# Nitrogen Saturation in the Rocky Mountains

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Nitrogen saturation is occurring throughout high-elevation catchments of the Colorado Front Range. Annual inorganic N loading in wet deposition to the Front Range of ~4 kg $ha^{-1}$ $yr^{-1}$ is about twice that of the Pacific States and similar to many sites in the northeastern United States. In the last ten years at Niwot Ridge/Green Lakes Valley and Glacier Lakes, annual minimum concentrations of $NO_3^-$ in surface waters during the growing season have increased from below detection limits to ~10 $\mu$equiv $L^{-1}$, indicating that these two catchments are at the threshold of N saturation. The Loch Vale watershed is N saturated, with annual minimum concentrations of $NO_3^-$ in surface waters generally above 10 $\mu$equiv $L^{-1}$; annual volume-weighted mean (VWM) concentrations of 16 $\mu$equiv $L^{-1}$ in surface waters are greater than that of ~11 $\mu$equiv $L^{-1}$ $NO_3^-$ in wet deposition. At these high-elevation catchments, there has been a shift in ecosystem dynamics from an N-limited system to an N-saturated system as a result of anthropogenically fixed N in wetfall and dryfall. Results from the Western Lakes Survey component of the National Surface Water Survey show that N saturation is a regional problem in the Colorado Front Range, with many lakes having ($NO_3^-$) concentrations greater than 10 $\mu$equiv $L^{-1}$. Foliar N:P ratios in bristlecone pine increase with elevation in the Colorado Front Range, indicating that at higher elevations P is translocated from foliar tissue more efficiently than N and that increasing atmospheric deposition of N with elevation is causing a change from N limitation to P limitation in the highest-elevation bristlecone pines. Current concepts of critical loads need to be reconsidered since only modest atmospheric loadings of N are sufficient to induce N leaching to surface waters in high-elevation catchments of the western United States.

## Introduction

Lakes in the Rocky Mountains are relatively uncontaminated compared to many other high-elevation lakes in the world, with the median value of $NO_3^-$ concentrations less than 1 $\mu$equiv $L^{-1}$ (*1*). However, these high-elevation ecosystems are relatively sensitive to changes in the flux of energy, chemicals, and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils, and short growing seasons (*2*). Hence, small changes in atmospheric deposition have the potential to result in large changes in ecosystem dynamics and water quality (*3*). Furthermore, these ecosystem changes may occur in alpine areas before they occur in downstream ecosystems. Ambient concentrations of N measured in the early 1980s at Niwot Ridge in the Colorado Front Range were 30-fold greater than preindustrial levels (*4*) and attributed to fossil fuel combustion (*5*). Previous research in Colorado has shown a statistically significant increase in the output of $NO_3^-$ from montane basins subjected to increasing deposition of N (*6*).

Here we investigate whether deposition of atmospheric N has caused N saturation in high-elevation catchments of the Colorado Front Range. Atmospheric deposition of N is known to alter the N cycle in forested ecosystems of northeastern United States (*1*) and northern Europe (*8*). Forested ecosystems are generally N-limited, characterized by efficient internal N cycling leading to a minimal loss of inorganic N in surface waters, groundwater, and gaseous loss through denitrification (*9*). When atmospheric deposition of anthropogenically fixed N becomes excessive, other nutrients or environmental factors constrain forest growth and inorganic N leaches below the rooting zone, a condition known as "nitrogen saturation" (*10*). Nitrogen saturation in forested ecosystems has been linked to serious environmental impacts, including direct effects such as an imbalance in N:Mg ratios causing chlorosis of foliage, premature needle drop, and decline in tree vigor (*11*) and indirect effects such as alteration of interspecific competitive ability and changes in nutrient use efficiency (*12*).

Historically, little attention has been paid to the effects of N deposition on surface waters of the western United States. The Environmental Protection Agency (EPA) in 1993 recommended removing its contribution for the wet deposition monitoring sites in the western United States operated by the National Acid Deposition Program/National Trends Network (NADP/NTN) program because rates of wet deposition of strong acid anions are generally lower

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west of the 100th meridian than further east. However, surface waters in the western United States can be more sensitive to atmospheric deposition than the eastern United States and so may be adversely impacted by lower deposition rates (*13*). For example, phytoplankton communities in the ultraoligotrophic Lake Tahoe, California–Nevada, have switched from colimitation by N and phosphorus to P limitation because of N in atmospheric deposition (*14*).

Our primary objective is to evaluate the response of high-elevation catchments in and near the Colorado Front Range to increases in ambient concentrations of atmospheric N. We discuss whether other high-elevation catchments in the Rocky Mountains and western United States are at risk. Last, we apply our results to the concept of critical loads in relation to N deposition to high-elevation catchments in the western United States.

## Methods

We define N saturation as a shift in ecosystem dynamics from no leakage of inorganic N into surface waters during the growing season to leakage of N in surface waters during the growing season (*15*). It is reasonable to ask if a concept originally developed for forested and agricultural catchments can be applied to high-elevation catchments. It is possible that such basins have insufficient capacity for N consumption in terrestrial systems to prevent the appearance of N in aquatic systems, because of a combination of N release from snow in an ionic pulse (*16*), a limited growing season (*17*), little vegetation, and poorly developed soils (*18*). Alternatively, for these same reasons, alpine basins may have a sufficient but limited ability to consume N and may be more sensitive to N saturation than forested ecosystems at lower elevation. Model simulations of terrestrial and aquatic N cycling at the high-elevation Loch Vale watershed in the Colorado Front Range using the nutrient-based CENTURY model (*19*) indicate that alpine ecosystems are N-limited at preindustrial levels of N deposition (*20*). Evaluation of the N-saturation concept at the high-elevation Emerald Lake catchment in the Sierra Nevada confirms the CENTURY modeling simulations, with no leakage of N in surface waters during the growing season (*21*). The conclusion was reached that application of the concept of N saturation to high-elevation catchments is valid (*21*).

We present time series data on N content in precipitation and surface waters from three high-elevation basins in and near the Colorado Front Range, all located on the east side of the Continental Divide (Figure 1). Niwot Ridge/Green Lakes Valley (NWT) is a 700-ha alpine/subalpine basin in which biogeochemical processes have been studied since 1985 as part of the Long-Term Ecological Research (LTER) network. The basin consists of a hydrologically linked linear chain of lakes; we present data from the outlet of Green Lakes 4, a second-order, 200-ha basin. The Loch Vale watershed (LVWS) is a second-order, 660-ha basin in Rocky Mountain National Park. Biogeochemical research began in 1983 and is conducted by the National Biological Service and the U.S. Geological Survey. The Glacier Lakes Ecosystem Experiments Site (GLEES) is a 300-ha catchment located in the Snowy Range of southeastern Wyoming in which research has been conducted by the U.S. Forest Service since 1987; we present results from the 80-ha Cascade Creek subdrainage. All catchments are glaciated alpine to subalpine basins underlain with crystalline bedrock and range in elevation from about 3000 to 4000 m, vegetation varies from alpine tundra to subalpine coniferous forest with growing seasons of at least 120 days, and soils are limited in area and generally located adjacent to perennial and ephemeral streams. All three catchments were selected for long-term research because they are representative of montane regions in the Rocky Mountains.

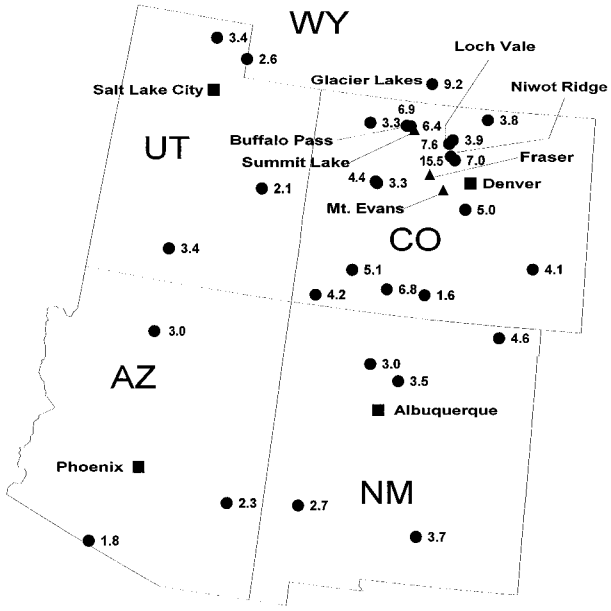


**FIGURE 1. Locations of Niwot Ridge/Green Lakes Valley (NWT), Loch Vale (LVWS), and Glacier Lakes (GLEES) in relation to Denver. The map includes the average annual loading of $NO_3^-$ (kg $ha^{-1}$ $yr^{-1}$) in wet deposition from 1989 to 1993 for all NADP sites in a four-state region, clearly illustrating that the Rocky Mountains receive more loading than do low-elevation areas. All NADP sites in Arizona, New Mexico, and Utah are less than 2500 m in elevation and all but one received less than 4.0 kg $ha^{-1}$ $yr^{-1}$ of $NO_3^-$ for this time period. In contrast, montane sites above 2500 m in Colorado received more than 4.0 kg $ha^{-1}$ $yr^{-1}$ $NO_3^-$ for the same time period.**

Precipitation and surface water samples are collected and analyzed at the three sites using similar protocols, so that chemical content may be compared among sites. All sites participate in the NADP/NTN network, which operates ~200 wet precipitation collectors throughout the continental United States (*22*). NADP collectors are located within 2 km of the stream sampling sites. Surface water samples are collected at daily to weekly intervals at the initiation of snowmelt and through the growing season and about bimonthly during the winter (*23*). Sample collection at NWT is at the outlet of Green Lake 4, at LVWS at the outlet of Loch Vale, and at GLEES at the inlet to West Glacier Lake. Detection limits for most solutes are less than 1 $\mu$equiv $L^{-1}$ and precision is better than 2%. Discharge is measured continuously during the ice-free period at all sites. The complete record of $NO_3^-$ measurements is shown for all three sites.

The response of forested ecosystems to N deposition was evaluated by measuring foliar N and P concentrations in bristlecone pine (*Pinus aristata*) along an elevational transect on Mt. Evans, located on the east slope of the Front Range ~50 km south of Green Lakes Valley and Niwot Ridge (Figure 1). Trees were sampled on an east aspect at elevations of 3450, 3550, and 3650 m. Five trees were sampled at each elevation and two replicates of five-needle fascicles were sampled for each tree. Foliage age was

**TABLE 1**

**Comparison of Annual Volume-Weighted Mean Concentrations[a] for $NH_4^+$, $NO_3^-$, and Total Annual Loading of Inorganic N from Selected NADP Sites, 1991–1993**

| site | $NH_4^+$ ($\mu$equiv $L^{-1}$) | $NO_3^-$ ($\mu$equiv $L^{-1}$) | inorg N (kg $ha^{-1}$ $yr^{-1}$) |
|---|---|---|---|
| NWT/GLV | 5.0 | 15.6 | 4.71 |
| LVWS | 7.2 | 11.6 | 2.73 |
| GLEES | 6.7 | 11.5 | 3.09 |
| Acadia NP, ME | 5.5 | 13.2 | 3.60 |
| Hubbard Brook, NH | 8.3 | 21.9 | 4.87 |
| Yosemite NP, CA | 8.3 | 8.4 | 2.53 |
| Olympia NP, WA | 1.1 | 1.6 | 1.04 |

[a]All means are arithmetic means of annual values.

determined by bud scars; for each year, two replicates of five-needle fascicles were analyzed. Concentrations of N and P were measured on a Lachet autoanalyzer QuichChem AE following standard protocols.

## Results

Annual loading of inorganic N ($NO_3^- + NH_4^+$) in wetfall to the Colorado Front Range is similar in magnitude to that of many sites in the northeastern United States and much larger than in montane sites in the far west. To illustrate using NADP data (Table 1), annual loading of inorganic N to the three watersheds ranged from 2.73 to 4.71 kg $ha^{-1}$ $yr^{-1}$ from 1991 through 1993. Measured N deposition to Niwot Ridge at 4.71 kg $ha^{-1}$ $yr^{-1}$ was more than that of Acadia National Park in Maine (3.60 kg $ha^{-1}$ $yr^{-1}$) and similar to Hubbard Brook in New Hampshire (4.87 kg $ha^{-1}$ $yr^{-1}$). In contrast, annual N deposition in wetfall to Olympic National Park in Washington of 1.04 kg $ha^{-1}$ $yr^{-1}$ was only 25% of that at NWT and the 2.53 kg $ha^{-1}$ $yr^{-1}$ at Yosemite National Park was about half of that at NWT. Within the intermountain region of Utah, Wyoming, Colorado, Arizona, and New Mexico, the highest rates of annual $NO_3^-$ deposition (in kg $ha^{-1}$ $yr^{-1}$ nitrate) were also in the Front Range (Figure 1). The 5-year average of annual $NO_3^-$ deposition from 1989 to 1993 shows that annual $NO_3^-$ deposition to NWT was 15.5 kg $ha^{-1}$ $yr^{-1}$, 7.6 kg $ha^{-1}$ $yr^{-1}$ at LVWS, and 9.2 kg $ha^{-1}$ $yr^{-1}$ at GLEES. It is worth noting that NADP sites just west of the Front Range had annual $NO_3^-$ deposition values over this time period of 6.4 and 6.9 kg $ha^{-1}$ $yr^{-1}$. These relatively high rates of N deposition in the Colorado Rocky Mountains are due in part to increasing orographic precipitation with elevation (*24*).

At the three test basins in the Front Range, annual $NO_3^-$ loading from wetfall increased in the late 1980s and the higher loading rates have been maintained (Figure 2). At NWT, NADP results show that there has been a ~200% increase in $NO_3^-$ loading from wet deposition over the last decade, increasing from ~8 kg $ha^{-1}$ $yr^{-1}$ for 1985–1987 to 16.5 kg $ha^{-1}$ $yr^{-1}$ for 1990–1992 (Figure 2). Earlier and comparable measurements of annual $NO_3^-$ deposition extend the record back to 1982 and indicate an even larger increase in $NO_3^-$ loading, with a mean $NO_3^-$ loading of 5.7 kg $ha^{-1}$ $yr^{-1}$ from 1982 to 1986 (*25*). A simple linear regression analysis shows that increases in precipitation amount account for about half the increase in annual $NO_3^-$ loading at NWT ($r^2 = 0.56$, $p = 0.01$) and about half comes from increases in the annual volume-weighted mean concentration of $NO_3^-$ ($r^2 = 0.59$, $p = 0.01$); a multiple

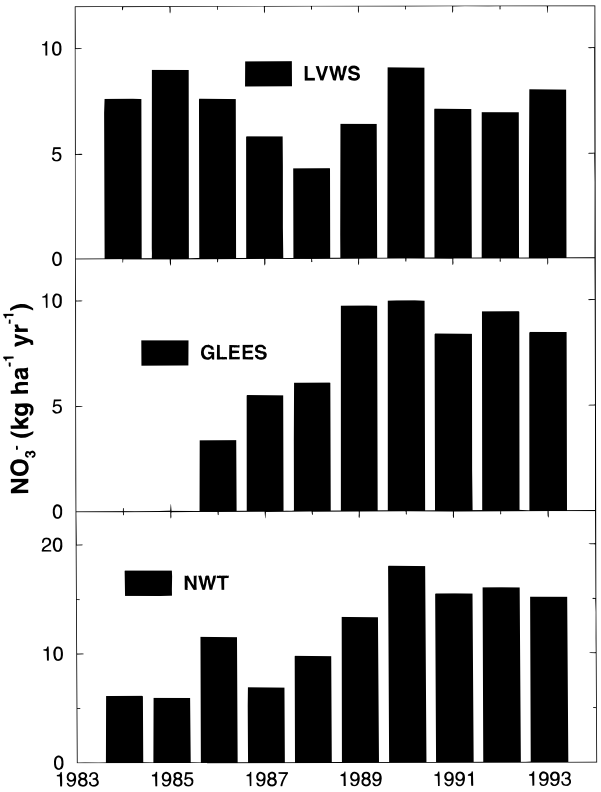


**FIGURE 2. Time series of annual $NO_3^-$ loading from NADP collectors at NWT, GLEES, and LVWS (complete time series shown for each site). Nitrate loading increased at all three sites in the late 1980s, and these elevated loading levels have persisted to the present.**

linear regression analysis shows that the combination of precipitation and concentration explains annual wet deposition of $NO_3^-$ ($r^2 = 0.99$, $p \ll 0.0001$) (*3*). The increase in annual $NO_3^-$ loading to GLEES has been more dramatic, increasing by ~300% from 3.35 kg $ha^{-1}$ $yr^{-1}$ in 1986 to 9.95 kg $ha^{-1}$ $yr^{-1}$ in 1990. Annual $NO_3^-$ loading is more variable at LVWS but does show an increase from 4.28 kg $ha^{-1}$ $yr^{-1}$ in 1988, a dry year, to 9.05 kg $ha^{-1}$ $yr^{-1}$ in 1990, a wet year. Ammonium loading from wet deposition shows a pattern similar to that of $NO_3^-$ loading at these sites, in both timing and magnitude. Dry deposition of N further compounds the N loading from wet deposition, with dry deposition of inorganic N during the growing season to NWT about equal to wet deposition of inorganic N (*26*).

Nitrate concentrations at all test basins show an annual peak during the onset of snowmelt runoff and an annual minimum during the growing season when discharge is primarily from base flow (Figure 3). Apparently in response to the increase in N deposition at NWT, there has been an increase in annual minimum $NO_3^-$ concentrations in surface waters during the growing season. At NWT in 1985 and 1986, $NO_3^-$ concentrations during the growing season were near or below detection limits (Figure 3). Biota apparently had the ability to utilize all available N from atmospheric deposition and were N-limited during the growing season. Starting in 1987, $NO_3^-$ began to leak out of the basin in surface waters during the growing season, reaching annual minimum concentrations of ~10 $\mu$equiv $L^{-1}$ in 1990. This increase in annual minimum concentrations of $NO_3^-$ in surface waters parallels the large increase in $NO_3^-$ loading from wetfall in the late 1980s.

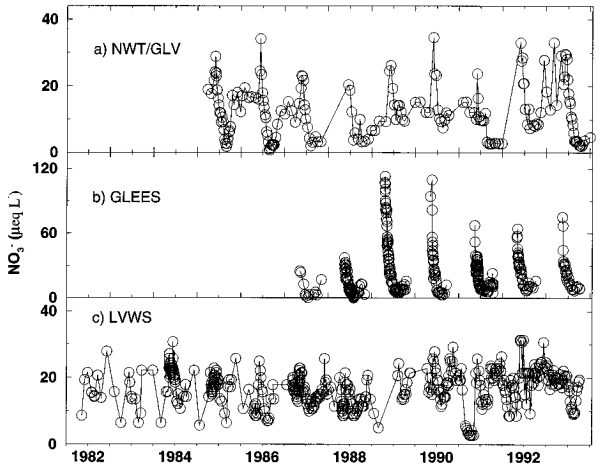


**FIGURE 3. Time series of $NO_3^-$ concentrations in surface waters from NWT, GLEES, and LVWS. Complete data set is shown for each site. NWT and GLEES appear to be approaching the threshold of stage 2 of N saturation; LVWS is N-saturated.**

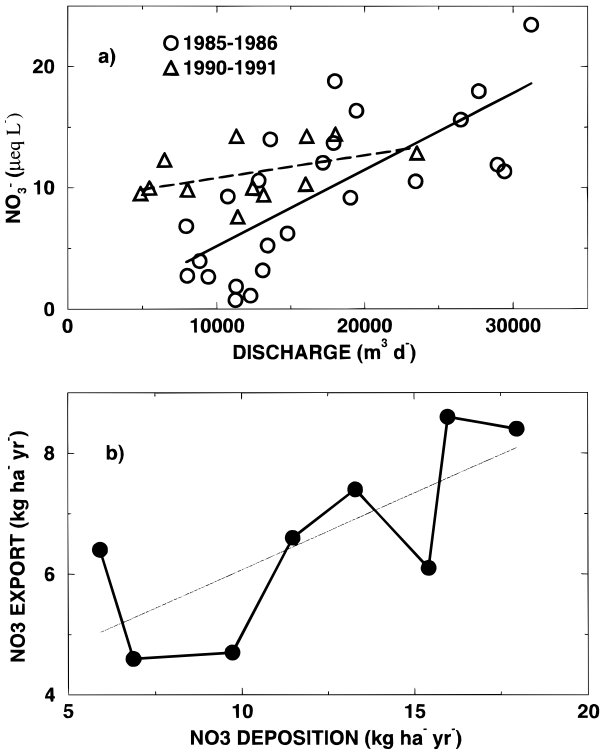


**FIGURE 4. (a) Changes in the relationship between streamwater $NO_3^-$ concentrations and discharge at NWT during the growing season. Growing season is defined as the recession limb of the hydrograph from maximum discharge in early June through August in 1985–1986 (circles) and 1989–1990 (triangles). In 1985–1986, the $NO_3^-$ intercept at zero discharge was not significantly different than zero. However, in 1989–1990 the zero-discharge intercept for $NO_3^-$ of 9 $\mu$equiv L$^{-1}$ was significantly greater than zero ($p < 0.01$). (b) Regression analysis between annual $NO_3^-$ input from wet deposition and output in surface waters at NWT. There is a significant increase in $NO_3^-$ export with increasing deposition.**

There has been a concurrent shift in the relationship of seasonal discharge to $NO_3^-$ concentrations at NWT. We examine the relationship between $NO_3^-$ concentrations and discharge during the growing season, investigating the recession limb of the discharge curve from maximum discharge in early June through August. In 1985 and 1986, the regression of $NO_3^-$ concentration as a function of discharge had a $y$ intercept of zero $NO_3^-$ (Figure 4a). In 1989 and 1990, the zero discharge intercept increased to 9 $\mu$equiv L$^{-1}$, indicating potentially increased $NO_3^-$ in the soil solution in excess of uptake capacity. We interpret this increase in $NO_3^-$ concentrations during the growing season to the leaching of N to deeper hydrologic flow paths that maintain summer base low.

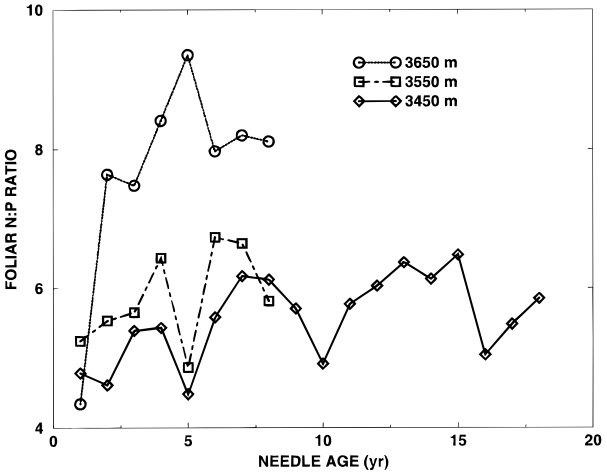


**FIGURE 5. Foliar N:P ratios in bristlecone pine along three elevational transects. N:P foliar ratios increase with elevation, indicating that at higher elevations P is translocated from foliar tissue more efficiently than N. Increasing atmospheric deposition of N with elevation may be causing a change from N limitation to P limitation in the highest-elevation bristlecone pines.**

Annual $NO_3^-$ yield from NWT increased by 50% from the period 1985–1988 (5.0 kg ha$^{-1}$ yr$^{-1}$) to 1989–1992 (7.5 kg ha$^{-1}$ yr$^{-1}$). There is a significant correlation ($p < 0.05$) between N loading in wet deposition and N export, with $r^2 = 0.53$ ($n = 8$) (Figure 4b). Most of this increase in N export from NWT occurred during the growing season of June, July, and August, consistent with the change from an N-limited system to an N-saturated system. Mass balance analysis shows that currently ~50% of the $NO_3^-$ loading from annual wet deposition is exported in streamwaters.

An increase in N availability should cause a corresponding change in the foliar chemistry of trees, with reduced translocation of nitrogen from foliage (*27*) and trees becoming P-limited rather than N-limited (*28*). If N saturation at high elevation causes changes in foliar chemistry, we should see these changes first at the highest elevations where forests occur. We tested this hypothesis by measuring the N and P concentrations in the foliage of bristlecone pine along an elevational transect on Mt. Evans in the Front Range, ~50 km south of Green Lakes Valley and Niwot Ridge. Bristlecone pine was chosen because it is a tree-line species that retains its foliage for ~20 yr at the lower elevation end of its range and ~8 yr at the upper end; foliage age on individual needles can be determined by bud scars. Analysis of the nutrient content in needles of bristlecone pines provides a surrogate method of evaluating changes in N and P foliar content with time.

Our results show that the foliar N:P ratio was greater in high-elevation trees compared to lower elevation trees (Figure 5). The N:P ratio in the foliage of bristlecone pine after year one ranged from 7.5 to 9.5 for trees sampled at the high elevation of 3650 m, compared to an N:P ratio ranging from 4 to 6 for trees at lower elevations of 3450–3550 m. These results suggest that P was translocated more efficiently than N in high-elevation trees, that P has become

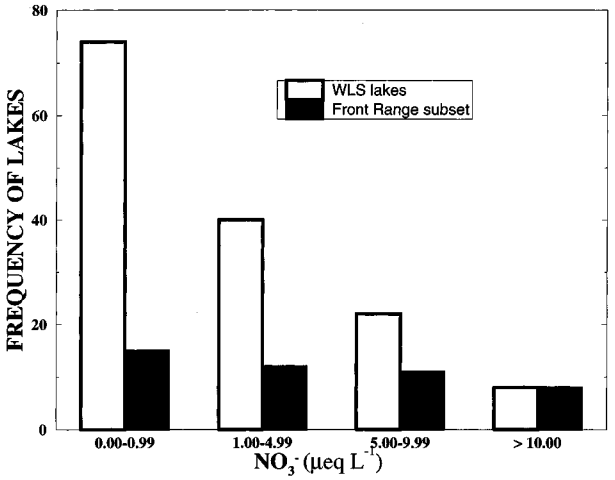


**FIGURE 6. Frequency analysis of $NO_3^-$ concentrations from the southern Rocky Mountain section of the Western Lakes Survey. Median $NO_3^-$ concentrations were less than 1 $\mu$equiv $L^{-1}$. All lakes with concentrations greater than 10 $\mu$equiv $L^{-1}$ were found in the Colorado Front Range.**

limiting in these high-elevation trees, and that N is no longer limiting. Thus, changes in N cycling in the forested ecosystems of the Colorado Front Range may be occurring in response to present levels of N deposition.

The Western Lakes Survey (WLS) component of the National Surface Water Survey extends these site-specific results to the Rocky Mountain region. The National Surface Water Survey was designed to provide a statistically rigorous and comparative synoptic survey of water quality for all acid-sensitive lakes in the United States (*29*). Most of the study areas of the WLS were at high elevations, with nearly two-thirds of the sampled lakes located in federally designated wilderness areas (*30*). Water samples were collected in the autumn of 1985 during base-flow conditions, with $NO_3^-$ and $NH_4^+$ concentrations throughout the western United States generally below 1 $\mu$equiv $L^{-1}$ (*15*). In the southern Rocky Mountain section of the WLS, $NO_3^-$ concentrations in most lakes were also below 1 $\mu$equiv $L^{-1}$, indicating no leakage of $NO_3^-$ from these basins (Figure 6). These results indicate that most catchments within the southern Rocky Mountains have the ability to assimilate all N from atmospheric deposition and are N-limited. However, lakes in the Colorado Front Range provided a disproportionately large amount of the lakes with $NO_3^-$ concentrations greater than 1 $\mu$equiv $L^{-1}$ (Figure 6). All 10 WLS lakes from the southern Rocky Mountain area with $NO_3^-$ concentrations greater than 10 $\mu$equiv $L^{-1}$ were located in the Colorado Front Range. These results are consistent with results from the three test basins and indicate that many high-elevation catchments within the Colorado Front Range are at some stage of N saturation. However, at the time of the WLS in 1985, basins outside of the Colorado Front Range were not N-saturated and were N-limited.

## Discussion

There are striking parallels between the changes in $NO_3^-$ concentration at NWT in response to increasing atmospheric deposition of N and the changes in $NO_3^-$ concentrations of surface waters induced by experimental loading of N at the West Bear Brook watershed (BBWM) in Maine (*31*). Comparison of our results at NWT to those of BBWM provides insight into the N dynamics of the Colorado Front Range. The BBWM is a headwater catchment, forested, and ~10 ha in area. Prior to increased loading at both sites, maximum $NO_3^-$ concentrations in surface waters were near 40 $\mu$equiv $L^{-1}$ and minimum concentrations were below detection limits. At each site, the relationship between $NO_3^-$ concentrations and discharge showed a zero $NO_3^-$ intercept at zero discharge. Following increased $NO_3^-$ loading at both sites, $NO_3^-$ export occurred during the growing season and the $NO_3^-$ intercept at zero discharge increased. And at both sites, the $NO_3^-$ yield in surface waters increased with increased $NO_3^-$ loading. The experimental N loading at BBWM induced nitrogen saturation. The increase in N loading to NWT in wetfall may have acted as a natural experiment, causing N saturation.

Nitrogen saturation proceeds in a series of steps (*15*). The first stage occurs when there is chronic export of N in surface waters during the nongrowing season. In alpine basins, the large concentrations of $NO_3^-$ that occur at the onset of snowmelt runoff are consistent with the release of $NO_3^-$ from the snowpack in the form of an ionic pulse (*32*). Piston pumping of nitrification products stored in soils under the seasonal snowpack may provide some amount of this $NO_3^-$ (*21*). Nitrate becomes a mobile anion at this time in part because assimilation of N by vegetation is limited by physical factors such as deep snow cover and low temperatures.

Nitrogen saturation is reached in stage 2, manifested by the chronic loss of N to surface waters during the growing season. We interpret our data to indicate that NWT is at the threshold of the second stage of N saturation. The GLEES catchment is also nearing the threshold of stage 2 of N saturation. Annual minimum concentrations at GLEES were below detection limits in 1987 and 1988 and started to rise in 1989, following a pattern similar to that of NWT (Figure 3). Presently, annual minimum concentrations of $NO_3^-$ at GLEES are ~8 $\mu$equiv $L^{-1}$.

In contrast, the LVWS appears to have been at stage 2 of N saturation for some years. The amplitude of $NO_3^-$ concentrations in surface waters of the LVWS is much less than at NWT and GLEES, with annual minimum concentrations generally ranging from 10 to 15 $\mu$equiv $L^{-1}$. Annual volume-weighted mean (VWM) concentrations of $NO_3^-$ in streamflow of 16 $\mu$equiv $L^{-1}$ are greater than annual VWM concentrations of $NO_3^-$ in wet deposition of ~11 $\mu$equiv $L^{-1}$ (Table 1). About 34% of the annual export of N from the LVWS occurs during the summer months; again consistent with N saturation. CENTURY model results suggest that tundra in LVWS was previously N-limited and then crossed the threshold from an N-limited ecosystem to an N-saturated ecosystem in the last several decades (*20*).

Prior results by Campbell et al. (*33*) suggest that the higher-elevation subcatchments at LVWS may be at the threshold of stage 3 saturation. Stage 3 occurs when the basin becomes a source of N rather than a sink, with N export exceeding atmospheric deposition of N (*15*). Annual input−output studies of N were conducted at LVWS in 1992 for each of the two first-order basins (each catchment ~200 ha in area) (*33*). All inorganic N in streamwaters was as $NO_3^-$ with annual VWM concentrations of 23 and 21 $\mu$equiv $L^{-1}$. The $NO_3^-$ export in streams was equivalent to annual VWM concentrations in deposition of 11 $\mu$equiv $L^{-1}$ $NO_3^-$ and 7 $\mu$equiv $L^{-1}$ $NH_4^+$, assuming ~25% evapotranspiration and/or dry deposition. We interpret these mass balance results to indicate that all the $NH_4^+$ in wet deposition was

assimilated and that net nitrification in the first-order subcatchments was equal to $NH_4^+$ deposition. High nitrification rates are symptomatic of the second and third stages of N saturation (*10*). Within years to decades at the first-order catchments of LVWS, continued inputs of N from deposition in combination with mineralization and nitrification may produce concentrations of $NO_3^-$ in surface waters that exceed concentrations of inorganic N in deposition alone.

Nitrogen saturation in high-elevation catchments of the Colorado Front Range may provide an early warning indicator for disruption of N cycling in forested ecosystems at lower elevations. Forested ecosystems in the Rocky Mountains are generally N-limited (*34*). At LVWS, mass balance studies indicate that the lower-elevation subalpine forest within the catchment is retaining N exported from the higher-elevation alpine subcatchments (*35*). CENTURY simulations suggest that, in response to this increase in available N, the subalpine forest within LVWS is undergoing increases in forest production, soil N mineralization rates, soil carbon, and accumulation rates of soil N (*20*).

Our results from the Colorado Front Range may act as an early warning indicator of N saturation for other high-elevation catchments in the Rocky Mountains and the western United States. Time series data from the high-elevation catchments west of NWT and LVWS show no evidence of N saturation at this time. At the Fraser Experimental Forest, located ~15 km west of NWT, N deposition is less than at NWT, $NO_3^-$ concentrations in streamwaters during the growing season are below detection limits (*36*), and 95% of inorganic N in wet deposition is retained in alpine and subalpine catchments (*37*). Data collected from 1985 to 1991 at the 11-ha Summit Lake, located just west of LVWS at an elevation of 3144 m in the Mt. Zirkel Wilderness Area, shows $NO_3^-$ concentrations always below detection limits (*38*). However, while these and other basins directly west of the Colorado Front Range are presently N-limited, deposition rates of atmospheric N are elevated. The Buffalo Pass NADP site near Summit Lake has $NO_3^-$ loading of 6.4 kg $ha^{-1}$ $yr^{-1}$ from 1989 to 1993 (Figure 1), only slightly less than rates reported from the Front Range. Furthermore, a 1992 synoptic survey of the chemical content of snow in the Rocky Mountains from New Mexico to Montana shows that the highest concentrations of $NO_3^-$ (15 $\mu$equiv $L^{-1}$) occurred in northern Colorado near Summit Lake, in part from coal-fired power plants downwind (*39*). Our results from the Colorado Front Range suggest that these and other high-elevation catchments may cross the threshold from N-limited to N-saturated ecosystems in the near future if present deposition rates of N persist or increase.

A key issue that demands attention is the ecosystem impacts of increasing N deposition to these high-elevation catchments. Increasing levels of N saturation may lead directly to increasing acidification of surface waters in these and other high-elevation catchments. High-elevation streams are particularly vulnerable to acidification because snowmelt runoff causes a decrease in surface water alkalinity through dilution of base cations (*40*). However, there were no reported cases of acidification in streamwaters west of the Mississippi River because of atmospheric deposition, until a recent report of episodic acidification at NWT in 1994 with pH values below 5.0 and negative alkalinities in stream flow during snowmelt runoff (*3*). The low pH values and negative alkalinities at NWT were associated with elevated levels of $NO_3^-$ and dilution of base cations during snowmelt runoff. Increasing N deposition may also affect rare and threatened alpine plants, many of which prefer snow accumulation sites and thus would be exposed to the greatest N loading from wet and dry deposition to snow cover (*41*). Terrestrial biota of high-elevation catchments have a very conservative ecological strategy with little genetic or phenotypic ability to respond to increases in nutrient loading from the atmosphere. Nitrogen fertilization experiments at NWT have shown that increasing N availability alters species composition in alpine tundra communities (*42*).

Current concepts of critical loads need to be reconsidered since only modest atmospheric loadings of N are sufficient to induce N leaching to surface waters of high-elevation catchments in the western United States. An important result of this analysis is the demonstration that high-elevation ecosystems may be nearly N-saturated at current levels of N deposition. These findings have important implications for policy relating to N emissions. The rapidity of the increase in $NO_3^-$ flux from these test basins was unexpected given the historically low rates of N deposition in the western United States, the modest increase in N loading, and the generally N-limited status of montane ecosystems in the western United States. Determining critical loads for N deposition has been problematical because of the inability to quantify ecosystem storage capacity of N (*7*). Critical load estimates for N deposition have been set at 10 kg $ha^{-1}$ $yr^{-1}$ for northern Europe, based on empirical results that showed no L leaching to surface waters below this value (*43*). Clearly, leakage of N to surface waters in the Colorado Front Range occurs at N-deposition values well below 10 kg $ha^{-1}$ $yr^{-1}$ N. Concepts of critical loads need to be reevaluated for mountain ecosystems in the western United States.

Our ability to effectively manage high-elevation catchments is constrained by a lack of process-level understanding of the nitrogen cycle. At present, we do not know the source of $NO_3^-$ in surface waters of the Colorado Front Range and other high-elevation catchments in the western United States. Snowmelt runoff is the dominant hydrologic event in these catchments. Nitrate concentrations in surface waters are generally consistent with the release of $NO_3^-$ from storage in the seasonal snowpack in the form of an ionic pulse (*21*), and the $NO_3^-$ in streamwaters is often assumed to be from wet and dry deposition (*32*). However, experiments conducted in 1993 at NWT indicate that microbial activity in snow-covered soils plays a key role in N cycling in alpine ecosystems prior to snowmelt runoff, with net mineralization rates from March 3 to May 4 ranging from 2.2 to 6.6 g of N $m^{-2}$ (*44*). Preliminary analysis tracing sources of streamwater $NO_3^-$ at LVWS during snowmelt runoff at LVWS using both the oxygen and nitrogen isotopic composition of nitrate suggests that atmospheric $NO_3^-$ eluted from the snowpack was a minor source of $NO_3^-$ in streamflow and that microbial activity was an important source of $NO_3^-$ in streamwaters (*45*). Innovative experiments and tools such as the dual-isotope analysis of $NO_3^-$ are needed for a mechanistic understanding of N dynamics in high-elevation ecosystems.

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## Literature Cited


(1) Psenner, R. *Aquatic Sci.* **1989**, *51*, 108−128.
(2) Baron, J. S. *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*; Ecological Studies Series 90; Springer-Verlag: New York, 1991.
(3) Williams, M. W.; Losleben, M.; Caine, N.; Greenland, D. *Limnol. Oceanogr.*, in press.
(4) Fahey, D. W.; Hubler, G.; Parish, D. D.; Williams, E. J.; Norton, R. B.; Ridley, B. A.; Singh, H. B.; Liu, S. C.; Fehsenfeld, F. C. *J. Geophys. Res.* **1986**, *91*, 9781−9793.
(5) Lewis, W. M., Jr.; Grant, M. C.; Saunders, J. F., III *Water Resour. Res.* **1984**, *20*, 1691−1704.
(6) Lewis, W. M., Jr.; Grant, M. C. *Ecology* **1979**, *60*, 1093−1097.
(7) Aber, J. D. **1992**, *7*, 220−223.
(8) van Breemen, N.; Driscoll, C. T.; Mulder, J. *Nature* **1984**, *307*, 599−604.
(9) Tamm, C. O. *Nitrogen in terrestrial ecosystems: questions of productivity, vegetational changes, and ecosystem stability*; Springer-Verlag: New York, 1991.
(10) Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. *BioScience* **1989**, *39*, 378−386.
(11) Skeffington, R. A.; Wilson, E. J. *Environ. Pollut.* **1988**, *54*, 159−184.
(12) Taylor, G. E., Jr.; Johnson, D. W.; Andersen, C. P. *Ecol. Appl.* **1994**, *4*, 662−689.
(13) Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Kellar, P. E.; Silverstein, M. E.; Schonbrod, R. D.; Crowe, R. E.; Linthurst, R. A.; Omernik, J. M.; Teague, S. A.; Meier, E. P. *Population descriptions and physico-chemical relationships*; EPA-600/3-86/054a; U.S. Environmental Protection Agency: Washington, DC, 1987; Vol. I.
(14) Jassby, A. D.; Reuter, J. E.; Axler, R. P.; Goldman, C. R.; Hackley, S. H. *Water Resour. Res.* **1994**, *30*, 2207−2216.
(15) Stoddard, J. L. Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In *Environmental Chemistry of Lakes and Reservoirs*; Baker, L. A., Ed.; Advances in Chemistry Series 237; American Chemical Society: Washington, DC, 1994; pp 223−284.
(16) Denning, A. S.; Baron, J. S.; Mast, M. A.; Arthur, M. A. *Water, Air, Soil Pollut.* **1991**, *59*, 107−123.
(17) Walker, M. D.; Webber, P. J.; Arnold, E. H.; Ebert-May, D. *Ecology* **1994**, *75*, 393−408.
(18) Burns, S. Alpine soil distribution and development, Indian Peaks, Colorado Front Range Ph.D. Thesis, Department of Geology, University of Colorado, Boulder, CO, 1980.
(19) Parton, W. J.; Scurlock, J. M. O.; Ojima, D. S.; Gilmanov, T. G.; Scholes, R. J.; Schimel, D. S.; Kirchner, T.; Minaut, J. C.; Seastedt, T.; Garcia-Moya, E.; Kimnalrut, A.; Kinyamario, J. I. *Global Biogeochem. Cycles* **1993**, *7*, 785−810.
(20) Baron, J. S.; Ojima, D. S.; Holland, E. A.; Parton, W. J. *Biogeochemistry* **1994**, *27*, 61−82.
(21) Williams, M. W.; Bales, R. C.; Melack, J.; Brown, A. *Biogeochemistry* **1995**, *28*, 1−31.
(22) NADP/NTN National Atmospheric Deposition Program. *NADP/NTN annual data summary, precipitation chemistry in the United States*; NADP/NTN Coordination Office, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 1984−1993.
(23) Baron, J. S. Biogeochemical fluxes. In *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*; Baron, J. S., Ed.; Ecological Studies Series 90; Springer-Verlag: New York, 1991.
(24) Baron, J. S. In *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*; Baron, J. S., Ed.; Ecological Studies Series 90; Springer-Verlag: New York, 1991.
(25) Reddy, M. M.; Caine, N. A small alpine basin budget: Front Range of Colorado. In *Proceedings, International Mountain Watershed Symposium, Lake Tahoe*; Poppoff, I. G., Goldman, C. R., Loeb, S. L., Leopold, L. B., Eds.; Tahoe Resource Conservation DIstrict: Tahoe, NY, 1988; pp 370−385.
(26) Sievering, H.; Burton, D.; Caine, N. *Global Biogeochem. Cycles* **1992**, *6*, 339−346.
(27) Flanagan, P. W.; Van Cleve, K. *Can. J. Forest Res.* **1983**, *13*, 795−817.
(28) McNulty, S. G.; Aber, J. D.; Boone, R. D. *Biogeochemistry* **1991**, *14*, 13−29.
(29) National Acid Precipitation Assessment Program. Integrated assessment. External Review Drafts, Washington, DC, 1990.
(30) Eilers, J. M.; Kanciruk, P.; McCord, R. A.; Overton, W. S.; Hook, L.; Blick, D. J.; Brakke, D. F.; Kellar, P. E.; DeHaan, M. S.; Silverstein, M. E.; Landers, D. H. Characteristics of lakes in the western United States, Vol. II; EPA-600/3-86/054b; U.S. Environmental Protection Agency: Washington, DC, 1987.
(31) Kahl, J. S.; Norton, S. A.; Fernandez, I. J.; Nadelhoffer, K. J.; Driscoll, C. T.; Aber, J. D. *Environ. Sci. Technol.* **1993**, *27*, 565−568.
(32) Williams, M. W.; Melack, J. M. *Water Resour. Res.* **1991**, *27*, 1575−1588.
(33) Campbell, D. H.; Clow, D. W.; Ingersoll, G. P.; Alisa Mast, M.; Turk, J. T.; Spahr, N. E. Nitrogen deposition and release in alpine watersheds, Loch Vale, Colorado, USA. In *Biogeochemistry of Seasonally Snow Covered Catchments*; Tonnessen, K., Williams, M. W., Tranter, M. IAHS-AIHS Publication 228; Int. Assoc. Hydrol. Sci.: Wallingford, UK, 1995; pp 243−254.
(34) Fahey, T. J.; Yavitt, J. B.; Pearson, J. A.; Knight, D. H. *Biogeochemistry* **1985**, *5*, 257−275.
(35) Baron, J. S.; Campbell, D. H. *Hydrol. Processes*, in press.
(36) Stottlemyer, R.; Troendle, C. A. *J. Hydrol.* **1992**, *140*, 179−208.
(37) Stottlemyer, R.; Troendle, C. A. Surface Water chemistry and chemical budgets, alpine and subalpine watersheds, Fraser Experimental Forest, CO. In *Biogeochemistry of Seasonally Snow Covered Catchments*; Tonnessen, K., Williams, M. W., Tranter, M., IAHS-AIHS Publication 228; Int. Assoc. Hydrol. Sci.: Wallingford, UK, in press.
(38) Campbell, D. H.; Turk, J. T.; Spahr, N. E. *Water Resour. Res.* **1991**, *27*, 2047−2060.
(39) Turk, J. T.; Campbell, D. H.; Ingersoll, G. P.; Clow, D. W. *Open File Rep−U.S. Geol. Surv.* **1992**, *No. 92−645*.
(40) Williams, M. W.; Brown, W. A.; Melack, J. M. *Limnol. Oceanogr.* **1993**, *38*, 775−797.
(41) Bowman, W. D. *Arctic Alpine Res.* **1992**, *24*, 211−215.
(42) Bowman, W. D.; Theodose, T. A.; Schardt, J. C.; Conant, R. T. *Ecology* **1993**, *74*, 2085−2097.
(43) Dise, N. B.; Wright, R. F. *For. Ecol. Manage.* **1995**, *71*, 153−161.
(44) Brooks, P. D.; Williams, M. W.; Schmidt, S. K. *Biogeochemistry*, in press.
(45) Kendall, C.; Campbell, D. H.; Burns, D. A.; Shanley, J. B.; Silva, S. R.; Chang, C. C. Y. Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate: pilot studies at three catchments. In *Biogeochemistry of Seasonally Snow Covered Basins*; Tonnessen, K. A., Williams, M. W., Tranter, M., Eds.; IAHS-AIHS Publication 228; Int. Assoc. Hydrol. Sci.: Wallingford, UK, 1995; pp 339−348.


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