discussed so far (forest, wetland, and tundra) all have established vegetation and developed soils that retain much of the N from atmospheric deposition; these areas do not contribute substantially to N export in surface water. Bedrock and talus are the only major landscape units that have not been eliminated as significant sources of N export in streamflow. Recent studies have suggested that landscapes classified primarily as bedrock may actually have substantial biological and geochemical activity for nitrogen assimilation [*Meixner et al.*, 1998]. Talus slopes were once believed to be of minimal importance hydrologically and biogeochemically, and as such, talus was often considered equivalent to exposed bedrock. However, this and other recent work indicate that talus deposits play a key role in controlling the hydrology and chemical composition of alpine streams [*Campbell et al.*, 1995b; *Williams et al.*, 1997], especially in Loch Vale where greater than 80% of the catchment is classified as unvegetated.

Groundwater springs discharging from talus deposits had concentrations of NO_3^- that greatly exceeded precipitation or snowmelt concentrations of DIN. The NH_4^+ from atmospheric deposition is absent from talus groundwater, indicating that it is either retained as NH_4^+ sorbed to cation exchange sites, assimilated by plants or microbes, nitrified to NO_3^-, or some combination of these. Adsorption may be a mechanism for temporary storage of atmospherically deposited NH_4^+, but the sorbed NH_4^+ remains readily available for and is in demand by other biogeochemical processes [*Williams et al.*, 1995]. The scarcity of vegetative cover limits opportunity for long-term nitrogen immobilization in plant biomass, leaving microbial assimilation, remineralization, and nitrification as the most likely fate of atmospherically derived NH_4^+ in talus.

Recent work in talus landscapes of nearby Niwot Ridge has demonstrated that the talus environment supports active microbial communities in both surface and subsurface pockets of fine material [*Williams et al.*, 1997]. In contrast to well-developed, vegetated soils, these soil-like pockets of fine material are very low in organic carbon, averaging approximately 1% by weight. While microbial communities may provide a short-term sink for N in infiltrating rain and snowmelt, this N pool probably turns over quite rapidly, as has been demonstrated for tundra soils during snowmelt [*Brooks et al.*, 1998] and thereafter [*Fisk and Schmidt*, 1995]. The combination of an active microbial community, a carbon-limited environment, and readily available NH_4^+ from atmospheric deposition favors nitrification [*Schlessinger*, 1991] and is consistent with high NO_3^- concentrations from the talus seeps. Because pools of organic nitrogen in tundra and talus are large relative to annual fluxes, small changes in pool sizes driven by microbial processes can substantially affect annual watershed fluxes of nitrogen [*Williams et al.*, 1997]. The landscape position of talus adjacent to and at lower elevation than the tundra makes it possible that some of the nitrogen that appears to be retained in the tundra is exported to the talus as organic nitrogen. Both inorganic and organic N may also reach the talus via subsurface flow paths and contribute to the high NO_3^- concentrations in the talus seeps.

The large areal extent of talus deposits, along with their high concentrations of NO_3^- and capacity to store groundwater, make talus the most likely source of NO_3^- in streamflow, especially during the growing season. The $\delta^{15}N$ and $\delta^{18}O$ isotopic signatures show that most of the stream water NO_3^- has been microbially cycled [*Kendall et al.*, 1995], indicating that talus areas support substantial biogeochemical processes but have little capacity for long-term retention of additional N inputs. N cycling in talus remains poorly understood and merits additional investigation, especially with respect to its potential for contributing to elevated concentrations of N in alpine and subalpine surface waters.

5.3. Climatic Controls on Fluxes of Water and Nitrogen

Spatial and temporal heterogeneity of precipitation contributes substantially to release of nitrogen from these alpine watersheds. Winter winds blowing off the Continental Divide scour snow from ridge tops and redeposit it on slopes adjacent to the valley bottom. This redistribution of snowfall causes atmospheric deposition to be less in ridge top tundra areas and greater in talus deposits compared to measured values at the NADP site in a forest clearing. This is demonstrated in depletion curves for the snow-covered area of Andrews Creek subbasin in 1994 and 1996, where maximum snow cover reached 60–80% in talus and bedrock areas compared to 20–50% in areas with developed soils [*Meixner et al.*, this issue].

Summer rainfall is not subject to redistribution by wind (as winter snow is); therefore the seasonal distribution of precipitation (snow versus rain) affects the spatial distribution of precipitation amount and wet deposition of nitrogen. In years with relatively more precipitation in winter than in summer, a larger percentage of the precipitation and nitrogen deposition go to talus deposit areas that have little nitrogen assimilation capacity. In years with more summer precipitation the opposite occurs, with more potential for assimilation in the tundra. Summer precipitation also promotes plant growth in the tundra (and in talus deposits) by preventing desiccation of the thin, coarse soils. These factors may explain the positive relation between annual N retention and summer (July–September) N deposition ($r^2 = 0.43$, $p = 0.02$, and $n = 12$ for the subbasins combined). This relation is leveraged by the 1994 water year, which had both the greatest N retention and a large amount of summer precipitation with high N concentrations. This high N deposition during the period of greatest ecosystem N demand was unlike most years, when most of the N from deposition is delivered to the ecosystem during snowmelt prior to peak demand for N in the summer. The interaction of spatially heterogeneous processes that are sensitive to seasonal variability indicates that a spatially distributed modeling approach is needed to account for nitrogen-cycling processes in these watersheds.

Physical stressors such as temperature and moisture likely are more important than nutrient limitations in controlling productivity of plant and microbial communities in high-elevation ecosystems. Climatic extremes limit the capacity of the ecosystem to sequester nitrogen inputs; the growing season is short in all alpine and subalpine areas, and redeposition of windblown snow favors talus deposit areas most sensitive to nitrogen deposition. In watersheds of the northeastern United States, years with cold winter temperatures had the greatest export of N, caused by release of N when soils froze [*Mitchell et al.*, 1996]. In most years the Rocky Mountains have sufficient snow cover to insulate soils and prevent freezing despite cold temperatures.

Previous studies have suggested the importance of seasonal snow cover in controlling microbial N assimilation in tundra landscapes and thus in controlling N export from the entire Loch Vale watershed [*Brooks et al.*, 1999]. Nitrogen assimilation in subalpine forests and meadows may explain those results because in this study of the alpine subbasins in Loch Vale, no significant relation was found between N export or retention and winter precipitation. This is likely because little N is assimilated in the alpine environment that dominates the upper subbasins, regardless of climatic conditions. Increased snow deposition may also have two opposing effects: While it may enhance N retention through microbial assimilation, it may hinder N retention by depositing more N in the most sensitive areas through wind redistribution of snow.

6. Conclusions

Alpine watersheds of Colorado are more sensitive to moderate rates of atmospheric deposition of NO_3^- than forested watersheds; symptoms of nitrogen excess are observed in alpine watersheds with as little as 3 kg N ha^{-1} yr^{-1} from wet deposition. The low threshold for nitrogen excess is caused in part by (1) large areal extent of sensitive landscapes such as talus and bedrock, (2) spatial variability in precipitation amount that causes deposition to be greatest in some of the most sensitive landscapes, and (3) release of large amounts of atmospherically deposited N during snowmelt when biological N demand is low.

In the talus landscapes, minimal vegetation limits nitrogen assimilation by plants and causes a carbon-poor environment that favors mineralization and nitrification by microbial populations. Mobile nitrate accumulates along subtalus flow paths through the winter and is flushed directly to surface water during snowmelt and throughout the growing season, with little opportunity for assimilation. Tundra landscapes contribute moderately to nitrogen release because of lower deposition rates and weak hydrologic linkages to surface water. Other areas such as forests and wetlands have moderate deposition of snow and relatively well-developed soils and vegetation that retain most of the nitrogen from atmospheric deposition. The sensitivity of alpine and subalpine ecosystems to N excess is likely a function of the areal coverage and slope position of talus and tundra landscapes with high deposition of windblown snow.

Locally enhanced deposition by windblown snow, a short growing season, and seasonal desiccation create a physically stressed environment in alpine ecosystems that is sensitive to atmospheric deposition. Some sensitive landscapes may have released nitrogen even before anthropogenic emissions elevated nitrogen-deposition levels. Prediction of ecosystem response to potential changes in atmospheric deposition of NO_3^- is confounded by the complexity of biogeochemical processes in these ecosystems. In this study, ecosystem retention of nitrogen increased with greater nitrogen deposition. At higher levels of nitrogen deposition than those measured in this study, nitrogen retention would likely reach a maximum as additional inputs could no longer be assimilated in forest landscapes currently retaining nitrogen [*Baron et al.*, 1994]. Thus increases in deposition of nitrogen may cause significant changes in the ecosystem as more landscapes and more watersheds reach a nitrogen-saturated state. In the short term, however, effects of natural climatic variability on deposition, nitrogen cycling, and watershed translocation of nitrogen will likely overwhelm any expected response of watershed N export to changes in anthropogenic emissions of N.

Federal land managers and regulators are required to make cause-and-effect linkages before declaring adverse impacts to class 1 areas or setting critical loads of inorganic N to protect most sensitive ecosystems from injury caused by air pollution. This type of landscape-level research can be used in the design of an effective monitoring program to relate long-term changes in deposition chemistry with biologically significant changes in ecosystem processes.

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