Evaluating Regional Patterns in Nitrate Sources to Watersheds in National Parks of the Rocky Mountains using Nitrate Isotopes

LEORA NANUS,*,† MARK W. WILLIAMS,‡
DONALD H. CAMPBELL,†
EMILY M. ELLIOTT,§ AND
CAROL KENDALL‖

U.S. Geological Survey, WRD-CWSC, Federal Center, Denver, Colorado, University of Colorado at Boulder and Institute of Arctic and Alpine Research, Boulder, Colorado, Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania, and U.S. Geological Survey, WRD-National Research Program, Menlo Park, California

In the Rocky Mountains, there is uncertainty about the source areas and emission types that contribute to nitrate (NO_3) deposition, which can adversely affect sensitive aquatic habitats of high-elevation watersheds. Regional patterns in NO_3 deposition sources were evaluated using NO_3 isotopes in five National Parks, including 37 lakes and 7 precipitation sites. Results indicate that lake NO_3 ranged from detection limit to 38 μeq/L, $\delta^{18}O$ (NO_3) ranged from −5.7 to +21.3‰, and $\delta^{15}N$ (NO_3) ranged from −6.6 to +4.6‰. $\delta^{18}O$ (NO_3) in precipitation ranged from +71 to +78‰. $\delta^{15}N$ (NO_3) in precipitation and lakes overlap; however, $\delta^{15}N$ (NO_3) in precipitation is more depleted than $\delta^{15}N$ (NO_3) in lakes, ranging from −5.5 to −2.0‰. $\delta^{15}N$ (NO_3) values are significantly related ($p < 0.05$) to wet deposition of inorganic N, sulfate, and acidity, suggesting that spatial variability of $\delta^{15}N$ (NO_3) over the Rocky Mountains may be related to source areas of these solutes. Regional patterns show that NO_3 and $\delta^{15}N$ (NO_3) are more enriched in lakes and precipitation from the southern Rockies and at higher elevations compared to the northern Rockies. The correspondence of high NO_3 and enriched $\delta^{15}N$ (NO_3) in precipitation with high NO_3 and enriched $\delta^{15}N$ (NO_3) in lakes, suggests that deposition of inorganic N in wetfall may affect the amount of NO_3 in lakes through a combination of direct and indirect processes such as enhanced nitrification.

Introduction

In the western United States, anthropogenic emissions of NO_x (nitrogen oxides) and NH_3 (ammonia) from energy generation activities, transportation, industry, and agricultural activities contribute to deposition of dissolved inorganic nitrogen (DIN = NO_3 + NH_4) in high-elevation watersheds (*1, 2*). There is considerable uncertainty about the source areas and emission types that contribute to deposition of DIN, which can adversely affect sensitive aquatic habitats of high-elevation lake basins (*3*). Deposition data indicate that DIN in wetfall has increased steadily over much of the Rocky Mountains in recent years for a variety of reasons (*4–6*), including increases in motor vehicle emissions which have offset reductions in NO_x emissions from fossil-fuel burning industries (*7*) and regional increases in ammonia emissions (*8*). The percent of DIN in wet deposition contributed by NH_4 has increased from 1992−1996 to 2002−2006, and is now approximately 50% of measured DIN in over half of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites in the Rocky Mountains (*8*), including sites located near national parks. A previous study that evaluated all major emission sources (including both stationary and mobile sources) across the Rocky Mountains found that the Colorado Front Range, which is located near large urban centers, has the highest N emissions (*2*). Spatial trends in deposition of DIN in wetfall over the Rocky Mountains show that deposition is greatest near Rocky Mountain National Park and Great Sand Dunes National Park and Preserve near the Colorado Front Range in the southern Rocky Mountains, compared to National Parks in the northern Rocky Mountains that are also located further west (*9*) (Supporting Information Figures SI-1 and SI-2).

Federal and state resource managers are investigating policy options to alleviate this problem by reducing anthropogenic emissions of NO_x and NH_3. However, identifying source areas and emission types is complicated (*10, 11*). Isotopic tracers of N measured in precipitation and water samples show promise in helping to identify these emission sources (*10, 11*). Previously published studies (*12, 13*) indicate $\delta^{15}N$ (NO_3) values in NO_x emissions from coal-fired power plants have isotopic values ranging from +6 to +13‰ (*12, 13*). $\delta^{15}N$ (NO_3) values from motor vehicle NO_x emissions in tailpipe exhaust range from −13 to −2‰ (*12*). The following $\delta^{15}N$ (NO_3) values have also been reported for vehicle NO_x emissions in tailpipe exhaust (+3.7‰) and roadside vegetation (+3.8‰) (*14, 15*). The use of these NO_3 isotopes has been limited in part because analytical techniques for NO_3 isotopes required large sample volumes that made it logistically difficult to sample in areas with topographically complex terrain.

Researchers have shown that elevated levels of atmospheric N deposition in the Front Range of Colorado have caused substantial changes in the state and function of terrestrial and aquatic ecosystems at high elevations (*1, 16–20*). In one study, inorganic N retention of DIN in wetfall averaged 72% in high-elevation ecosystems (*21*). N deposition in excess of the total combined plant and microbial demand can cause watershed N saturation and increased rates of N leaching from soils to aquatic ecosystems (*22*), which is occurring in the Colorado Rockies (*20, 23*). This excess N can result in a cascade of ecological effects in surface waters that includes acidification, eutrophication, and increased emissions of N_2O, a greenhouse gas. Eutrophication increases primary productivity in lakes and streams and alters diatom species distributions that form the base of the food web in many high-elevation lakes (*24*). The combined effects of increasing N deposition and drought have sharply increased stream-water concentrations of NO_3 in Rocky Mountain National Park (Rocky) in recent years (*20*). Changes in the water quality of the headwater systems affects not only fish, wildlife, and

* Corresponding author phone: 303/236-4882 ext. 250; fax: 303/236-4912; e-mail: lnanus@usgs.gov: mailing address: U.S. Geological Survey, WRD-CWSC, Federal Center, PO Box 25046, MS 415, Lakewood, Colorado 80225.
† U.S. Geological Survey, Denver, Colorado.
‡ University of Colorado at Boulder and Institute of Arctic and Alpine Research.
§ University of Pittsburgh.
‖ U.S. Geological Survey, Menlo Park, California.

ecosystem integrity, but also downstream ecosystems and water users.

Increased aquatic productivity resulting from eutrophication accelerates the accumulation of organic matter in the water column and in lake sediments. Decomposition of this organic matter promotes hypoxia in lakes when they are ice-covered during winter, and may adversely affect fish populations (25). In Rocky, mineralization of organic N in pond sediments has caused concentrations of dissolved ammonia in vernal ponds to reach levels that may be harmful to threatened amphibians that breed there (26). Although N deposition is greatest in the Front Range of Colorado, other high-elevation sites in the Rocky Mountains also show symptoms of early stage N saturation. The progression toward N saturation is expected to continue if N deposition continues at current or higher levels in the future (27).

The denitrifier method to determine the dual isotopic composition ($\delta^{15}N$ and $\delta^{18}O$) of NO_3 is well suited for studies of NO_3 contributions to streams and lakes (28). This method requires only 20–60 nmol of NO_3 and enables high throughput of samples (29, 30). The development of a new analytical technique for analyzing $\delta^{15}N$ (NH_4) holds promise in terms of tracing other sources of N deposition. However, it requires large sample volumes and is beyond the scope of this study.

To evaluate NO_3 sources, we analyzed both $\delta^{15}N$ and $\delta^{18}O$ of NO_3 using the denitrifier method in samples collected from lakes in the Rocky Mountains that span a range of NO_3 deposition (31). The objectives of this study were to (1) evaluate the spatial distribution of $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) in lake samples from five National Parks collected during baseflow conditions; and (2) compare the isotopic composition of the lake water from these watersheds with that of precipitation collected at nearby NADP/NTN sites. This study is the first comprehensive evaluation using NO_3 isotopes to investigate the possible relationship between atmospheric deposition of NO_3 in wetfall and the NO_3 in lakes of the Rocky Mountains.

Experimental Section

Study Area and Field Methods. The five National Parks in the Rocky Mountains included in this study are Glacier National Park (Glacier), Yellowstone National Park (Yellowstone), Grand Teton National Park (Grand Teton), Rocky Mountain National Park (Rocky), and Great Sand Dunes National Park and Preserve (Great Sand Dunes) (Supporting Information Figure SI-2). The areas under investigation are in the headwaters of most of the major rivers in the western United States, and their airsheds extend across state and national political boundaries. Precipitation chemistry was measured at 7 NADP/NTN sites located near National Parks (Supporting Information Figure SI-2). The precipitation samples collected weekly at NADP/NTN sites from 2000 were pooled into bimonthly, volume-weighted-mean composites, and analyzed for NO_3 concentrations and for $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) (10). For this study, bimonthly $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) values were aggregated into average annual wet deposition values. Sample duplicates had an average standard deviation of 0.6‰ for $\delta^{18}O$ (NO_3) and 0.4‰ for $\delta^{15}N$ (NO_3). Dry deposition was not included in this evaluation.

Lakes were randomly selected for sampling during late summer 2004 and are spatially distributed within each of the National Parks. The 56 sampled lakes range in elevation from 2000 to 3800 m and from 1 to 46 ha in area, with 65% of the lakes less than 5 ha in area. Surface waters were collected from the outflow of each lake as grab samples during the low-flow period from August to September. Samples were collected at baseflow when NO_3 concentrations in surface waters are generally near or at their annual minima as a result of biological assimilation (2). Surface waters that have elevated NO_3 concentrations (i.e., greater than about 5 μeq/

L) during baseflow conditions may be approaching the initial stage of N saturation (2) and may be particularly susceptible to inputs of DIN in wetfall. Polyethylene bottles (250 mL) were soaked with deionized (DI) water overnight and then rinsed with DI water 5 times; bottles were further rinsed 3 times with sample water at the time of collection. Samples were frozen after collection and transported to the Kiowa Environmental Chemistry Laboratory (32) run by the Niwot Ridge Long-Term Ecological Research Program (University of Colorado, INSTAAR), which specializes in analysis of dilute waters such as those found in the study area (33).

Laboratory Analyses. All lake samples were analyzed for pH, acid neutralizing capacity (ANC), conductance, and major ions. ANC and pH were measured immediately after melting or after return to the laboratory using the Gran titration technique. Subsamples were immediately filtered through prerinsed (300 mL), 47-mm Gelman A/E glass fiber filters with ca. 1-μM pore size. Filtered samples were stored in the dark at 4 °C for subsequent analyses within 1−4 weeks. Anions were measured using ion chromatography (Dionex DX 500) employing chemical ion suppression and conductivity detection. Base cations were analyzed with a Varian AA6 atomic absorption spectrophotometer using an air-acetylene flame. Quality assurance for this study was addressed with field duplicate samples separated by 10−15 samples in each run. Analytical precision for all solutes was less than 2% and detection limits were less than 1 μeq/L.

Frozen aliquots were analyzed for $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) using the denitrifier method at the USGS Stable Isotope Laboratory in Menlo Park. In this method, denitrifying bacteria (*Pseudomonas aureofaciens*) quantitatively convert the N and O from NO_3 into gaseous nitrous oxide (N_2O) for isotopic analysis (29, 30). A minimum of 20 nmol NO_3 was required to analyze samples on a Micromass IsoPrime isotope ratio mass spectrometer (IRMS). Sample duplicates had an average standard deviation of 0.7‰ for $\delta^{18}O$ (NO_3) and 0.2‰ for $\delta^{15}N$ (NO_3).

To evaluate regional differences in spatial patterns, $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) values from lakes were compared to $\delta^{15}N$ (NO_3) values in precipitation from collocated NADP/NTN sites. Also, isotopic values of NO_3 in lakes were compared with emissions within a specified buffer distance calculated using emissions inventories (2, 7, 10). For this study, stationary source NO_x emission inventory data that are readily available (7) were used as a surrogate for various anthropogenic N emission sources that are not as readily available including motor vehicles, agriculture, feedlots, power plants, and other industrial emission sources (2).

Basin characteristics were evaluated to determine their potential influence on spatial patterns in NO_3 concentrations, $\delta^{18}O$ (NO_3), and $\delta^{15}N$ (NO_3) values. Forty-eight basin characteristics were derived using Geographic Information Systems (GIS) software, and included bedrock type, slope, aspect, elevation, lake area, soil type, and vegetation type, following the protocols presented in ref 34.

Results and Discussion

NO_3 concentrations in the 56 lakes sampled ranged from below the detection limit (~1 μeq/L) to 38 μeq/L (Supporting Information Figure SI-3). Mean values were highest in Rocky (20 μeq/L) and lowest in Yellowstone (0.2 μeq/L). An analysis of variance test (ANOVA) shows that mean concentrations of NO_3 varied significantly among National Parks ($n = 56$, $p < 0.001$). A follow-up Tukey−Kramer HSD test shows that the mean value of 20 μeq/L for NO_3 at Rocky was significantly higher than that of the other 4 parks.

Of the 56 lakes sampled, 37 lakes had sufficient mass of NO_3 to analyze for $\delta^{15}N$ (NO_3) and $\delta^{18}O$ (NO_3) (Supporting Information Table SI-1). Lake samples with NO_3 mass greater
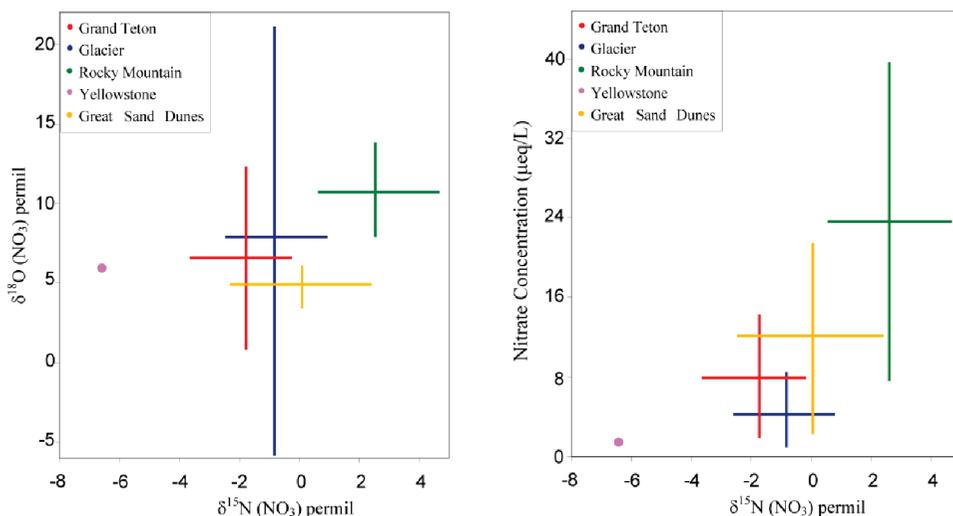
FIGURE 1. Range in lake $\delta^{15}N$ (NO_3) values compared with range in lake $\delta^{18}O$ (NO_3) values (1a) and range in lake NO_3 concentrations (1b).
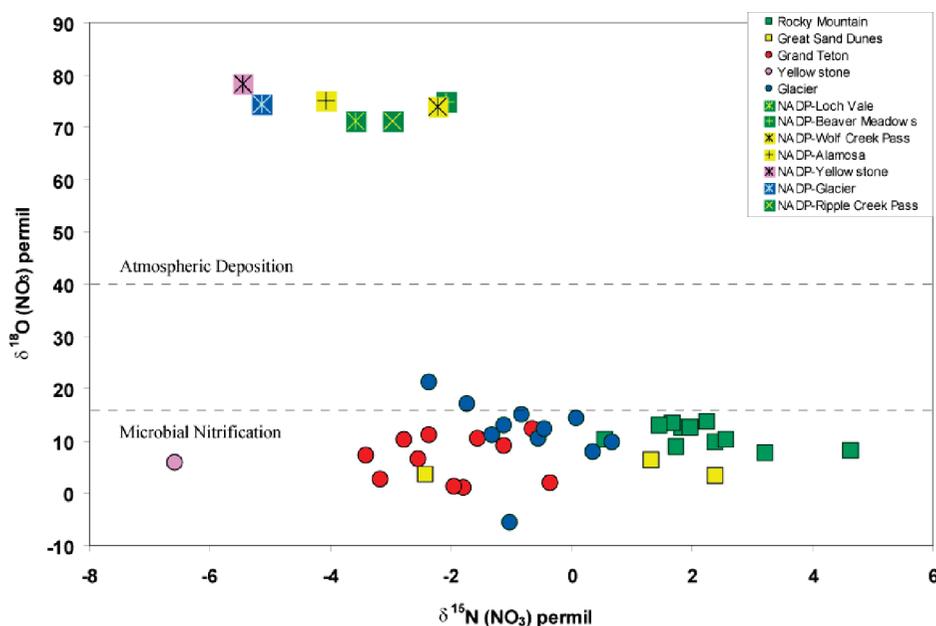
FIGURE 2. $\delta^{15}N$ (NO_3) values compared with $\delta^{18}O$ (NO_3) values at NADP/NTN sites and at lakes. Dashed lines represent estimated $\delta^{18}O$ (NO_3) end-members.

than 20 nmoles were distributed among the parks as follows: Glacier ($n = 11$), Grand Teton ($n = 11$), Great Sand Dunes ($n = 3$), Rocky ($n = 11$), and Yellowstone ($n = 1$).

$\delta^{18}O$ (NO_3) values in lake samples ranged from -5.7 to $+21.3‰$, with a median value of $+10.1$ (Figure 1a). Both of the lakes with elevated $\delta^{18}O$ (NO_3) values are located in Glacier and receive direct input from glacier outflow, which may explain the enriched $\delta^{18}O$ (NO_3) values. $\delta^{15}N$ (NO_3) values for the 37 lakes ranged from -6.6 to $+4.6‰$ (Figure 1a), with a median value of $-0.6‰$. Somewhat surprisingly, this range in $\delta^{15}N$ (NO_3) values is similar to $\delta^{15}N$ (NO_3) values in wet NO_3 deposition from NADP/NTN sites across the Northeastern and Mid-Atlantic U.S. (*10*). A plot of $\delta^{15}N$ (NO_3) values compared to NO_3 concentration, color coded by park, is shown in Figure 1b. In general, there was a trend for the lake $\delta^{15}N$ (NO_3) values to increase with increasing NO_3 concentrations ($r^2 = 0.5$; $p < 0.05$). Lake $\delta^{18}O$ (NO_3) values, however, did not increase with increasing NO_3 concentrations ($r^2 = 0.02$; $p > 0.1$).

We compared the isotopic composition of NO_3 from these catchments to the isotopic composition of NO_3 in precipitation collected at the 7 nearby NADP/NTN sites in Figure 2

(Supporting Information Table SI-2). The $\delta^{18}O$ (NO_3) values in precipitation ranged from $+71$ to $+78‰$, significantly more enriched than the -5.7 to $+21.3‰$ of samples in lake water ($p < 0.001$). The $\delta^{18}O$ (NO_3) values in lake water are not indicative of a direct atmospheric source (Figure 2). The $\delta^{15}N$ (NO_3) values in precipitation tended to be significantly more depleted than values in lake waters ($p < 0.001$), ranging from -5.5 to $-2.0‰$ (Figure 2). $\delta^{15}N$ (NO_3) values in precipitation generally increased from north to south. For example, $\delta^{15}N$ (NO_3) values were $-5.5‰$ for Glacier, and increased to $-2.0‰$ continuing south toward Wolf Creek Pass, Colorado. There was a significant positive trend for the atmospheric $\delta^{15}N$ (NO_3) values to increase with increasing NO_3 concentrations ($r^2 = 0.7$; $p < 0.01$).

The occurrence of higher NO_3 concentrations and enriched $\delta^{15}N$ (NO_3) values in precipitation in National Parks characterized by higher NO_3 concentrations and enriched $\delta^{15}N$ (NO_3) values in lake waters suggests that atmospheric deposition of DIN in wetfall affects the amount of NO_3 in lakes. $\delta^{15}N$ (NO_3) values in both precipitation and lakes are more enriched in Colorado parks than in the northern parks in Wyoming and Montana. The correspondence of enriched
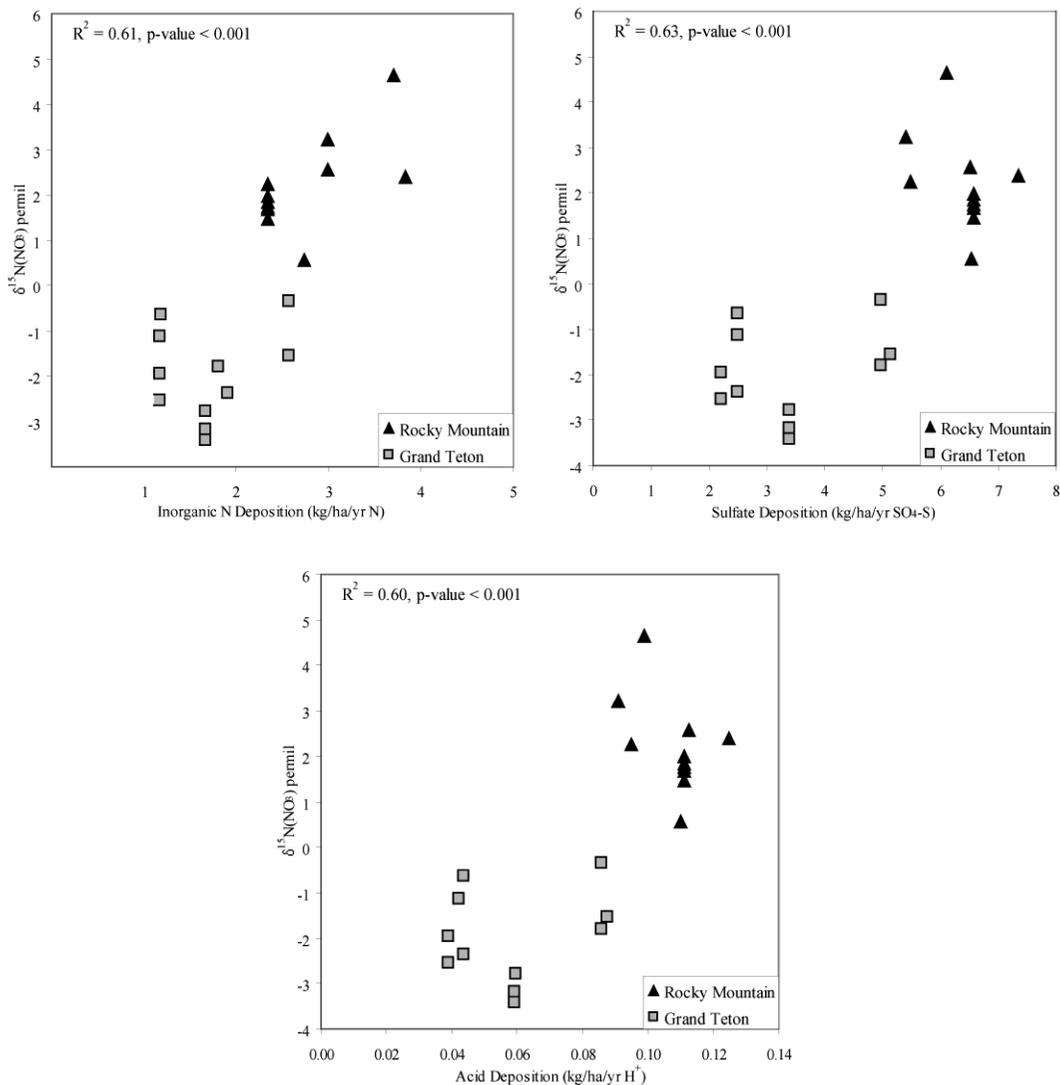
FIGURE 3. $\delta^{15}N$ (NO$_3$) values of lake water compared to average annual deposition of inorganic N (DIN), SO$_4$, and H$^+$ in wetfall for two parks (estimates of wetfall from ref **31**).

$\delta^{15}N$ with higher concentrations of NO$_3$ in precipitation and lakes suggests that areas with higher deposition are affected by a source of anthropogenic N emissions that is enriched in $\delta^{15}N$. These results are similar to an earlier study in which significant correlations between $\delta^{15}N$ (NO$_3$) values in precipitation and stationary source NO$_x$ emissions within source areas of 500−600 km in the eastern U.S. were attributed to regional transport of NO$_x$ (*10*).

To evaluate this idea, isotopic values of $\delta^{15}N$ (NO$_3$) from lake water were compared with total stationary source NO$_x$ emissions in USEPA Region 8 during 1990−1999, the longest recent period of record (*7*), as a proxy for total anthropogenic N emissions (*2*). Total stationary source NO$_x$ emissions within a variety of buffer distances ranging from 50 to 600 km were tested, and 300 km was the most highly correlated with the data for all parks. Results for Colorado and Wyoming indicate that there is a significant positive correlation ($r^2 = 0.8$, $p < 0.05$) between $\delta^{15}N$ (NO$_3$) from lake waters and NO$_x$ emissions within a 300 km buffer for Rocky, Grand Teton, Great Sand Dunes, and Yellowstone (Supporting Information Figure SI-4). For Glacier, there are no reported stationary sources of NO$_x$ emissions within a 300 km buffer during 1990−1999 (*7*). As NO$_x$ emissions increase, $\delta^{15}N$ (NO$_3$) values in NO$_3$ from lakes increase, suggesting a relationship between spatial variations in $\delta^{15}N$ across the Rocky Mountains and N emissions. This correlation suggests a contribution of regional anthropogenic N emission sources. This is particularly

apparent for National Parks in Colorado (Rocky and Great Sand Dunes) which are located near larger anthropogenic N emission sources compared to parks in northern Wyoming (Grand Teton and Yellowstone).

To further evaluate a potential connection between atmospheric deposition of pollutants and NO$_3$ in lake waters, lake $\delta^{15}N$ (NO$_3$) values were compared with average annual deposition estimates of DIN, SO$_4$, and H$^+$ in wetfall (*31*) at Rocky and Grand Teton (Figure 3). Results indicate that lake water $\delta^{15}N$ (NO$_3$) values are significantly correlated ($p < 0.001$) with average annual deposition estimates of DIN ($r^2 = 0.61$), SO$_4$ ($r^2 = 0.63$), and H$^+$ ($r^2 = 0.60$). This correlation is consistent with the spatial variability of $\delta^{15}N$ (NO$_3$) in lake waters being related to the atmospheric deposition of pollutants in wetfall (Figure 3).

Modeling results using 48 GIS attributes for each watershed show that there is a significant positive relation ($p < 0.05$) between elevation for lakes located at elevations greater than 2500 m and $\delta^{15}N$ (NO$_3$) values in lake water (Figure 4a). There was no significant relation between $\delta^{18}O$ (NO$_3$) values in lake waters and any GIS attribute. Geographic patterns of NO$_3$ concentrations of high-elevation lakes in the Rockies have previously been reported and results show particularly high NO$_3$ concentrations in Rocky (*35*). Here we show an increase in $\delta^{15}N$ (NO$_3$) values of lake waters with increasing elevation of the lakes (Figure 4a). There was also a trend for $\delta^{15}N$ (NO$_3$) values in precipitation to increase with increasing
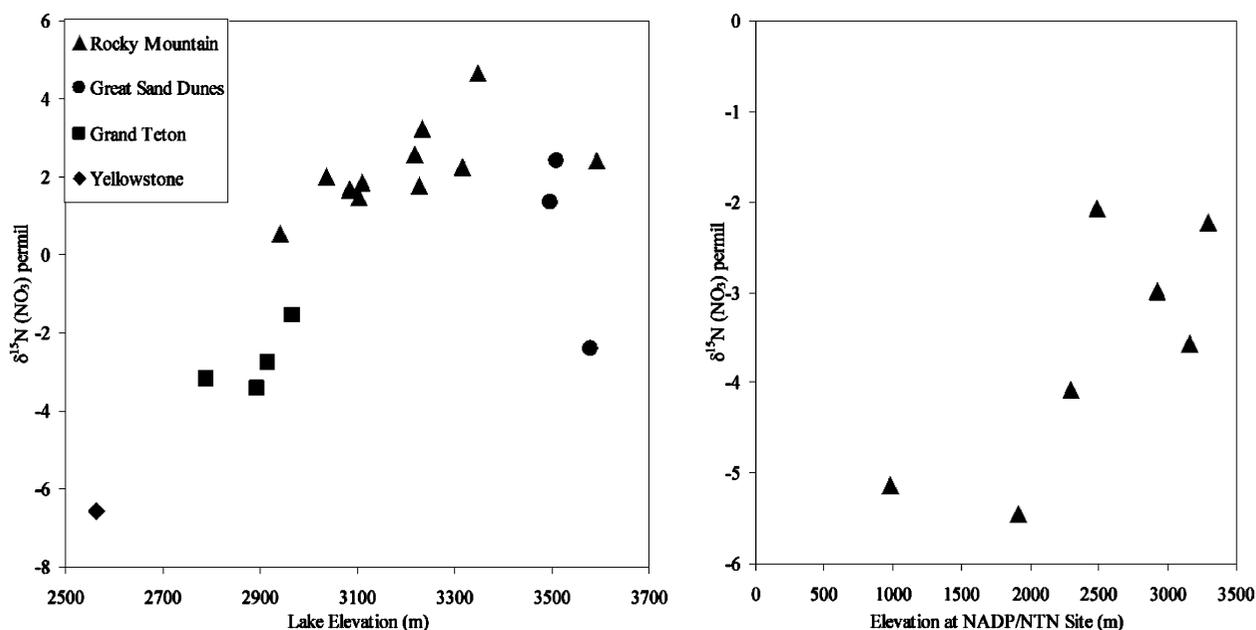
FIGURE 4. Lakes with elevation greater than 2500 m compared with $\delta^{15}N(NO_3)$ values in lake water (4a) and $\delta^{15}N(NO_3)$ values in NADP/NTN precipitation compared with elevation (4b).

elevation ($p < 0.05$) (Figure 4b). It is possible that the enriched $\delta^{15}N$ (NO_3) values in precipitation with increasing elevation may be influencing the NO_3 isotopic values collected from lake water.

The source of NO_3 in lake and stream waters from mountain catchments in the Sierra Nevada has previously been examined with a simple end-member mixing analysis using $\delta^{18}O$ (NO_3) values (36). Here we have direct measurements of the atmospheric end-member, where $\delta^{18}O$ (NO_3) values range from +71 to +78‰. The range in $\delta^{18}O$ (NO_3) values of lake water is from −5.7 to + 21.3 (Figure 2), with 95% of samples having $\delta^{18}O$ (NO_3) values less than +15‰ (Figure 2). However, the terrestrial end-member is difficult to parameterize without direct measurements of subsurface $\delta^{18}O$ (NO_3) values. The generally accepted upper limit for $\delta^{18}O$ of microbial NO_3 is +15‰ for the terrestrial end-member (11).

Several previous studies have evaluated N sources in streamwater draining undisturbed catchments using a dual NO_3 isotope approach ($\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3)) to differentiate watershed NO_3 sources (18, 37, 38). NO_3 in streamwater was found to be mainly derived from nitrification in the Catskill mountains of New York (37). Most of the NO_3 in streamflow was nitrified within two forested catchments in New Hampshire (38). Similarly, most of the streamwater NO_3 in Rocky had an isotope signature indicative of substantial biological cycling of atmospherically derived N prior to release from the ecosystem (18).

However, assuming a $\delta^{18}O$ (NO_3) value of less than +15‰ for a terrestrial source could underestimate the actual contribution of atmospheric NO_3 to the NO_3 in lake waters. Laboratory incubation experiments and field studies have shown that the $\delta^{18}O$ (NO_3) formed by microbial nitrification range between +2 and +14‰, assuming that soil−water $\delta^{18}O$ (NO_3) values vary between −15 and −5‰ (39). In the Catskill Mountains of New York, $\delta^{18}O$ (NO_3) values from +13.2 to +16.0‰ were measured for NO_3 derived by nitrification in incubated soil samples (37). In Sleepers River, a snowmelt-dominated catchment in Vermont, $\delta^{18}O$ values of stream NO_3 ranged from −7.7 to +18.3‰ and generally were correlated with NO_3 concentrations (28). It was concluded that a significant amount of NO_3 during snowmelt was directly from atmospheric deposition of NO_3 (28). A $\Delta^{17}O$ in surface water

did not undergo biologic processing before being exported from the system (40). Thus, it is possible that the direct atmospheric contribution to NO_3 may be underestimated in earlier reports. A quantitative source apportionment of atmospheric NO_3 to the NO_3 in lake waters is difficult because of the wide range of $\delta^{18}O$ values from microbial nitrification.

The trend toward increasing $\delta^{15}N$ (NO_3) values with increasing concentrations of NO_3 in lake waters, which in turn are associated with increasing elevation and increasing inputs of DIN in wetfall, is intriguing. One potential explanation that deserves additional study is that the more enriched values of $\delta^{15}N$ (NO_3) may result from increasing rates of net nitrification in the watersheds. Well-drained soils typically show an increase in total soil-$\delta^{15}N$ with increasing soil depth and age (11). This increase in $\delta^{15}N$ is attributed to fractionation during net mineralization and generally results from the metabolism of microbial heterotrophs that produce $\delta^{15}N$-enriched biomass as a result of $\delta^{15}N$-depleted waste (41, 42). DIN deposition in wetfall in the Rocky Mountains increases with increasing elevation (>2500 m) compared to lower elevations (<2500 m), due in part to orographically enhanced precipitation amounts at high elevations (2, 31). This increased DIN deposition in wetfall may lead to enhanced N cycling in high-elevation watersheds. The percent of DIN in wet deposition contributed by NH_4 is now approximately 50% of measured DIN in the Rocky Mountains (8). However, export of NH_4 in these watersheds is small, making up less than 6% of DIN compared to approximately 94% of DIN that is NO_3 in the baseflow lake outlet samples. This indicates that at least some of the NH_4 in atmospheric deposition of DIN in wetfall is mineralized and nitrified to NO_3 that is exported to lake waters (17). Research in high-elevation areas of the Colorado Rockies show high rates of N-mineralization (43) and less NH_4 assimilation due to a lack of vegetation, particularly in talus areas (44). These areas tend to be carbon limited (45), driving systems toward net nitrification (43, 46). It is possible that high rates of DIN deposition in wetfall at high elevations in the Colorado Rockies (2, 3), characterized by enriched $\delta^{15}N$ (NO_3) values (10), may lead to enhanced nitrification and more enriched $\delta^{15}N$ values in the NO_3 exported to lake waters.

The role of denitrification in these systems was also considered, however, denitrification does not appear to

substantially affect $\delta^{15}N$ (NO_3). If denitrification were important in these systems, a progression toward decreased NO_3 concentration would be expected. This trend does not exist in the data. Instead, the data show a significant correlation with increasing NO_3 concentrations and increasing $\delta^{15}N$ (NO_3) values in lake waters suggesting that enhanced nitrification may be important in these systems. Our results are consistent with previous work evaluating pathways for NO_3 release from an alpine watershed using $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) which found that denitrification does not affect fluxes of NO_3 from surface water or talus springs (18).

The results presented in this study suggest that relatively high anthropogenic emissions of NO_x may be contributing to high NO_3 concentrations in high-elevation lakes in the southern Rocky Mountains through a combination of direct and indirect processes such as enhanced nitrification. This study provides valuable information on spatial patterns in $\delta^{15}N$ (NO_3) in lakes and precipitation across the Rocky Mountains and has important implications as N emissions (stationary and mobile sources) and inorganic N deposition continue to increase into the future. Results of this study may be helpful to resource managers who are considering the best way to reduce N emissions to control inorganic N deposition in sensitive, protected areas.

Acknowledgments

Supporting Information Available

Four additional figures including a national map of DIN deposition (Figure SI-1), a map of the study sites (Figure SI-2), nitrate concentrations at 56 lakes aggregated by National Park (Figure SI-3), and $\delta^{15}N$ (NO_3) values compared with NO_x emissions (Figure SI-4). Two additional tables including a table of NO_3 concentration, $\delta^{18}O$ (NO_3) and $\delta^{15}N$ (NO_3) values for National Park lakes (Table SI-1) and NADP/NTN precipitation sites (Table SI-2). This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Baron, J. S.; Rueth, H. M.; Wolfe, A. M.; Nydick, K. R.; Allstott, E. J.; Minear, J. T.; Moraska, B. Ecosystem responses to nitrogen deposition in the Colorado Front Range. *Ecosystems* **2000**, *3*, 352–368.

(2) Williams, M. W.; Tonnessen, K. A. Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. *Ecol. Appl.* **2000**, *10*, 1648–1665.

(3) Burns, D. A. The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and Southern Wyoming, USA - A critical review. *Environ. Pollut.* **2004**, *127*, 257–269.

(4) Baumgardner, R. E., Jr.; Lavery, T. F.; Rogers, C. M.; Isil, S. S. Estimates of the atmospheric deposition of sulfur and nitrogen species: Clean Air Status and Trends Network, 1990−2000. *Environ. Sci. Technol.* **2002**, *36*, 2614–2629.

(5) Fenn, M. E.; Haeuber, R.; Tonnesen, G. S.; Baron, J. S.; Grossman-Clarke, S.; Hope, D.; Jaffe, D. A.; Copeland, S.; Geiser, L.; Reuth, H. M.; Sickman, J. O. Nitrogen emissions, deposition, and monitoring in the western United States. *Bioscience* **2003**, *53*, 391–403.

(6) Nilles, M. A.; Conley, B. E. Changes in the chemistry of precipitation in the United States, 1981−1998. *Water, Air Soil Pollut.* **2001**, *130*, 409–414.

(7) U.S. Environmental Protection Agency. *National Quality and Emissions Trends Report 1998*; EPA-454/R-00-003; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 2000.

(8) National Atmospheric Deposition Program. *National Atmospheric Deposition Program 2006 Annual Summary*; NADP Data Report, 2007-01; Illinois State Water Survey: Champaign, IL, 2007.

(9) *National Atmospheric Deposition Program: NRSP-3*; NADP Program Office, Illinois State Water Survey, 5 2204 Griffith Dr., Champaign, IL 61820, 2008.

(10) Elliott, E. M.; Kendall, C.; Wankel, S. D.; Burns, D. A.; Boyer, E. W.; Harlin, K.; Bain, D. J.; Butler, T. J. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. *Environ. Sci. Technol.* **2007**, *41*, 7661–7667.

(11) Kendall, C. Tracing nitrogen sources and cycling in catchments. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J. J., Eds.; Elsevier:, Amsterdam, 1998.

(12) Heaton, T. H. E. $^{15}N/^{14}N$ ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus* **1990**, *42*, 304–307.

(13) Kiga, T.; Watanabe, S.; Yoshikawa, K.; Asano, K.; Okitsu, S.; Tsunogai, U.; Narukawa, K. *Evaluation of NO_x Formation in Pulverized Coal Firing by Use of Nitrogen Isotope Ratios*; Presented at ASME 2000 International Joint Power Generation Conference, Miami Beach, FL, July 23−26, 2000; ASME: Miami Beach, FL, 2000.

(14) Ammann, M.; Siegwolf, R.; Pichlmayer, F.; Suter, M.; Saurer, M.; Brunold, C. Estimating the uptake of traffic-derived NO_2 from ^{15}N abundance in Norway spruce needles. *Oecologia* **1999**, *118*, 124–131.

(15) Pearson, J.; Wells, D. M.; Seller, K. J.; Bennett, A.; Soares, A.; Woodall, J.; Ingrouille, M. J. Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses. *New Phytol.* **2000**, *147*, 317–326.

(16) Burns, D. A. Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming-A review and new analysis of past study results. *Atmos. Environ.* **2003**, *37*, 921–932.

(17) Campbell, D. H.; Baron, J. S.; Tonnessen, K. A.; Brooks, P. D.; Schuster, P. F. Controls on nitrogen flux in alpine/subalpine watersheds of Colorado. *Water Resour. Res.* **2000**, *36*, 37–47.

(18) Campbell, D. H.; Kendall, C.; Chang, C.C.Y.; Silva, S. R.; Tonnessen, K. A. Pathways for nitrate release from an alpine watershed: Determination using $\delta^{15}N$ and $\delta^{18}O$. *Water Resour. Res.* **2002**, *38* (5), 10.1029/2001WR000294.

(19) Mast, M. A.; Campbell, D. H.; Ingersoll, G. P.; Foreman, W. T.; Krabbenhoft, D. P. *Atmospheric Deposition of Nutrients, Pesticides, and Mercury in Rocky Mountain National Park, Colorado*;USGS WRIR 03-4241; USGS: Washington, DC, 2003.

(20) Williams, M. W.; Baron, J.; Caine, N.; Sommerfield, R. Nitrogen saturation in the Rocky Mountains. *Environ. Sci. Technol.* **1996**, *30*, 640–646.

(21) Sickman, J. O.; Melack, J. M.; Stoddard, J. L. Regional analysis of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rocky Mountains. *Biogeochemistry* **2002**, *57/58*, 341–374.

(22) Aber, J. D.; Nadelhoffer, K. J.; Steudler, P.; Melillo, J. M. Nitrogen saturation in northern forest ecosystems: Excess nitrogen from fossil fuel combustion may stress the biosphere. *Bioscience* **1989**, *39*, 378–386.

(23) Baron, J. S. Hindcasting nitrogen deposition to determine an ecological critical load. *Ecol. Appl.* **2006**, *16*, 433–439.

(24) Wolfe, A. M.; Baron, J. S.; Cornett, J. R. Anthropogenic nitrogen deposition induces rapid ecological change in alpine lakes of the Colorado Front Range (U.S.A.). *J. Paleolimnol.* **2001**, *25*, 1–7.

(25) Vitousek, P. M.; Aber, J. D.; Howarth, R. W.; Likens, G. W.; Matson, P. A.; Schindler, D. W.; Schlesinger, W. H.; Tilman, D. G. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl.* **1997**, *7*, 737–750.

(26) Campbell, D. H.; Muths, E.; Turk, J. T.; Corn, P. S. Sensitivity to acidification of subalpine ponds and lakes in north-western Colorado. *Hydrol. Process.* **2004**, *18*, 2817–2834.

(27) Campbell, D. H. Atmospheric deposition and its effects in the Intermountain West. In *Acid Rain: Are the Problems Solved? Proceedings of the Conference, May 2−3, 2001*; White, J., Ed.; American Fisheries Society: Bethesda, MD, 2003.

(28) Ohte, N.; Sebeysten, S. D.; Shanley, J. B.; Doctor, D. H.; Kendall, C.; Wankel, S. D.; Boyer, E. W. Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique. *Geophys. Res. Lett.* **2004**, *31*, doi:10.1029/2004GL020908.

(29) Sigman, D. M.; Casciotti, K. L.; Andreani, M.; Barford, C.; Galanter, M.; Bohlke, J. K. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* **2001**, *73*, 4145–4153.

(30) Casciotti, K. L.; Sigman, D. M.; Hastings, M. G.; Bohlke, J. K.; Hilkert, A. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* **2002**, *74*, 4905–4912.

(31) Nanus, L.; Campbell, D. H.; Ingersoll, G. P.; Clow, D. W.; Mast, M. A. Atmospheric deposition maps for the Rocky Mountains. *Atmos. Environ.* **2003**, *37*, 4881–4892.

(32) Seibold, C. CU-LTER Kiowa Wet Chemistry Laboratory Manual; 2001; http://snowbear.colorado.edu/Seiboldc/Kiowa.html.

(33) Williams, M. W.; Hood, E.; Caine, N. The role of organic nitrogen in the nitrogen cycle of a high-elevation catchment, Colorado Front Range, USA. *Water Resour. Res* **2001**, *37* (10), 2569–2582.

(34) Nanus, L.; Campbell, D. H.; Williams, M. W. *Sensitivity of alpine and subalpine lakes to acidification from atmospheric deposition in Grand Teton National Park and Yellowstone National Park, Wyoming*;USGS SIR 05-5023; USGS: Washington, DC, 2005.

(35) Clow, D. W.; Striegl, R.; Nanus, L.; Mast, M. A.; Campbell, D. H.; Krabbenhoft, D. P. Chemistry of selected high-elevation lakes in seven National Parks in the Western United States. *Water, Air Soil Pollut. Focus 2* **2002**, 139–164.

(36) Sickman, J. O.; Leydecker, A.; Chang, C. C. Y.; Kendall, C.; Melack, J. M.; Lucero, D. M.; Schimel, J. Mechanisms underlying export of N from high-elevation catchments during seasonal transitions. *Biogeochemistry* **2003**, *64*, 1–24.

(37) Burns, D. A.; Kendall, C. Analysis of δ^{15}N and δ^{18}O to differentiate NO_3^- sources in runoff in two watersheds in the Catskill Mountains of New York. *Water Resour. Res.* **2002**, *38*, doi:10.1029/2001WR000292.

(38) Pardo, L. H.; Kendall, C.; Pett-Ridge, J.; Chang, C. C. Y. Evaluating the source of streamwater nitrate using Δ^{17} in nitrate in two watersheds in New Hampshire. *USA. Hydrol. Process.* **2004**, *18*, 2699–2712.

(39) Mayer, B.; Bollwerk, S. M.; Mansfeldt, T.; Huetter, B.; Veizer, J. The oxygen isotope composition of nitrate generated by nitrification in acid rain forest floors. *Geochim. Cosmochem. Acta.* **2001**, *65* (16), 2743–2756.

(40) Michalski, G.; Meixner, T.; Fenn, M.; Hernandez, L.; Sirulnik, A.; Allen, E.; Theimens, M. Tracing atmospheric nitrate deposition in a complex semiarid ecosystem using Δ^{17}O. *Environ. Sci. Technol.* **2004**, *38*, 2175–2181.

(41) Nadelhoffer, K. J.; Fry, B. Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *J. Soil Sci. Soc. Amer.* **1988**, *52*, 1633–1640.

(42) Nadelhoffer, K. J.; Fry B. Nitrogen isotope studies in forest ecosystems. In *Stable Isotopes in Ecology*; Lajtha, K., Michener, R., Eds.; Blackwell: Oxford, 1994.

(43) Brooks, P. D.; Williams, M. W. Snowpack controls on nitrogen cycling. *Hydrol. Process.* **1999**, *13*, 2177–2190.

(44) Williams, M. W.; Davinroy, T.; Brooks, P. D. Organic and inorganic nitrogen pools in talus soils and water, Green Lakes Valley, Colorado Front Range. *Hydrol. Process.* **1997**, *11*, 1747–1760.

(45) Ley, R.; Williams, M. W.; Schmidt, S. K. Microbial population dynamics in an extreme environment: controlling factors in talus soils at 3750 m in the Colorado Rocky Mountains. *Biogeochemistry* **2004**, *68*, 313–335.

(46) Williams, M. W.; Knauf, M.; Cory, R.; Caine, N.; Liu, F. J. Nitrate content and potential microbial signature of rock glacier outflow, Colorado Front Range. *Earth Surf. Process.* **2007**, DOI: 10.1002/esp.1455.