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Spatial patterns of atmospheric deposition of nitrogen and sulfur using ion-exchange resin collectors in Rocky Mountain National Park, USA

David W. Clow^{a,*}, Heidi A. Roop^{a,b}, Leora Nanus^c, Mark E. Fenn^d, Graham A. Sexstone^a^a United States Geological Survey, Denver Federal Center, MS 415, Denver, CO, 80225, USA^b GNS Science, 1 Fairway Drive, Avalon, Lower Hutt, 5010, New Zealand^c Department of Geography and Environment, San Francisco State University, 1600 Holloway Avenue, San Francisco, CA, 94132, USA^d US Forest Service, Pacific Southwest Research Station, 4955 Canyon Crest Drive, Riverside, CA 92507, USA

H I G H L I G H T S

- Deposition of NO₃⁻ and DIN were positively related to elevation.
- Summer DIN deposition was 25–50% greater on the east side of the park than on the west.
- A high-resolution geospatial model of summer DIN deposition was created for the park.
- Emissions sources and climate patterns affect spatial patterns in N and S deposition.
- Seasonal patterns in NO₃⁻ isotopes may reflect variations in emissions sources.

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Lakes and streams in Class 1 wilderness areas in the western United States (U.S.) are at risk from atmospheric deposition of nitrogen (N) and sulfur (S), and protection of these resources is mandated under the Federal Clean Air Act and amendments. Assessment of critical loads, which are the maximum exposure to pollution an area can receive without adverse effects on sensitive ecosystems, requires accurate deposition estimates. However, deposition is difficult and expensive to measure in high-elevation wilderness, and spatial patterns in N and S deposition in these areas remain poorly quantified. In this study, ion-exchange resin (IER) collectors were used to measure dissolved inorganic N (DIN) and S deposition during June 2006–September 2007 at approximately 20 alpine/subalpine sites spanning the Continental Divide in Rocky Mountain National Park. Results indicated good agreement between deposition estimated from IER collectors and commonly used wet + dry methods during summer, but poor agreement during winter. Snowpack sampling was found to be a more accurate way of quantifying DIN and S deposition during winter. Summer DIN deposition was significantly greater on the east side of the park than on the west side (25–50%; $p \leq 0.03$), consistent with transport of pollutants to the park from urban and agricultural areas to the east. Sources of atmospheric nitrate (NO₃⁻) were examined using N isotopes. The average $\delta^{15}\text{N}$ of NO₃⁻ from IER collectors was 3.5‰ higher during winter than during summer ($p < 0.001$), indicating a seasonal shift in the relative importance of regional NO_x sources, such as coal combustion and vehicular sources of atmospheric NO₃⁻. There were no significant differences in $\delta^{15}\text{N}$ of NO₃⁻ between east and west sides of the park during summer or winter ($p = 0.83$), indicating that the two areas may have similar sources of atmospheric NO₃⁻. Results from this study indicate that a combination of IER collectors and snowpack sampling can be used to characterize spatial variability in DIN and S deposition in high-elevation wilderness areas. These data can improve our ability to model critical loads by filling gaps in geographic coverage of deposition monitoring/modeling programs and thus may enable policy makers to better protect sensitive natural resources in Class 1 Wilderness areas.

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* Corresponding author.

E-mail address: dwclow@usgs.gov (D.W. Clow).

1. Introduction

In the western United States (U.S.), and globally, mountain environments provide vital ecosystem services that humans rely on. Their seasonal snowpacks and glaciers store freshwater used by more than half of the world's population for drinking, agriculture, and industry; they are home to unique and diverse assemblages of flora and fauna; and they are popular destinations for tourism and recreation (Grêt-Regamey et al., 2012). Thus, the ecological integrity of mountain ecosystems is critically important; however, many mountainous areas are undergoing rapid change in response to anthropogenic activities. Many high-elevation ecosystems are highly sensitive to nitrogen (N) and sulfur (S) pollutants emitted from agricultural, mobile (e.g. vehicles), and stationary (e.g., power plants) sources, which contribute to nutrient enrichment and acidification of surface water (Baron et al., 2000; Campbell et al., 1995; Fenn et al., 2003; Williams and Tonnessen, 2000). This sensitivity stems from a prevalence of thin, poorly developed soils, sparse vegetation, and short growing seasons, which limit the ability of ecosystems to assimilate N or neutralize acidity (Clow and Sueker, 2000).

Rocky Mountain National Park (RMNP), in the northern Front Range of Colorado, USA, has over 150 lakes and 720 km of streams, and is bisected by the north-south trending Continental Divide (Fig. 1). Surface-water nitrate (NO_3^-) concentrations in the park's high-elevation lakes and streams are well above natural background levels, particularly on the east side of the park, and lake sulfate (SO_4^{2-}) shows a similar pattern (Clow et al., 2002b). The elevated lake NO_3^- concentrations have caused changes in the composition of aquatic biota in high-elevation RMNP lakes (Baron et al., 2000; Wolfe et al., 2003), and effects on terrestrial biota have been noted in the park as well (Baron et al., 2000; Bowman et al., 2012; McDonnell et al., 2014). It has generally been assumed that the east-side/west-side patterns in surface-water NO_3^- reflect greater N deposition on the east side of the park because of emissions from vehicles and power plants in the Denver–Fort Collins urban corridor east of the Front Range, and agriculture sources on the Eastern Plains (Fig. 1; Baron et al., 2000; Benedict et al., 2013; Burns, 2003). Although this assumption seems reasonable given higher N emissions and atmospheric

reactive N concentrations east of the park than to the west (Benedict et al., 2013), spatially distributed data on N deposition in the park to test this assumption have been lacking. An alternative explanation is that certain basin characteristics, such as an abundance of steep terrain and exposed bedrock and talus, make lakes and streams on the east side of the park especially sensitive to atmospherically deposited N and S and predispose them to high NO_3^- and SO_4^{2-} concentrations (Clow et al., 2002b; Clow and Sueker, 2000).

There are many Class I wilderness areas in the mountains of the western U.S. (Fig. S1), and 94% of RMNP is designated wilderness; these areas receive special protection for “Air Quality Related Values” under the federal Clean Air Act and amendments (Porter et al., 2005). Although S deposition has been declining nationwide since passage of the 1990 Clean Air Act Amendments, N deposition has been stable or increasing in much of the western U.S. (Lehmann et al., 2005; Morris et al., 2014). Resource managers with the National Park Service and other agencies have developed a protection strategy for Class I wilderness areas focusing on critical loads, which are the maximum exposure to pollution an area can receive without adverse effects on sensitive ecosystems (Nilsson and Grennfelt, 1988; Porter et al., 2005). Critical loads estimates rely, in part, on accurate N and S deposition estimates as the “dose” in a “dose–response” relationship. However, spatial patterns of deposition in mountain areas generally are poorly known because of complex relations between deposition and terrain, and a paucity of deposition monitoring sites at high elevation (Weathers et al., 2000, 2006). In the U.S., the most commonly used estimates for wet and dry deposition are from the National Atmospheric Deposition Program – National Trends Network (NADP-NTN) and Clean Air Status and Trends Network (CASTNET), respectively. The NADP-NTN operates wet-deposition collectors at approximately 260 sites across the country, however, only 9 of the sites (<4%) are at elevations over 3000 m (Fig. S2; <http://nadp.sws.uiuc.edu/nadpdata/ntnsites.asp>; accessed 10/16/13). The CASTNET program models dry deposition based on air quality and meteorological measurements at 90 sites, of which only one is over 3000 m (http://java.epa.gov/castnet/epa_jsp/sites.jsp; accessed 10/16/13). The paucity of NADP-NTN and CASTNET sites at high elevation reflects the difficulty of access and a lack of electrical power in wilderness areas.

Characterizing complex spatial patterns in N and S deposition in high-elevation wilderness areas requires simple, unobtrusive monitoring equipment that is inexpensive, easy to operate, and does not require frequent site visits. Ion-exchange resin (IER) collectors have been used to measure throughfall in forest ecosystems at high spatial resolution (Fenn and Poth, 2004; Root et al., 2013; Simkin et al., 2004; Weathers et al., 2000); however, there are no published reports of their use in high-elevation areas with deep seasonal snowpacks. The IER collectors consist of a funnel connected to a column containing ion-exchange resin that is usually mounted on top of a fence post. Bulk deposition falling on the funnel surface washes down into the column during rain or snowmelt events. The IER collectors may be deployed for extended periods (e.g. months), and equipment costs are low, making it feasible to deploy a large number of collectors to characterize spatial patterns in N and S deposition at high resolution.

Identifying sources of N in atmospheric deposition is another key issue for protection of sensitive resources in Class I wilderness areas. Important sources of N in atmospheric deposition include emissions of nitrogen oxide gases (NO_x) from motor vehicles, power plants, and industrial boilers during high-temperature combustion of fossil fuels; and from fertilized agricultural soils (<http://epa.gov/climatechange/ghgemissions/gases/n2o.html> and <http://www.epa.gov/airtrends/aqtrnd95/no2.html>; accessed 9/10/14).

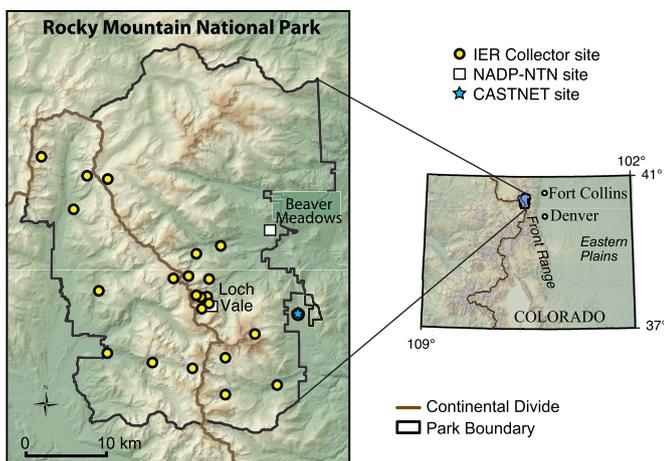


Fig. 1. Map showing locations of ion-exchange resin (IER) collector, NADP-NTN, and CASTNET sites in Rocky Mountain National Park. Base map from U.S. Geological Survey digital data; color scale represents elevation above mean sea level from minimum 2200 m (green) to maximum 4700 m (dark brown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Recent studies using dual isotope analyses of NO_3^- ($\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^-) in wet deposition indicate that isotopes of NO_3^- can be useful for evaluating the relative importance of atmospheric sources of N (Kendall, 1998; Nanus et al., 2008). A recent laboratory study tested whether mixed bed ion-exchange resin could be used for monitoring $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- in atmospheric deposition; results generally were positive, with the caveat that IER columns should not be subjected to high temperatures ($>40^\circ\text{C}$) or high rates of N loading (Templer and Weathers, 2011). Very few studies have been published on using IER columns to collect atmospheric deposition samples for isotope analyses of NO_3^- (e.g., Proemse et al., 2013; Templer and McCann, 2010).

In this study, IER collectors were used to examine the spatial variability of N and S deposition in RMNP. The primary objective was to develop spatially distributed estimates of N and S deposition that can be used to improve deposition maps in the western U.S., and thus inform critical loads analyses. This paper focuses on the main N and S compounds in atmospheric deposition: dissolved inorganic N (DIN; primarily NO_3^- and NH_4^+) and dissolved S (primarily SO_4^{2-}).

Specific objectives include:

- Compare deposition estimates from IER collectors, snowpack sampling, and NADP-NTN and CASTNET programs.
 - Can IER collectors provide accurate estimates of N and S deposition in alpine/subalpine environments with deep seasonal snowpacks?
- Characterize spatial patterns in DIN and SO_4^{2-} deposition in RMNP.
 - Do DIN and SO_4^{2-} deposition vary with elevation?
 - Are there significant differences in DIN and SO_4^{2-} deposition between the east and west sides of the Continental Divide?
- Evaluate possible sources of atmospheric NO_3^- in RMNP using isotopes of NO_3^- in bulk deposition.

2. Methods

2.1. Study sites

Rocky Mountain National Park is in the northern Front Range of Colorado, approximately 50 km west of the Denver–Fort Collins urban corridor and agricultural lands on the Eastern Plains (Fig. 1). The park covers 1075 km², of which 94% is Class 1 wilderness (<http://www.nps.gov/romo/naturescience/wilderness.htm>; accessed 10/19/13). Terrain is complex, with high relief, which may strongly affect patterns of atmospheric deposition. Elevations range from 2330 to 4346 m above sea level. Montane forest dominates the lower elevations, giving way to subalpine forest above 2700 m, and alpine tundra above 3500 m. Approximately one-quarter of RMNP is above tree line, and the park has 72 peaks higher than 3700 m.

Climate in the park is typical of high-elevation, mid-continental mountains, with cold, snowy winters and warm, dry summers with frequent afternoon thunderstorms. Snowfall usually begins in mid-October, accumulating in deep seasonal snowpacks that often persist through June or July, depending on elevation and year. Prevailing winds are predominantly from the west during the winter, with occasional reversals during upslope (easterly) wind conditions (Baron and Denning, 1993; Benedict et al., 2013; Clow et al., 2012). Winds are more variable during summer, and frequent afternoon thunderstorms can help mix the atmosphere and carry pollutants to the park from source areas to the east (Baron and Denning, 1993; Benedict et al., 2013).

The IER collectors were deployed at 19 sites in 2006 and 21 sites in 2007, with locations on both sides of the Continental Divide

(Fig. 1). Site elevations ranged from 2612 to 3642 m, covering high-elevation areas, where few NADP-NTN and CASTNET sites exist (Fig. S2). There were two NADP-NTN sites (Loch Vale, CO98, elevation 3159 m; and Beaver Meadows, CO19, elevation 2477 m), and one CASTNET site (ROM406, elevation 2743 m) in RMNP at the time of the study; all were on the east side of the park (Fig. 1) (<http://nadp.sws.uiuc.edu/sites/sitemap.asp?state=co>; accessed 4/10/14).

2.2. IER materials and methods

Bulk deposition of N and S was monitored in RMNP from June 2006 through September 2007 using IER collectors constructed and operated as described in Fenn and Poth (2004) and Simkin et al. (2004), with minor modifications. The IER collectors consisted of a 17.3 cm diameter plastic funnel with a mesh screen near the base; the funnel was connected to a 1.27 cm × 30 cm polyvinyl chloride (PVC) pipe, which was filled with 38 ml of pre-rinsed Amberlite™ IRN 150 mixed-bed nuclear-grade ion-exchange resin; polyester floss placed at the top and bottom of the PVC pipe acted as a filter and support for the resin. The IER collectors were installed approximately 0.5 m above ground level on rocky talus slopes or in forest clearings, and the data obtained represent bulk deposition (wet plus dry) with little or no throughfall. Collectors were deployed in pairs to test reproducibility (Table S1), and each site had a field blank consisting of a capped resin column, which was used to test for potential contamination from the equipment and resin.

The IER collectors were installed during mid-June 2006, shortly after snow had melted from trails and sites became accessible. Resin columns were replaced with fresh columns in early October 2006, shortly before the accumulation of seasonal snowpack. Columns were replaced again during mid-June 2007, soon after sites again became accessible, and columns were removed at the end of September 2007. These exposure periods yielded two sets of 'summer season' deposition (approximately mid-June through September/early October) values and one set of 'snow season' deposition values (approximately early October through mid-June). Variations in timing of snow accumulation and melt resulted in some variability in deployment times among sites (usually ± 10 days); these variations were accounted for by normalizing deposition rates to the average deployment duration for all sites in a given season. During site visits to replace columns, funnels were cleaned while disconnected from the columns by wiping them with clean, lint-free tissue paper, followed by a triple rinse with distilled water.

Results are summarized primarily by 'summer season' and 'snow season.' In addition to the deployment periods mentioned above, IER collectors were deployed at Loch Vale from April 1 through mid-June 2007 to obtain data for Spring 2007 (see Section 2.3 for more details).

2.3. Comparisons to deposition estimates from other methods

Deposition values obtained using the IER method were compared to estimates from several other methods, including wet deposition reported by the NADP-NTN program for site CO98 (Loch Vale), dry deposition from the CASTNET program for site ROM406, and winter bulk deposition from snowpack sampling.

Snowpack samples were collected at the Loch Vale IER site just prior to the time of maximum snow accumulation (April 1), using methods described in Ingersoll et al. (2002). Briefly, a snow pit was dug at each site and an integrated snowpack sample was collected from the snow surface to within 5 cm of the ground using ultraclean methods. Samples were placed in pre-cleaned Teflon bags

and kept frozen until analysis. Snowpack water content (SWE) was measured using a density cutter and scale, and SWE was multiplied by snow solute concentrations to obtain winter NH_4^+ , NO_3^- , DIN, and SO_4^{2-} deposition.

To obtain data for Spring 2007 at the snowpack sampling site, IER collectors were installed on the day of snow sampling and operated through mid-June 2007, when columns were swapped. For the springtime measurements, the IER collectors were installed on 1.5 m posts with 1 m 'snow-tube' extensions to capture precipitation that fell as either rain or snow (Fenn and Ross, 2010).

2.4. Analytical methods

Analytical methods followed those in Fenn and Poth (2004), Simkin et al. (2004), and Fenn et al. (2013). Resin columns underwent two sequential extractions in the laboratory, each consisting of 200 ml of 1 M potassium iodide (KI). The extracts were diluted 1:10 with nanopure deionized water (≥ 18.2 M-ohm) and analyzed for dissolved NO_3^- , SO_4^{2-} , and phosphate (PO_4^{3-}) by high performance ion chromatography on a Dionex DX-500 ion chromatograph. Ammonium (NH_4^+) was analyzed colorimetrically on a TRAACS 800 autoanalyzer. Concentrations were multiplied by the eluent volume to obtain the mass of ion in solution, and results for each of the two sequential extractions were summed to obtain the total mass of ion eluted from each resin column. Solute mass was divided by funnel surface area to obtain deposition in kilograms per hectare (kg ha^{-1}). A small blank correction (≤ 0.03 kg ha^{-1}) was applied based on results from the field blanks; this was followed by a correction for extraction efficiency, which was 88% for NH_4^+ , 100% for NO_3^- , and 95% for SO_4^{2-} . All deposition values reported herein use elemental units (NH_4^+ and NO_3^- as N, and SO_4^{2-} as S), and NH_4^+ and NO_3^- were summed to obtain total DIN. Results are presented as the average of the two columns deployed at each site, except in instances where one of the IER collectors was either damaged by animals (documented in the field) or contaminated (as indicated by elevated PO_4^{3-} concentrations; Fenn and Poth, 2004).

A subset of samples was analyzed for $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NO}_3^-$ at the USGS Reston Stable Isotope Lab using the microbial-denitrifier method (Casciotti et al., 2002). Samples with at least 0.002 mg NO_3^- -N were analyzed by bacterial conversion of NO_3^- to nitrous oxide (N_2O), with subsequent measurement on a continuous-flow isotope ratio mass spectrometer. The uncertainty of $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NO}_3^-$ results for samples with NO_3^- -N concentrations greater than 0.06 mg L^{-1} was 0.5%. Samples for $\delta^{15}\text{N}$ analyses of NH_4^+ were tested, but interferences prevented reliable measurements.

2.5. Statistical methods

Solute deposition and NO_3^- isotopic composition data fit a normal distribution, based on Shapiro–Wilk test for each solute and season, fulfilling a key requirement for parametric statistical tests (Helsel and Hirsch, 1992). Two-sample *t*-tests were used to compare solute deposition and isotopic composition on the east side of the Continental Divide to that on the west side. The influence of elevation on deposition rates was investigated by performing an analysis of covariance (ANCOVA) on combined summer 2006 and summer 2007 data, with site elevation as a continuous variable and side of the Continental Divide as a categorical variable (east or west).

For solutes that had a significant relation between deposition and elevation, predictive equations from the ANCOVA were applied to a digital elevation model (DEM) with 30-m resolution to develop gridded estimates of summer solute deposition. The gridded estimates were adjusted by adding interpolated model residuals to

account for local-scale variations in solute deposition; interpolation was performed using inverse-distance weighting (IDW) based on the 12 nearest sites.

3. Results and discussion

3.1. Comparison of deposition estimates

Average summer NO_3^- deposition from IER collectors was 0.27 ± 0.19 kg ha^{-1} (average ± 1 standard deviation) less than the

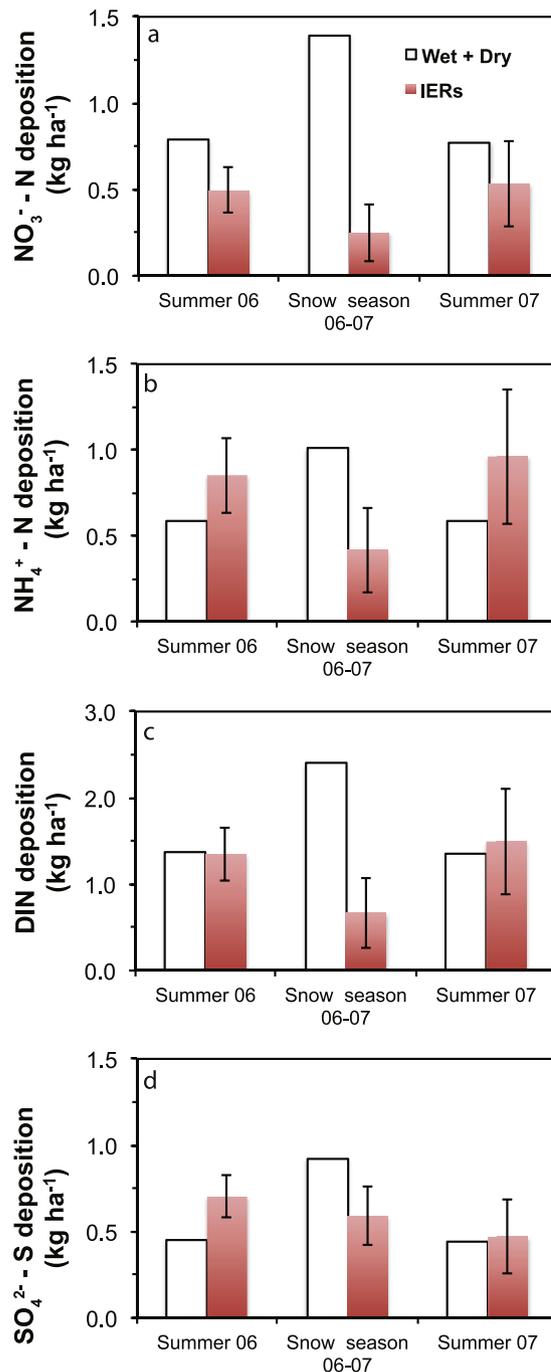


Fig. 2. Comparison of (a) NO_3^- , (b) NH_4^+ , (c) DIN, and (d) SO_4^{2-} in wet + dry deposition and from IER collectors. Wet deposition data are from the NADP-NTN program (site CO98); dry deposition estimates are from the CASTNET program (site ROM406); data from the IERs represent averages, with standard deviations indicated by whiskers ($n = 19-21$).

sum of estimated wet and dry (wet + dry) deposition from the NADP-NTN and CASTNET sites (Fig. 2a). In contrast, average summer NH_4^+ deposition from IERs was $0.32 \pm 0.31 \text{ kg ha}^{-1}$ greater than wet + dry estimates (Fig. 2b). These differences partially offset, and summer DIN deposition estimated from the two data sets differed by less than 4%, with IER-based deposition $0.05 \pm 0.46 \text{ kg ha}^{-1}$ less than estimated wet + dry deposition (Fig. 2c). Conversion of NH_4^+ to NO_3^- (via nitrification) in wet deposition may explain most of the differences in deposition estimates between methods for N-species. Previous studies have noted that NH_4^+ tends to be greater in winter bulk deposition than in wet deposition at co-located NADP-NTN sites, and these differences were attributed to nitrification in wet deposition during sample storage and transport (Clow et al., 2002a). For SO_4^{2-} , estimated summer deposition from IER collectors was $0.14 \pm 0.17 \text{ kg ha}^{-1}$ greater than wet + dry estimates (Fig. 2d), and differences were much more variable between summer seasons than for the N-species.

Compared to the summer season, agreement between IER and wet + dry deposition estimates for the snow season was poor, with estimates from IER collectors ranging from 18% to 64% of those from wet + dry (Fig. 2). Because the IER collectors were installed near the ground, they became buried by snow as the snowpack accumulated. This was intended, and prior to the study it was hypothesized that as the snowpack melted at the end of the snow season, meltwater would percolate downward into the IER funnel and through the column. The low deposition values obtained using the IERs (compared to wet + dry) might be caused by meltwater following preferential pathways during snowmelt (Albert et al., 1999); if this was the case, the IER funnels may have intercepted only a fraction of the meltwater released from the snowpack. Although the present study documented probable undercatch of N and S deposition by IER collectors during winter, the IER method

has been shown to work well during winter at sites with shallower snowpacks, such as the Athabasca region in Canada (Fenn and Ross, 2010; Proemse et al., 2013). In the Athabasca study, the IER collectors did not become buried by snow because they were mounted on posts. Thus, preferential melt pathways should not have appreciably affected the IER results in the Athabasca study.

Snowpack sampling provides an alternative method for measuring winter N and S deposition at remote wilderness sites (Clow et al., 2002a; Fenn et al., 2009; Ingersoll et al., 2002). Fig. 3a shows winter deposition of NO_3^- , NH_4^+ , DIN, and SO_4^{2-} from wet + dry estimates and snowpack samples collected at Loch Vale. Snowpack NO_3^- deposition was 0.12 kg ha^{-1} greater than wet + dry estimates, and snowpack NH_4^+ deposition was 0.12 kg ha^{-1} less than wet + dry estimates. The differences between methods offset, and as a result, differences in DIN deposition estimates were less than 1% (Fig. 3a and left side of Fig. 3b). Snowpack SO_4^{2-} deposition at Loch Vale was 0.14 kg ha^{-1} greater than wet + dry estimates, a difference of approximately 20%. These results are consistent with a study comparing snowpack and winter wet-deposition chemistry in the Rocky Mountains, which documented no significant differences in concentrations for NO_3^- and SO_4^{2-} (Clow et al., 2002a).

Total annual deposition at Loch Vale, calculated using a combination of snowpack-based estimates for winter deposition and IER-based estimates for spring and summer, was within 0.26 kg ha^{-1} (7%) of wet + dry estimates for the 2007 water year (Fig. 3b). Results for SO_4^{2-} (not shown) were similar, with a difference of 0.21 kg ha^{-1} for the 2007 water year. These results indicate that spatially distributed estimates of total annual DIN and S deposition can be obtained for high-elevation wilderness using a combination of snowpack and IER methods.

3.2. Spatial patterns in N and S deposition

Elevation had a modest influence on summertime NO_3^- and DIN deposition in the park ($p < 0.002$ and $p = 0.07$, respectively; Fig. 4), and no significant influence on NH_4^+ or SO_4^{2-} deposition ($p > 0.3$), based on ANCOVA results. These results may have important implications for development of deposition maps, such as those produced by the NADP-NTN program (e.g., <http://nadp.sws.uiuc.edu/NTN/maps.aspx>; accessed 9/26/14). Although the NADP-NTN maps take elevation (and other terrain-related features) into account when modeling precipitation amount, they do not directly

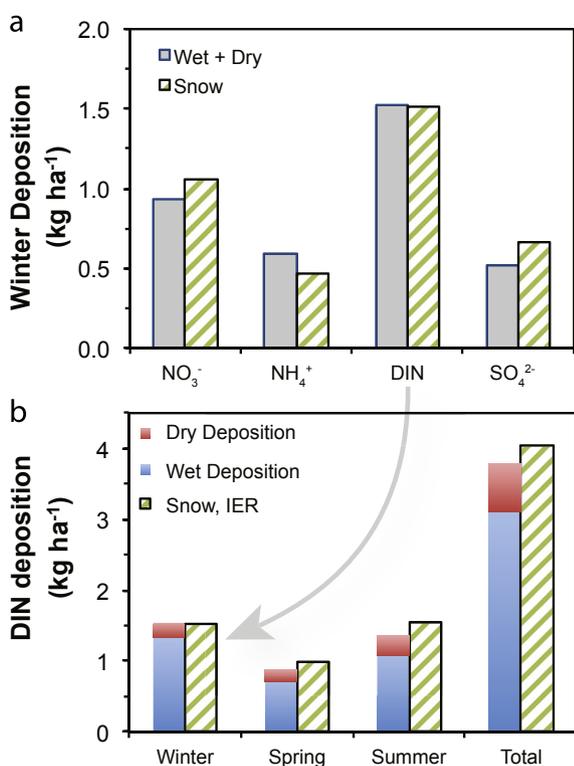


Fig. 3. Comparison of (a) winter deposition of NO_3^- , NH_4^+ , DIN, and SO_4^{2-} from wet + dry estimates (CO98 and ROM406) and snowpack sample collected at Loch Vale, and (b) winter, spring, summer, and total annual DIN deposition from wet + dry estimates, snowpack sampling (winter), and IER collectors (spring and summer).

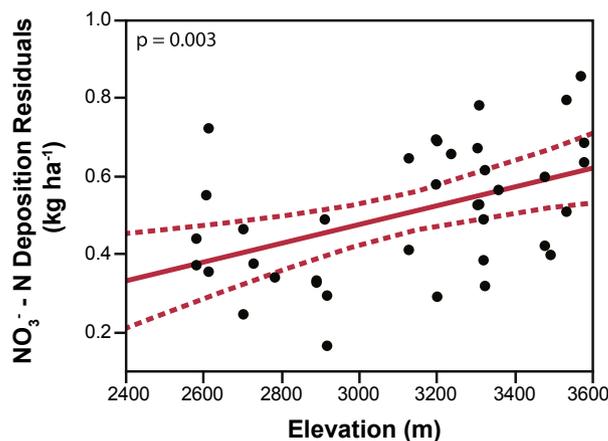


Fig. 4. Relation between NO_3^- deposition and elevation, after accounting for side of the Continental Divide. Solid red line represents slope of regression based on ANCOVA analysis; dashed red lines indicate 95% confidence interval of regression slope. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

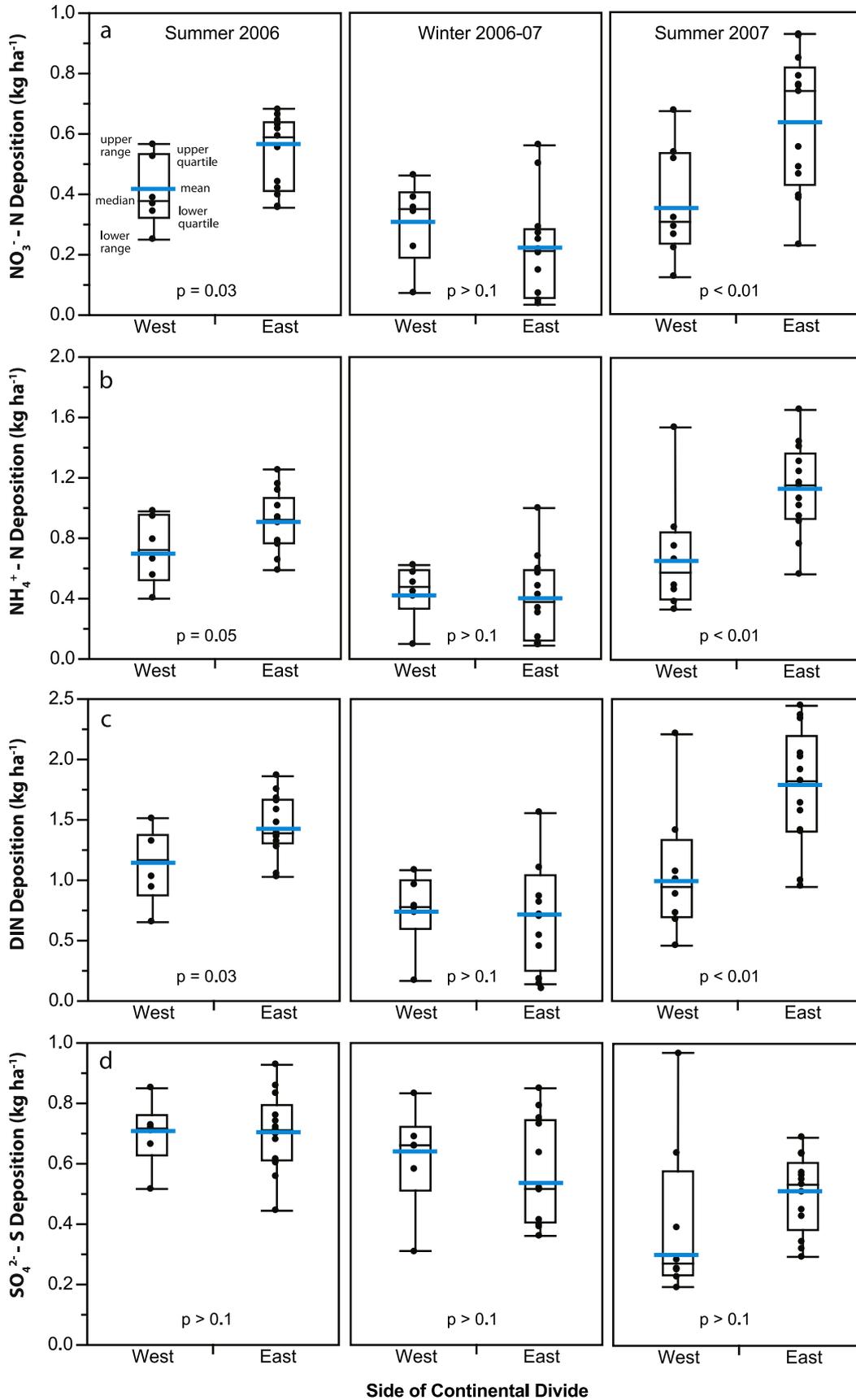


Fig. 5. Distributions of (a) NO_3^- , (b) NH_4^+ , (c) DIN, and (d) SO_4^{2-} deposition on east and west sides of Continental Divide, summer 2006 through summer 2007. P-values represent results from *t*-test on means.

account for elevation dependence when modeling precipitation chemistry (<http://nadp.sws.uiuc.edu/data/mapProcess.aspx>; accessed 11/11/14). As a result, the NADP-NTN maps usually show an increase in deposition with elevation, but this may not be accurate for some solutes. The lack of a positive relation between deposition and elevation for NH_4^+ and SO_4^{2-} in the present study may reflect opposing patterns in precipitation amount and solute concentration with respect to elevation. Previous studies have shown that precipitation amount often increases with elevation in mountainous terrain (Barry, 2008; Daly et al., 2008), and solute concentrations in precipitation often have the opposite pattern (Latysh and Wetherbee, 2012); this can result in no relation between deposition and elevation.

There were strong differences in NO_3^- and NH_4^+ deposition between east and west sides of the Continental Divide in the park. During summer 2006, NO_3^- deposition was significantly less on the west side of the Continental Divide ($0.41 \pm 0.12 \text{ kg ha}^{-1}$) than on the east side ($0.53 \pm 0.12 \text{ kg ha}^{-1}$; $p = 0.03$; Fig. 5). Summer 2006 NH_4^+ deposition showed a similar pattern, with average deposition of $0.72 \pm 0.22 \text{ kg ha}^{-1}$ on the west side and $0.91 \pm 0.20 \text{ kg ha}^{-1}$ on the east side ($p = 0.05$; Fig. 5). Total DIN deposition also was less on the west side ($1.13 \pm 0.31 \text{ kg ha}^{-1}$) than on the east side ($1.45 \pm 0.25 \text{ kg ha}^{-1}$) of the park during summer 2006 ($p = 0.03$; Fig. 5). Differences in deposition of NO_3^- , NH_4^+ , and DIN between west side and east side of the Continental Divide were even greater during summer 2007 (Fig. 5). Interestingly, there were no significant differences in SO_4^{2-} deposition between west-side and east-side sites during any of the seasons (Fig. 5).

A map of summer DIN deposition in RMNP illustrates the combined influences of elevation and site location, with lesser deposition values along valley bottoms than along ridges and peaks, and greater values on the east side of the Continental Divide

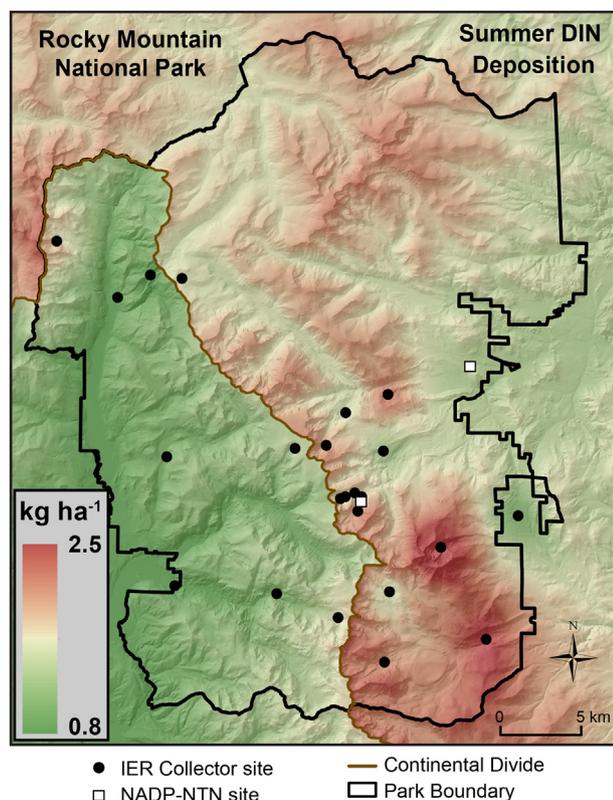


Fig. 6. Modeled summer dissolved inorganic nitrogen (DIN) deposition in Rocky Mountain National Park and vicinity.

than on the west side (Fig. 6). Summer DIN deposition was notably greater in the southeastern part of the park than elsewhere, reflecting local-scale variations in deposition that might be associated with wind patterns and proximity to emissions sources. It is uncertain whether annual DIN deposition has the same spatial pattern as that of summertime deposition. It should be possible to develop high-resolution annual DIN deposition maps through targeted monitoring that includes snowpack sampling (for winter) and IER collector measurements (for spring and summer) at multiple sites in the park. This would improve the accuracy of annual deposition estimates at high elevation, where deposition currently is interpolated based on sparse data. These estimates are essential for development of critical loads maps depicting ecosystem sensitivity to atmospheric deposition of N (e.g., Nanus et al., 2012).

3.3. Sources of N in atmospheric deposition

The spatial patterns in N and S deposition documented in this study likely reflect variations in the type, magnitude, and transport of emissions from upwind sources. Easterly transport of atmospheric N pollution is indicated by results from several studies conducted as part of the 2006–2009 Rocky Mountain Atmospheric Nitrogen and Sulfur (RoMANS) project. A study of reactive N species in the atmosphere along an east–west transect in northern Colorado indicated elevated concentrations of reduced N (primarily NH_3 and NH_4^+) in agricultural areas on the Eastern Plains, and elevated concentrations of oxidized N (NO_x) in the Denver–Fort Collins urban area (Benedict et al., 2013). Benedict et al. (2013) also documented that concentrations of atmospheric NH_4^+ and NO_3^- in RMNP were highest during easterly upslope wind events, indicating that sources to the east of RMNP likely were important (Benedict et al., 2013). Source apportionment of atmospheric N in RMNP using back-trajectory analyses revealed complex patterns of sources that varied by season and pollutant (Gebhart et al., 2011). Results were consistent with emissions of reduced N in agricultural areas on the Eastern Plains and of oxidized N in the Denver–Fort Collins urban corridor (Gebhart et al., 2011). In contrast to the results for atmospheric N, the source apportionment study indicated that the main sources of atmospheric SO_x (SO_2 and SO_4^{2-}) appeared to be west of the Continental Divide, with approximately 20–30% derived from

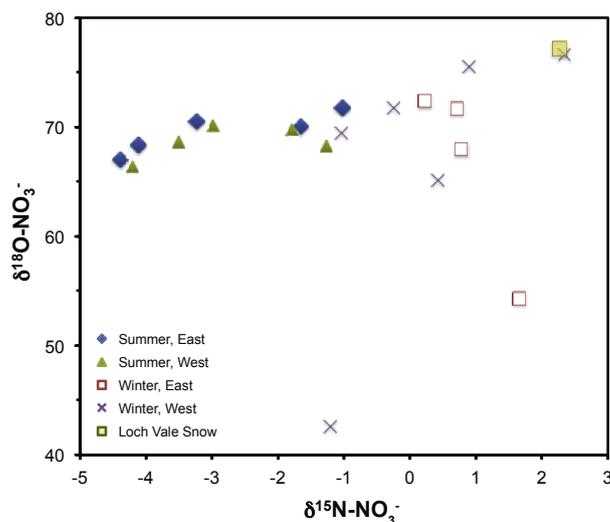


Fig. 7. Variation in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- from IER collector samples from Rocky Mountain National Park and snowpack sample from Loch Vale.

western Colorado, and approximately one-half to two-thirds from outside the state (Gebhart et al., 2011). The importance of regional sources of atmospheric SO_x (as opposed to more local sources) helps explain the lack of significant difference in SO₄²⁻ deposition on the east and west sides of the Continental Divide in RMNP found in the present study.

Spatial and temporal variations in the isotopic composition of NO₃⁻ provide additional insight into possible variations in NO_x emissions sources. The δ¹⁵N-NO₃⁻ of summer bulk deposition in RMNP ranged from approximately -1 to -4‰ (Fig. 7), similar to other sites in the Rocky Mountains (-2 to -5‰; Nanus et al., 2008), and slightly higher than values in Yosemite National Park (YOSE; -4 to -6‰; Fig. S4). The δ¹⁵N-NO₃⁻ of winter bulk deposition in RMNP was significantly higher than that of summer bulk deposition in the park, ranging from -1 to 2‰ (*p* = 0.001; Fig. 7). The seasonal difference in δ¹⁵N-NO₃⁻ of bulk deposition in this study is consistent with past work in RMNP, where the average δ¹⁵N-NO₃⁻ of winter snowpack was approximately 4‰ higher than that of summer bulk precipitation (Campbell et al., 2002). Seasonal shifts in δ¹⁵N-NO₃⁻ of bulk deposition may be caused by shifts in source regions and variation in the relative importance of NO_x sources (Elliott et al., 2007; Freyer, 1991; Hastings et al., 2004). Previous studies have documented δ¹⁵N-NO₃⁻ in emissions from coal-fired power plants ranging from 6 to 13‰ (Felix et al., 2012; Heaton, 1990), while those from motor vehicles range from -13 to -2‰ (Heaton, 1990). The seasonal differences in δ¹⁵N-NO₃⁻ of bulk deposition documented in this study suggest that in RMNP the importance of emissions from coal-fired power plants may increase during winter, and the importance of emissions from motor vehicles may increase during summer. These shifts may, in turn, be related to changes in source regions and wind flow patterns, with predominantly westerly winds during winter, and easterly winds more common during spring and summer (Baron and Denning, 1993; Benedict et al., 2013; Clow et al., 2012; Gebhart et al., 2011). Source regions to the west of RMNP have substantial coal combustion emissions of NO_x, while vehicular NO_x emissions sources are important east of the park along the Front Range urban corridor (Benedict et al., 2013).

Somewhat surprisingly, there were no statistically significant differences in the δ¹⁵N-NO₃⁻ of bulk deposition on the east side compared to the west side of RMNP (*p* = 0.83). The lack of significant difference between δ¹⁵N-NO₃⁻ in bulk deposition on the east and west sides of the park is interesting, particularly because summer N deposition is significantly higher (25–50%) on the east side of the park than on the west side. These results suggest that, although NO_x sources or dominant source regions vary seasonally, they affect the east and west sides of the park similarly. This might be caused by strong atmospheric mixing, which is facilitated by complex terrain, persistent winds at high elevation, and convective storms; these factors may allow N to be transported over the Continental Divide during both winter and summer.

The δ¹⁸O-NO₃⁻ of summer bulk deposition from IER collectors in RMNP ranged from 66 to 72‰ (Fig. 7), similar to values in wet deposition at other high-elevation sites in the Rocky Mountains (71–78‰; Nanus et al., 2008), and in YOSE (65–70‰; Fig. S4). These δ¹⁸O-NO₃⁻ values are at the upper end of the range in values observed for precipitation in previous studies (14–75‰; Kendall, 1998); this, and the relatively narrow range of δ¹⁸O-NO₃⁻ in summer deposition found in the present study are noteworthy because they suggest that the δ¹⁸O-NO₃⁻ of summer deposition in mountains of the western U.S. may be distinct and well defined. Winter bulk deposition in RMNP and YOSE had a much wider range of δ¹⁸O-NO₃⁻ values (43–77‰) than summer deposition, which may reflect variations in sources, fractionation processes within the atmosphere, or a combination of the two.

4. Conclusions

This study demonstrated that IER collectors provide a useful method for obtaining spatially distributed data on N and S deposition during summer in high-elevation wilderness areas. The IER collectors performed poorly during winter, probably because of preferential flow through the snowpack during snowmelt; however, as in previous studies, winter deposition measured by snowpack sampling agreed well with wet + dry deposition estimates from the NADP-NTN and CASTNET programs. A combination of snowpack sampling (for winter) and IER collectors (for spring and summer) is likely the optimum strategy for obtaining year-round, spatially distributed data on N and S deposition in wilderness areas.

Elevation and location with respect to side of the Continental Divide were shown to have strong influences on summer NO₃⁻ and DIN deposition in RMNP. Geospatial modeling was used to create a high-resolution map of summer DIN deposition in the park. It should be possible to create similar maps showing annual DIN deposition in the future, if targeted monitoring is conducted that incorporates snowpack sampling and IER collector techniques. Accurate, high-resolution maps of annual DIN deposition are essential for developing improved critical loads exceedance maps that show spatial patterns in ecosystem sensitivity to N deposition in high-elevation areas.

The IER collectors show promise for characterizing shifts in sources of NO₃⁻ in bulk deposition through application of N-isotope techniques. Seasonal variations in δ¹⁵N-NO₃⁻ may be indicative of shifts in source regions, with a stronger coal-combustion signature during winter, and an increase in the relative contribution from vehicle emissions during summer. These differences are consistent with typical seasonal patterns of wind flow in the park, and with previous studies of atmospheric chemistry and transport.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.11.027>.

References

- Albert, M., Koh, G., Perron, F., 1999. Radar investigations of melt pathways in a natural snowpack. *Hydrol. Proc.* 13, 2991–3000.
- Baron, J., Denning, A.S., 1993. The influence of mountain meteorology on precipitation chemistry at low and high elevations of the Colorado Front Range, USA. *Atmos. Environ.* 27A, 2337–2349.
- Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T., Moraska, B., 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. *Ecosystems* 3, 89–99.
- Barry, R.G., 2008. *Mountain Weather and Climate*. Cambridge University Press, New York.
- Benedict, K.B., Day, D., Schwandner, F.M., Kreidenweis, S.M., Schichtel, B., Malm, W.C., Collett Jr., J.L., 2013. Observations of atmospheric reactive nitrogen species in Rocky Mountain National Park and across northern Colorado. *Atmos. Environ.* 64, 66–76.
- Bowman, W.D., Murgel, J., Blett, T., Porter, E., 2012. Nitrogen critical loads for alpine vegetation and soils in Rocky Mountain National Park. *J. Environ. Manag.* 103, 165–171.

- Burns, D.A., 2003. Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming—a review and new analysis of past study results. *Atmos. Environ.* 37, 921–932.
- Campbell, D.H., Clow, D.W., Ingersoll, G.P., Mast, M.A., Spahr, N.E., Turk, J.T., 1995. Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains. *Water Resour. Res.* 31, 2811–2821.
- Campbell, D.H., Kendall, C., Chang, C.C.Y., Silva, S.R., Tonnessen, K.A., 2002. Pathways for nitrate release from an alpine watershed: determination using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. *Water Resour. Res.* 38.
- Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* 74, 4905–4912.
- Clow, D.W., Ingersoll, G.P., Mast, M.A., Turk, J.T., Campbell, D.H., 2002a. Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition. *Atmos. Environ.* 36, 2337–2348.
- Clow, D.W., Nanus, L., Verdin, K.L., Schmidt, J., 2012. Evaluation of SNODAS snow depth and snow water equivalent estimates for the Colorado Rocky Mountains, USA. *Hydrol. Proc.* 26, 2583–2591.
- Clow, D.W., Striegl, R., Nanus, L., Mast, M.A., Campbell, D.H., Krabbenhoft, D.P., 2002b. Chemistry of selected high-elevation lakes in seven national parks in the Western United States. *Water Air Soil Pollut. Focus* 2, 139–164.
- Clow, D.W., Sueker, J.K., 2000. Relations between basin characteristics and stream-water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. *Water Resour. Res.* 36, 49–61.
- Daly, C., Halbleib, M., Smith, J.L., Gibson, W.P., Doggett, M.K., Taylor, G.H., Curtis, J., Pasteris, P.P., 2008. Physiographically sensitive mapping of climatological temperature and precipitation across the conterminous United States. *Int. J. Climatol.* 28, 2031–2064.
- Elliott, E.M., Kendall, C., Wankel, S.D., Burns, D.A., Boyer, E.W., Harlin, K., Bain, D.J., Butler, T.J., 2007. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States. *Environ. Sci. Technol.* 41, 7661–7667.
- Felix, J.D., Elliott, E.M., Shaw, S.L., 2012. Nitrogen isotopic composition of coal-fired power plant NO_x : influence of emission controls and implications for global emission inventories. *Environ. Sci. Technol.* 46, 3528–3535.
- Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.H., Neitlich, P., 2003. Ecological effects of nitrogen deposition in the western United States. *BioScience* 53, 404–420.
- Fenn, M.E., Poth, M., 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: a field test in the San Bernadino Mountains. *J. Environ. Qual.* 33, 2007–2014.
- Fenn, M.E., Ross, C.S., 2010. Sulfur and nitrogen deposition monitoring in the Athabasca oil sands region: extended abstract 2010-A-664-AWMA. In: *The Air and Waste Management Association 103rd Annual Conference and Exhibition*, Calgary, Alberta, Canada.
- Fenn, M.E., Ross, C.S., Schilling, S.L., Baccus, W.D., Larrabee, M.A., Lofgren, R.A., 2013. Atmospheric deposition of nitrogen and sulfur and preferential canopy consumption of nitrate in forests of the Pacific Northwest, USA. *For. Ecol. Manag.* 302, 240–253.
- Fenn, M.E., Sickman, J.O., Bytnerowicz, A., Clow, D.W., Molotch, N.P., Pleim, J.E., Tonnesen, G.S., Weathers, K.C., Padgett, P.E., Campbell, D.H., 2009. Methods for measuring atmospheric nitrogen inputs in arid and montane ecosystems of western North America. In: Legge, A.H. (Ed.), *Relating Atmospheric Source Apportionment to Vegetation Effects: Establishing Cause-effect Relationships*. Elsevier, Amsterdam, pp. 179–228.
- Freyer, H.D., 1991. Seasonal variation of $^{15}\text{N}/^{14}\text{N}$ ratios in atmospheric nitrate species. *Tellus B* 43, 30–44.
- Gebhart, K.A., Schichtel, B.A., Malm, W.C., Barna, M.G., Rodriguez, M.A., Collett Jr., J.L., 2011. Back-trajectory-based source apportionment of airborne sulfur and nitrogen concentrations at Rocky Mountain National Park, Colorado, USA. *Atmos. Environ.* 45, 621–633.
- Grêt-Regamey, A., Brunner, S.H., Kienast, F., 2012. Mountain ecosystem services: who cares? *Mt. Res. Dev.* 32, S23–S34.
- Hastings, M.G., Steig, E.J., Sigman, D.M., 2004. Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: implications for the study of nitrate in snow and ice cores. *J. Geophys. Res. Atmos.* 109, D20306.
- Heaton, T.H.E., 1990. $^{15}\text{N}/^{14}\text{N}$ ratios of NO_x from vehicle engines and coal-fired power stations. *Tellus* 42B, 304–307.
- Helsel, D.R., Hirsch, R.M., 1992. *Statistical Methods in Water Resources*. Elsevier, Amsterdam, The Netherlands.
- Ingersoll, G.P., Turk, J.T., Mast, M.A., Clow, D.W., Campbell, D.H., Bailey, Z.C., 2002. Rocky Mountain Snowpack Chemistry Network: History, Methods, and the Importance of Monitoring Mountain Ecosystems. U.S. Geological Survey, Denver, Colorado, p. 14.
- Kendall, C., 1998. Tracing nitrogen sources and cycles in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam, pp. 519–576.
- Latysh, N.E., Wetherbee, G.A., 2012. Improved mapping of national atmospheric deposition program wet-deposition in complex terrain using PRISM-gridded data sets. *Environ. Monit. Assess.* 184, 913–928.
- Lehmann, C.M.B., Bowersox, V., Larson, S.M., 2005. Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. *Environ. Pollut.* 135, 347–361.
- McDonnell, T.C., Belyazid, S., Sullivan, T.J., Sverdrup, H., Bowman, W.D., Porter, E.M., 2014. Modeled subalpine plant community response to climate change and atmospheric nitrogen deposition in Rocky Mountain National Park, USA. *Environ. Pollut.* 187, 55–64.
- Morris, K., Mast, A., Clow, D., Wetherbee, G., Baron, J., Taipale, C., Blett, T., Gay, D., Heath, J., 2014. 2012 Monitoring and Tracking Wet Nitrogen Deposition at Rocky Mountain National Park. National Park Service, Denver, Colorado, p. 24.
- Nanus, L., Clow, D.W., Saros, J.E., Stephens, V.C., Campbell, D.H., 2012. Mapping critical loads of nitrogen deposition for aquatic ecosystems in the Rocky Mountains, USA. *Environ. Pollut.* 166, 125–135.
- Nanus, L., Williams, M.W., Campbell, D.H., Elliott, E.M., Kendall, C., 2008. Evaluating regional patterns in nitrate sources to watersheds in national parks of the Rocky Mountains using nitrate isotopes. *Environ. Sci. Technol.* 42, 6487–6493.
- Nilsson, J., Grennfelt, P., 1988. *Critical Loads for Sulphur and Nitrogen*. Nordic Council of Ministers, Copenhagen.
- Porter, E., Blett, T.F., Potter, D.U., Huber, C., 2005. Protecting resources on federal lands: implications of critical loads for atmospheric deposition of nitrogen and sulfur. *BioScience* 55, 603–612.
- Proemse, B.C., Mayer, B., Fenn, M.E., Ross, C.S., 2013. A multi-isotope approach for estimating industrial contributions to atmospheric nitrogen deposition in the Athabasca oil sands region in Alberta, Canada. *Environ. Pollut.* 182, 80–91.
- Root, H.T., Geiser, L.H., Fenn, M.E., Jovan, S., Hutten, M.A., Ahuja, S., Dillman, K., Schirokauer, D., Berryman, S., McMurray, J.A., 2013. A simple tool for estimating throughfall nitrogen deposition in forests of western North America using lichens. *For. Ecol. Manag.* 306, 1–8.
- Simkin, S.M., Lewis, D.N., Weathers, K.C., Lovett, G.M., Schwarz, K., 2004. Determination of sulfate, nitrate, and chloride in throughfall using ion-exchange resins. *Water Air Soil Pollut.* 153, 343–354.
- Templer, P., McCann, T., 2010. Effects of the Hemlock woolly adelgid on nitrogen losses from urban and rural northern Forest ecosystems. *Ecosystems* 13, 1215–1226.
- Templer, P.H., Weathers, K.C., 2011. Use of mixed ion exchange resin and the denitrifier method to determine isotopic values of nitrate in atmospheric deposition and canopy throughfall. *Atmos. Environ.* 45, 2017–2020.
- Weathers, K.C., Lovett, G.M., Likens, G.E., Lathrop, R., 2000. The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. *Ecol. Appl.* 10, 528–540.
- Weathers, K.C., Simkin, S.M., Lovett, G.M., Lindberg, S.E., 2006. Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecol. Appl.* 16, 1590–1607.
- Williams, M.W., Tonnessen, K.A., 2000. Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. *Ecol. Appl.* 10, 1648–1665.
- Wolfe, A.P., Van Gorp, A.C., Baron, J.S., 2003. Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): a response to anthropogenic nitrogen deposition. *Geobiology* 1, 153–168.