# Journal of Environmental Management 103 (2012) 165-171

Contents lists available at SciVerse ScienceDirect



Journal of Environmental Management



journal homepage: www.elsevier.com/locate/jenvman

# Nitrogen critical loads for alpine vegetation and soils in Rocky Mountain National Park

William D. Bowman<sup>a,b,\*</sup>, John Murgel<sup>a,b,1</sup>, Tamara Blett<sup>c</sup>, Ellen Porter<sup>c</sup>

<sup>a</sup> Mountain Research Station, Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA <sup>b</sup> Department of Ecology and Evolutionary Biology, University of Colorado, Boulder, CO 80309, USA <sup>c</sup> National Park Service, Air Resources Division, Lakewood, CO 80225, USA

#### ARTICLE INFO

Article history: Received 23 June 2011 Received in revised form 27 December 2011 Accepted 2 March 2012 Available online 18 April 2012

Keywords: Acidification Alpine tundra Base cations Critical loads Diversity response Eutrophication Mountain ecosystems Nitrogen deposition Rocky Mountain National Park

#### ABSTRACT

We evaluated the ecological thresholds associated with vegetation and soil responses to nitrogen (N) deposition, by adding NH<sub>4</sub>NO<sub>3</sub> in solution at rates of 5, 10 and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> to plots in a species rich dry meadow alpine community in Rocky Mountain National Park receiving ambient N deposition of 4 kg N ha<sup>-1</sup> yr<sup>-1</sup>. To determine the levels of N input that elicited changes, we measured plant species composition annually, and performed one-time measurements of aboveground biomass and N concentrations, soil solution and resin bag inorganic N, soil pH, and soil extractable cations after 3 years of N additions. Our goal was to use these dose-response relationships to provide N critical loads for vegetation and soils for the alpine in Rocky Mountain National Park. Species richness and diversity did not change in response to the treatments, but one indicator species, Carex rupestris increased in cover from 34 to 125% in response to the treatments. Using the rate of change in cover for C. rupestris in the treatment and the ambient plots, and assuming the change in cover was due solely to N deposition, we estimated a N critical load for vegetation at 3 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Inorganic N concentrations in soil solution increased above ambient levels at input rates between 9 kg N ha<sup>-1</sup> yr<sup>-1</sup> (resin bags) and 14 kg N ha<sup>-1</sup> yr<sup>-1</sup> (lysimeters), indicating biotic and abiotic sinks for N deposition are exhausted at these levels. No changes in soil pH or extractable cations occurred in the treatment plots, indicating acidification had not occurred after 3 years. We conclude that N critical loads under 10 kg  $ha^{-1}$  yr<sup>-1</sup> are needed to prevent future acidification of soils and surface waters, and recommend N critical loads for vegetation at 3 kg N ha<sup>-1</sup> yr<sup>-1</sup> as important for protecting natural plant communities and ecosystem services in Rocky Mountain National Park.

© 2012 Elsevier Ltd. All rights reserved.

# 1. Introduction

Emissions of reactive nitrogen (N) by agricultural development and fossil fuel combustion have increased the deposition of N more than threefold over the past 160 years (Galloway et al., 2008). The environmental impact of these N inputs on terrestrial ecosystems varies according to vegetation type, chemistry of the soil parent material, and the rate and accumulated input of N deposition (Aber et al., 1998; Clark and Tilman, 2008). Enhanced net primary production (eutrophication) may occur where N remains the limiting resource for plant growth (e.g. Binkley and Högberg, 1997; Thomas et al., 2010). Greater N availability often results in losses of plant diversity (Gough et al., 2000; Stevens et al., 2004; Suding et al., 2005; Bobbink et al., 2010) and greater establishment of invasive species (Yoshida and Allen, 2004; Rao and Allen, 2010). Once plants, microorganisms, and soils cease to take up N entering the system from deposition, leaching of nutrient base cations, increases in soluble aluminum, and soil acidification can occur, eventually leading to decreases in plant growth and continued losses in diversity (Stevens et al., 2004; Bowman et al., 2008).

The environmental impacts of N deposition on terrestrial systems have been recorded primarily for industrialized regions such as northern and central Europe and the eastern United States (Bobbink et al., 1998; Driscoll et al., 2001). However, symptoms of ecological changes due to N deposition are showing up in more remote regions, including national parks and wilderness areas in the Rocky Mountains and Sierra Nevada in the U.S. (Burns, 2003; Fenn et al., 2003; Geiser and Neitlich, 2007). These symptoms include elevated surface water nitrate concentrations and greater abundances of nitrophilic lichen and diatom species in areas with elevated N deposition. Mountain ecosystems are especially sensitive to inputs of N deposition due to thin soils and low rates of net

<sup>\*</sup> Corresponding author. Mountain Research Station, Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA. Tel.: +1 303 492 2557; fax: +1 303 492 8699.

E-mail address: william.bowman@colorado.edu (W.D. Bowman).

<sup>&</sup>lt;sup>1</sup> Present address: Department of Horticulture and Landscape Architecture, Colorado State University, Fort Collins, CO 80523, USA.

<sup>0301-4797/\$ —</sup> see front matter  $\odot$  2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.jenvman.2012.03.002

primary production, limiting the uptake and stabilization of reactive N (Williams and Tonnessen, 2000; Weathers et al., 2006).

The ecological changes in ecosystems subjected to elevated N deposition, from initial eutrophication and loss of diversity, to decreased productivity and acidification, may occur as thresholds of N inputs are reached and exceeded (Aber et al., 1998; Groffman et al., 2006). The reversibility from one stage of impact to another is uncertain, as biological and geochemical feedbacks may create substantial inertia. For example, changes in plant diversity due to N deposition may enhance rates of N cycling of existing soil organic matter, with higher rates of net mineralization and nitrification increasing pools of soil inorganic N (Bowman and Steltzer, 1998). Depletion of base cations may shift the soil buffering system toward an aluminum dominated system (Chadwick and Chorover, 2001). Thus the best approach to mitigating environmental impacts of N deposition is to recognize the initial ecological responses and associated deposition rates, and manage air pollutant emissions to minimize further ecosystem changes.

The critical load concept uses sensitive ecological indicators to help minimize detrimental environmental impacts (Burns et al., 2008). A critical load is defined as the level of input of one or more pollutants below which there are no significant negative impacts on sensitive environmental elements (Nilsson and Grennfelt, 1988; Porter et al., 2005). Critical loads for nitrogen deposition have been established using modeling and empirical approaches. The latter often uses observations of ecological changes across gradients of N deposition, as well as experimental manipulations. The occasional use of high levels of N inputs in experiments to determine thresholds of ecological response, and relatively high ambient levels of N deposition, can result in somewhat arbitrary determinations of critical loads.

The goal of the research described here was to determine the responses of vegetation and soils in a sensitive alpine community in Rocky Mountain National Park to a gradient of relatively low-level N applications  $(5-30 \text{ kg N ha}^{-1} \text{ yr}^{-1})$  to help determine the critical load for N. The Clean Air Act Amendments of 1977 designated Rocky Mountain National Park as a Class I air quality area, and Congress directed park managers to preserve air pollution-sensitive resources unimpaired for future generations (NPS ARD, 2002). N critical loads for vegetation and soils can be used to manage the park's resources more effectively and to ensure that sensitive resources are protected from air pollution now and in the future.

# 2. Materials and methods

# 2.1. Study site

The research was performed in a dry meadow community approximately 2 km east of Chapin Pass in the Mummy Range, Rocky Mountain National Park (40° 26' 03.25" N, 105° 43' 3.45" W). The site was located on a west-facing slope at 3560 m elevation above sea level. An alpine dry meadow site was selected for this work as 1) it is one of the most sensitive communities due to inherently low rates of nutrient cycling and associated plant adaptations to low nutrient supply (Bowman and Bilbrough, 2001), 2) plant species density is high ( $\sim 30$  species/m<sup>2</sup>), increasing the probability of finding indicator species, and 3) these communities make up a significant part of the alpine landscape (~40%, Komárková, 1979). Dry meadows are dominated by the sedge Kobresia myosuroides, with additional sedges, primarily Carex rupestris, grasses, and forbs making up the remaining cover (Komárková, 1979). Soils are cryumbrepts derived from metamorphic granitoid parent material. The C:N ratios for mineral soil (0–10 cm depth) at the site are  $13.3 \pm 0.1$  (mean  $\pm$  s.e.m., n = 20). Climate at the site is characterized by long cold winters and a short growing season of 10–12 weeks.

Total ambient inorganic N deposition at the site is 4 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Baron, 2006), estimated from wet deposition measurements at a nearby National Atmospheric Deposition Program sampler (Loch Vale, 3159 m elevation, 17 km south on the same side of the Continental divide) and dry deposition estimates from a lower elevation CASTNet Dry Deposition monitor (Beaver Meadows, 2743 m elevation, 16 km east southeast, on the same side of the Continental divide). Wet deposition accounts for 75% and dry deposition accounts for 25% of the total N deposition. Deposition of reactive N consists of 41% NH<sup>4</sup><sub>4</sub>–N and 59% NO<sub>3</sub><sup>-</sup>–N (EPA CASTNET, http://epa.gov/castnet). Given the projected population growth for the Front Range cities in the Denver megalopolis and the rate of agricultural development, N deposition is expected to increase steadily in Rocky Mountain National Park over the next several decades, with rates approaching 1.5 times current rates by 2030 (Fenn et al., 2003; Dentener et al., 2006).

### 2.2. Experimental procedures

Experimental N additions consisted of ambient N deposition (4 kg N ha<sup>-1</sup> yr<sup>-1</sup>), and addition of 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> added to 5 replicate 1 m  $\times$  1.5 m plots. These levels represent 1.25 $\times$ ,  $2.5\times$ , and  $7.5\times$  ambient deposition rates. This range of N additions allowed estimation of response curves of soils and vegetation to increasing N deposition, facilitating a quantitative estimation of N critical loads (Bowman et al., 2006). Nitrogen was added as NH<sub>4</sub>NO<sub>3</sub> in solution, sprayed onto the plots three times during the growing season. The maximum solution concentrations added to the plots ranged from 4.5 mmol N in the +5 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatment to 26.8 mmol N in the +30 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatment, which are well below levels that cause toxicity to plants. Control plots received an equivalent amount of water (4 L  $plot^{-1}$  application<sup>-1</sup>). The amount of water added to plots represented a 5% increase in mean summer precipitation, well within the range of interannual variation, and therefore not a substantial treatment effect. Half of the N addition was added in the first application in early June, to better reflect that approximately half of annual input of N occurs as a pulse during snowmelt (Bowman, 1992). No overland flow of the treatment solutions was observed. The plots were arranged in 5 blocks, with one replicate plot of each treatment in each of the blocks (total of 20 plots). Treatment plots were separated by a minimum of a 2 m buffer zone. The uphill  $1 \text{ m} \times 1 \text{ m}$  portion of each plot was used for measurement of vegetation cover. The downhill 0.5 m  $\times$  1 m portion was used for soil sampling. The plots were established in 2006 and received the N additions each year for four years.

To evaluate the effect of the N treatments on the vegetation, cover of individual vascular plant species, bare ground, rocks, scat (proxy for herbivory), and litter were estimated using the point-intercept method, with 100 points in each plot. Cover estimates were made annually during the growing season when all species were present and identifiable, in mid- to late-July. The effect of the N treatments on aboveground net primary production (NPP) was estimated using a clip harvest of all aboveground biomass collected in late-July 2008. Three  $0.2 \text{ m} \times 0.2 \text{ m}$  subplots were used for biomass harvesting. The biomass was field sorted into three groups: Kobresia (dominant species), other graminoids (grasses and sedges), and forbs. The harvested biomass was dried to a constant mass by placing in a drying oven for 48 h at 70 °C, and then weighed to the nearest mg. The influence of N treatment on tissue N concentrations was evaluated by grinding the dried biomass with a mortar and pestle, and then analyzing the ground tissue using a CHN Analyzer. The uptake of N by the aboveground tissues was evaluated by multiplying the tissue N concentrations by the biomass accumulation measured by the clip harvests.

Soil responses to N inputs included soil solution inorganic N, resin bag N, soil pH, and extractable cations. Soil solution and resin bag inorganic N were collected in the third year of the experiment

(2008). Soil water was collected using vacutainers attached to the microlysimeters (Rhizon soil moisture samplers, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands), which was analyzed for inorganic N using a Lachat QuikChem 8000 Spectophotometric Flow Injection Analyzer and a Dionex DX 500 System IonPac AS11 Ion Chromatograph (Sunnyvale, California, USA). Inorganic N leaching below the rooting zone was estimated using ion exchange resin bags, constructed of plastic cylinders (4.9 cm<sup>2</sup> and 2.5 cm height) filled with mixed-bed ion exchange resins (J.T. Baker, IONAC NM-60 H/OH; Phillipsburg, New Jersey, USA) and covered with nylon mesh. Two resin bags per plot were inserted into the edge of an excavated hole below a column of undisturbed soil at a 15 cm depth, which is below the zone of maximum rooting density for dry meadow plants (10 cm, Webber and May, 1977). The resin bags were deployed in June 2008 and removed at snowmelt in June 2009. After retrieval the bags were opened, and the resin extracted using 2 N KCl. The extractant was analyzed for inorganic N as described above.

Soil pH and extractable cations were measured in the first year of the experiment (2006) and again in the third year of the experiment (2008). Two soil cores (A horizon, 1.5 cm diameter, 10 cm depth) were collected from each plot, sieved to 2 mm, and then composited for each plot and air dried. Soil pH was measured using a Beckman 340 pH probe on a 1:2 soil: distilled water paste determined after 30 min of shaking. Another subset of the soil was extracted with 0.1 M BaCl, and the extractant was analyzed for Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> using an ARL 3410 Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES; Thermo Electron, Waltham, MA, USA).

# 2.3. Data analyses

Changes in the cover of individual plant species in response to increases in N inputs were evaluated using repeated measures general linear model MANOVA, with block as a categorical covariate in the model to account for potential microsite influences. Significant effects of the N treatments on cover were evaluated using the year  $\times$  treatment interaction terms (Wilks lambda), which indicate whether temporal changes in the cover of species differed among the treatments. The effect of the N treatments on aboveground NPP, tissue N concentrations and N uptake, soil solution and resin bag inorganic N, soil pH, and extractable base cations was evaluated using a one-way general linear model ANOVA, with block as a categorical covariate when significant. All data sets were evaluated prior to ANOVA testing to assure they met the assumptions of the tests. Arcsine transformations were needed for the resin bag and soil solution inorganic N data to meet the assumptions of the tests.

# 3. Results

#### 3.1. Effect of N treatments on plant species cover

A total of 43 vascular plant species occurred within the plots  $(9-24 \text{ species m}^{-2} \text{ plot})$ , with the sedges *K. myosuroides* and *C. rupestris* making up the greatest amount of cover (average of 41% and 26% cover, respectively). Neither species richness nor the Shannon–Wiener diversity index (H'), which incorporates both the richness and evenness of species, changed with treatment or time. The only species that exhibited a significant response to the N treatments was *C. rupestris*, which increased in a dose dependent manner (significant treatment × time interaction in repeated measures ANOVA, *F* = 4.59, Wilks lambda *P* = 0.02, Fig. 1a). The mean cover of *C. rupestris* increased by 34%, 69%, 86%, and 125% over the four year period in the 0 (ambient), 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatments, respectively.



**Fig. 1.** Cover (a, symbols are means  $\pm$  s.e.m., n = 5) and rate of change in cover (b, each plot represented by a triangle) for *Carex rupestris* in an alpine dry meadow in Rocky Mountain National Park subjected to ambient deposition (control), and additions of 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup>. The data were fit with a sigmoidal dose response curve (solid line,  $r^2 = 0.67$ , 95% confidence interval shown by the dotted lines). The extrapolation of the line to the *x*-axis in b provides an estimate of the threshold of N input at which significant increases in cover of *C. rupestris* occurs due to N deposition.

# 3.2. Estimate of N critical load for vegetation change

The N critical load for changes in vegetation was estimated as the N input level below which no increase in C. rupestris cover would occur, as indicated here by the threshold at which cover increased. We assumed that no other factor contributed to the observed change in C. rupestris cover at the research site; e.g. climate change in this region has been minimal or non-significant (Pepin and Losleben, 2002; Clow, 2010). An analysis of growing season temperatures at the nearest site for which long-term data are available (Loch Vale) indicated the mean monthly temperatures for June, July, and August during 2006–2009 (June: 9.7  $\pm$  0.4, July: 13.4  $\pm$  0.2, August: 11.9  $\pm$  0.3) were not different from the 1983–2005 averages (June: 9.5  $\pm$  0.1, July: 13.2  $\pm$  0.1, August: 12.1  $\pm$  0.1). Furthermore past experiments at Niwot Ridge have determined that N, but not P or water, limits the growth of C. rupestris (Bowman et al., 1995). We estimated the N input threshold for changes in C. rupestris cover in all plots using linear regression analyses of the rate of change in projected cover for each of the 20 plots. The response function for the change in C. rupestris cover per year versus the N input rate (including ambient deposition) was estimated using a sigmoidal dose response curve (Fig. 1b), with the x-intercept providing the N critical load for vegetation. This approach yielded a N critical load for vegetation change of 3 kg N ha<sup>-1</sup> yr<sup>-1</sup>.

# 3.3. Changes in aboveground biomass and tissue N concentrations and N content

The total aboveground biomass did not change significantly in response to the N treatments after 3 years (Fig. 2a). However, there



**Fig. 2.** Biomass (a) and N content (b) of aboveground vegetation in an alpine dry meadow in Rocky Mountain National Park subjected to 3 years of ambient deposition (control), and additions of 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Plant tissues were separated into the dominant species (*Kobresia*), all other sedges and grasses (graminoids), and forbs. Bars are means  $\pm$  s.e.m. (n = 5).

was a significant increase in biomass of graminoids (which includes *C. rupestris*) (F = 13.6, P < 0.01). There was a significant influence of microsite on total biomass (block effect, F = 9.1, P = 0.001), but not on the other components of biomass.

Nitrogen concentrations in aboveground tissues increased significantly with increasing N inputs for the graminoids (F = 13.4, P < 0.01) and forbs (F = 10.9, P < 0.01), but not for *Kobresia* (F = 0.54, P = 0.48) (Table 1). Concentrations increased by an average of 40% in graminoids and 27% in forbs between the 0 and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatments.

The total pool of N in aboveground biomass increased with increasing N input as a result of both increases in tissue N concentrations and biomass in the graminoids (F = 27.1, P < 0.001 for graminoids N content, F = 5.2, P = 0.04 for total biomass N content). Nitrogen content in aboveground biomass increased 29% between the 0 and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatments (Fig. 2b).

#### 3.4. Effects of N treatments on soil inorganic N, cations and pH

Soil solution NO<sub>3</sub><sup>-</sup>–N and NH<sub>4</sub><sup>+</sup>–N both increased significantly with the N treatments (Fig. 3a, F = 18.0, P < 0.001 for NO<sub>3</sub><sup>-</sup>–N; F = 17.4, P < 0.001 for NH<sub>4</sub><sup>+</sup>–N). Significant deviation from the control soil solution concentrations of NO<sub>3</sub><sup>-</sup>–N occurred between 9 and 14 kg N ha<sup>-1</sup> yr<sup>-1</sup>, based on the 95% confidence interval of the regression analysis.

Resin bag NO<sub>3</sub><sup>-</sup>–N concentrations also increased significantly with the N treatments (Fig. 3b, F = 18.0, P < 0.001), and there was

#### Table 1

Tissue N concentrations for above ground biomass collected in plots treated with 0 (control), 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> in an alpine dry meadow, Rocky Mountain National Park. Values are means (%)  $\pm$  s.e.m.

Treatment:	0	5	10	30	
Biomass component:					
Kobresia	$1.60\pm0.10$	$1.74\pm0.12$	$1.69\pm0.06$	$1.76\pm0.17$	
Graminoids <sup>a</sup>	$1.21 \pm 0.09$	$1.27\pm0.09$	$1.54\pm0.11$	$1.69\pm0.09$	
Forbs <sup>a</sup>	$1.52 \pm 0.04$	$\textbf{1.67} \pm \textbf{0.13}$	$1.77 \pm 0.05$	$1.93 \pm 0.10$	

<sup>a</sup> Significant treatment effect at P < 0.01.

a trend of an increase for NH<sup>+</sup><sub>4</sub>–N (F = 2.9, P = 0.09). Significant deviation from the control (0) resin bag concentrations of NO<sup>-</sup><sub>3</sub>–N occurred above 9 kg N ha<sup>-1</sup> yr<sup>-1</sup>, based on the 95% confidence interval of the regression analysis.

Extractable soil cations were dominated by Ca<sup>2+</sup>, with Mg<sup>2+</sup> making up the next greatest contribution (Table 2), indicating that the soil buffering system was dominated by base cations. Extractable Al<sup>3+</sup> was a relatively minor component of the soil cation pool. The N treatments did not influence the concentrations of extractable cations in 2008 nor were the levels of extractable cations different from the pretreatment levels measured in 2006 (data not shown). However there was a trend for all of the base cations to have lower means in the 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> treatment in 2008, which was not apparent in 2006. Soil pH values did not change with the N treatments nor between 2006 and 2008 (mean =  $5.83 \pm 0.06$  s.e.m.), but there was a significant microsite influence (block effect, F = 7.5, P = 0.002).

# 4. Discussion

The determination of a N critical load for vegetation change was greatly facilitated by the response of a relatively abundant sedge of alpine dry meadow communities, C. rupestris. Increases in the cover of this N indicator species were proportional to the amount of N added. The rate of increase in cover plotted as a function of N input provided a N critical load of 3 kg N ha<sup>-1</sup> yr<sup>-1</sup>. This result is very similar to the N critical load evaluation for a dry meadow on Niwot Ridge, approximately 45 km south (Bowman et al., 2006), with a N critical loads for vegetation change at 4 kg N ha<sup>-1</sup> yr<sup>-1</sup> and whole community response at 10 kg N  $ha^{-1}$  yr<sup>-1</sup>. These empirically derived N critical loads indicate vegetation changes are already ongoing on the east side of the continental divide in the Colorado Front Range. The current N deposition rates for the Chapin Pass research site, and most of the alpine areas of the eastern side of the continental divide from Rocky Mountain National Park to the south along the Denver airshed, are in excess of this critical load (Baron et al., 2000; Williams and Tonnessen, 2000; Burns, 2003; Baron, 2006). Much of this area is designated as Class I and given special protection by the Clean Air Act Amendments of 1977 (NPS ARD, 2002).

Initially we anticipate that diversity of vascular plant species will increase in most alpine communities as N deposition increases over background levels, based on responses in N fertilization experiments (Theodose and Bowman, 1997; Molau and Alatalo, 1998; Heer and Körner, 2002; Bowman et al., 2006; Olofsson and Shams, 2007), as well as theoretical considerations of the relationship between resource supply and diversity (Loreau et al., 2002). As nitrophilic species become more dominant, however, diversity will decrease with more rare species excluded by competition (Suding et al., 2005). Decreasing diversity due to N deposition has been reported in numerous ecosystems, primarily in developed countries with deposition rates >10 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Stevens et al., 2004; Bobbink et al., 2010). Critical loads for similar high elevation grassland systems in Europe have generally been set



**Fig. 3.** Changes in soil solution inorganic N (a) and resin bag NO<sub>3</sub><sup>-</sup>-N (b) from plots in an alpine dry meadow in Rocky Mountain National Park subjected to 3 years of ambient deposition (control), and additions of 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Symbols are means  $\pm$  s.e.m. (n = 5).

at higher levels (~10 kg N ha<sup>-1</sup> yr<sup>-1</sup>, Achermann and Bobbink, 2003) than suggested here (3 kg N ha<sup>-1</sup> yr<sup>-1</sup>), and it is possible that initial changes in species composition have already occurred in alpine grasslands in some parts of Europe. Stevens et al. (2004) suggested many low elevation grasslands in the U.K. have already lost plant species as a result of current N deposition rates between 5 and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup>, with as much as a 23% loss at an average deposition rate for all grasslands of 17 kg N ha<sup>-1</sup> yr<sup>-1</sup>.

While there is evidence to support ongoing changes in the abundance of plant species in the southern Rocky Mountains as a result of current N deposition rates, thresholds for the response of soil metrics related to acidification do not appear to be exceeded at this time. Ecosystem uptake of inorganic N at loading rates up to 10 kg ha<sup>-1</sup> yr<sup>-1</sup> appears to be sufficient to minimize NO<sub>3</sub> leaching in dry meadow communities, as indicated by the lack of change in inorganic N concentrations in soil water and in resins placed below the main rooting zone. This apparent stabilization was not entirely the result of increases in plant uptake, as changes in aboveground N uptake combined with estimated belowground N uptake (assumed to be  $1.5 \times$  aboveground (Fisk et al., 1998)), could not account for disappearance of all of N added. Although NPP of dry meadow and other alpine plant communities have been assumed to be limited by the supply of N (Bowman et al., 1993, 1995), there was no significant increase of aboveground biomass to the N inputs, and even when significant increases have been noted, interannual variation in NPP was greater than the N treatment effect (Bowman et al., 2006). The previous investigations of N limitation of NPP in these ecosystems have used higher inputs of N, and the majority of the biomass response was the result of a turnover in species composition. This turnover resulted in a higher abundance of nitrophilic species with greater capacity to increase biomass as N supply increased (Theodose and Bowman, 1997). Thus the stabilization of N seen in the present experiment is probably the result of a combination of greater uptake by microbial biomass (Fisk and Schmidt, 1996) and possibly by soil organic matter (Davidson

#### Table 2

Extractable cation concentrations from soils collected in year 3 of an N addition treatment of 0 (control), 5, 10, and 30 kg N ha<sup>-1</sup> yr<sup>-1</sup> in an alpine dry meadow, Rocky Mountain National Park. Values are mg/kg dry mass soil  $\pm$  s.e.m.

Treatment:	0	5	10	30
Cation:				
$Ca^{2+}$	$7631 \pm 1193$	$7667 \pm 1352$	7773 + 1206	$5707 \pm 351$
$Mg^{2+}$	$809\pm114$	$864 \pm 164$	$887 \pm 157$	$628\pm45$
$K^+$	$240\pm43$	$244\pm45$	$250\pm37$	$179\pm32$
Na <sup>+</sup>	$31\pm11$	$30\pm9$	$30\pm9$	$13\pm7$
$Mn^{2+}$	$26\pm5$	$29\pm 6$	$30\pm9$	$18\pm5$
Al <sup>3+</sup>	$\textbf{3.8} \pm \textbf{1.2}$	$10.9\pm5.1$	$7.5\pm3.5$	$10.9\pm6.3$
Fe <sup>3+</sup>	$\textbf{2.4} \pm \textbf{1.0}$	$1.6 \pm 0.5$	$2.1 \pm 0.9$	$1.3 \pm 0.7$

et al., 2003). Changes in litter and soil organic matter chemistry, i.e. decreases in C:N ratios, will likely have positive feedbacks to N cycling rates and enhanced pools of soil inorganic N are likely to occur (Baron et al., 2000; Bowman, 2000).

The threshold for increases in NO<sub>3</sub><sup>-</sup> leaching below the rooting zone was estimated at 9 kg N ha<sup>-1</sup> yr<sup>-1</sup>, and for increases in soil solution  $NO_3^-$  at 14 kg ha<sup>-1</sup> yr<sup>-1</sup>, using a conservative estimate that there was no impact of ambient N deposition on  $NO_3^-$  leaching in vegetated soils. Above these thresholds the biotic and abiotic sinks for N deposition are exceeded. Increases in soil  $NO_{\overline{3}}$  leaching can initiate acidification, as soil cations are removed from cation exchange sites and replaced by protons (van Breemen et al., 1983; Binkley and Richter, 1987). Increases in NH<sub>4</sub><sup>+</sup> can enhance rates of nitrification, which will also acidify soils. There was no indication that acidification is currently occurring within the treatment plots at the Chapin Pass experimental site after 3 years, as extractable basic cation concentrations were not significantly affected by the treatments, nor did soil pH decrease. Soil acidification was noted after 11 years of experimental N additions above a threshold of 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> at Niwot Ridge (Lieb et al., 2011), as indicated by significant decreases in base cations, soil pH, and acid neutralizing capacity, as well as increases in extractable aluminum. Generally levels of extractable base cations are higher in soils at the Chapin Pass site relative to Niwot Ridge. Soil acidification, losses of nutrient cations, and increases in soluble Al can increase susceptibility to stress, lower growth rates, and increase mortality in plants (Aber et al., 1998; Driscoll et al., 2001; Högberg et al., 2006; Bowman et al., 2008). Long-term inputs of low levels of N deposition can lower the thresholds for acidification as N builds up in the soil organic matter pool, enhancing internal N cycling rates and potentially increasing nitrification and leaching of NO<sub>3</sub>.

The metrics used to establish N critical loads should consider the long-term ecological implications of maintaining N deposition rates at a given level (Porter et al., 2005). For relatively pristine areas such as national parks and wilderness areas, using sensitive vegetation based N critical loads, such as those described here and in Bowman et al. (2006), or lichen composition and chemistry (Geiser et al., 2010), will help protect and maintain natural plant communities that evolved under low nitrogen conditions. N critical loads will also help prevent more severe and relatively irreversible changes, such as acidification, from occurring. Once base cations are depleted, it may take decades to centuries of weathering and deposition to replace them. Recovery from acidification due to high levels of S deposition has been ongoing in industrialized regions that have reduced S emissions, but this recovery has been slowed by continued, and in some cases, enhanced N deposition (Stoddard et al., 1999; Bouwman et al., 2002; Warby et al., 2009). Preventing acidification of soils and surface waters in regions exhibiting initial symptoms of ecological changes due to N deposition should be an important goal of land managers and air quality policy makers.

# 5. Conclusions

The critical loads we estimated for vegetation change (3 kg N ha<sup>-1</sup> yr<sup>-1</sup>) and NO<sub>3</sub> leaching (9–14 kg N ha<sup>-1</sup> yr<sup>-1</sup>) for alpine ecosystems of Rocky Mountain National Park are lower than most forest and shrubland ecosystems, but similar to other infertile ecosystems (Bobbink et al., 2010). The results indicate that changes in vegetation are already occurring in the park, similar to reports for neighboring areas (Bowman et al., 2006) and for aquatic biota in the park (Baron, 2006). No losses of soil cations or increases in soil pH were found in treatment plots, but sustained enhancement of NO<sub>3</sub> leaching may eventually lead to more severe and less reversible geochemical changes in soils.

# Acknowledgments

We thank Isabel Ashton, Jane Smith, Jenifer Hall-Bowman, Gordon Bowman, Miles Bowman, Courtney Meier, Melissa Maxa, Kaleb Keyserling, Samantha Swatling-Holcomb, Evan Fricke, Anna Lieb, and Ben Kamark for field assistance. Laboratory analyses were expertly performed by the staff of the Niwot Ridge LTER program, supervised by Chris Seibold, the Laboratory for Environmental and Geological Studies, and Chris Washenberger/Diana Nemergut (CHN analyses). Constructive comments on a previous version of this manuscript were provided by three anonymous reviewers and Harrison Carpenter's Spring 2012 Graduate Writing Seminar course.. Funding was provided by the National Park Service, Air Resources Division, through a Rocky Mountain Cooperative Ecosystem Studies Units grant.

# References

- Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L., Fernandez, I., 1998. Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. BioScience 11, 921–934.
- Achermann, B., Bobbink, R. (Eds.), 2003. Empirical Critical Loads for Nitrogen. Environmental Documentation No. 164 Air. Swiss Agency for Environment, Forest and Landscape SAEFL, Berne, p. 327.
- 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, 352–368.
- Baron, J.S., 2006. Hindcasting nitrogen deposition to determine an ecological critical load. Ecol. Appl. 16, 433–439.
- Binkley, D., Högberg, P., 1997. Does atmospheric deposition of nitrogen threaten Swedish forests? For. Ecol. Manage. 92, 119–152.
- Binkley, D., Richter, D., 1987. Nutrient cycles and H+ budgets of forest ecosystems. Adv. Ecol. Res. 16, 1–51.
- Bobbink, R., Hornung, M., Roelofs, J.G.M., 1998. The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. J. Ecol. 86, 717–738.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.-W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., De Vries, W., 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecol. Appl. 20, 30–59.
- Bouwman, A.F., Van Vuuren, D.P., Derwent, R.G., Posch, M., 2002. A global analysis of acidification and eutrophication of terrestrial ecosystems. Water, Air, Soil Pollut. 141, 349–382.
- Bowman, W.D., Bilbrough, C.J., 2001. Influence of a pulsed nitrogen supply on growth and nitrogen uptake in alpine graminoids. Plant Soil 233, 283–290.
- Bowman, W.D., Steltzer, H., 1998. Positive feedbacks to anthropogenic nitrogen deposition in Rocky Mountain alpine tundra. Ambio 27, 514–517.
- Bowman, W.D., Theodose, T.A., Schardt, J.C., Conant, R.T., 1993. Constraints of nutrient availability on primary production in two alpine tundra communities. Ecology 74, 2085–2097.
- Bowman, W.D., Theodose, T.A., Fisk, M.C., 1995. Physiological and production responses of plant growth forms to increases in limiting resources in alpine tundra: implications for differential community response to environmental change. Oecologia 101, 217–227.

- Bowman, W.D., Gartner, J.L., Holland, K., Wiedermann, M., 2006. Nitrogen critical loads for alpine vegetation and terrestrial ecosystem response – are we there yet? Ecol. Appl. 16, 1183–1193.
- Bowman, W.D., Cleveland, C.C., Halada, L., Hreško, J., Baron, J.S., 2008. Negative impact of nitrogen deposition on soil buffering capacity. Nat. Geosci. 1, 767–770.
- Bowman, W.D., 1992. Inputs and storage of nitrogen in winter snowpack in an alpine ecosystem. Arct. Alp. Res. 24, 211–215.
- Bowman, W.D., 2000. Biotic controls over ecosystem response to environmental change in alpine tundra of the Rocky Mountains. Ambio 29, 396–400.
- Burns, D.A., Blett, T., Haeuber, R., Pardo, L.H., 2008. Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants. Front. Ecol. Environ. 6, 156–159.
- 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.
- Chadwick, O.A., Chorover, J., 2001. The chemistry of pedogenic thresholds. Geoderma 100, 321–353.
- Clark, C.M., Tilman, D., 2008. Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. Nature 451, 712–715.
- Clow, D.W., 2010. Changes in the timing of snowmelt and streamflow in Colorado: a response to recent warming. J. Clim. 23, 2293–2306. Davidson, E.A., Chorover, J., Dail, D.B., 2003. A mechanism of abiotic immobilization
- Davidson, E.A., Chorover, J., Dail, D.B., 2003. A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Glob. Change Biol. 9, 228–236.
- Dentener, F., Drevet, J., Lamarque, J.F., Bey, I., Eickout, B., et al., 2006. Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation. Global Biogeochem. Cy. 20, GB4003.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. BioScience 51, 180–198.
- Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., Sickman, J.O., 2003. Nitrogen emissions, deposition, and monitoring in the western United States. BioScience 53, 391–403.
- Fisk, M.C., Schmidt, S.K., 1996. Microbial responses to nitrogen additions in alpine tundra soil. Soil Biol. Biochem. 28, 751–755.
- Fisk, M.C., Schmidt, S.K., Seastedt, T.R., 1998. Topographic patterns of above- and belowground production and N cycling in alpine tundra. Ecology 79, 2253–2266.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320, 889–892.
- Geiser, L.H., Neitlich, P.N., 2007. Air pollution and climate gradients in western Oregon and Washington indicated by epiphytic macrolichens. Environ. Pollut. 145, 203–218.
- Geiser, L.H., Jovan, S.E., Glavich, D.A., Porter, M.K., 2010. Lichen-based critical loads for atmospheric nitrogen deposition in Western Oregon and Washington Forests, USA. Environ. Pollut. 158, 2412–2421.
- Gough, L., Osenberg, C.W., Gross, K.L., Collins, S.L., 2000. Fertilization effects on species density and primary production in herbaceous plant communities. Oikos 89, 428–439.
- Groffman, P.M., Baron, J.S., Gold, A.J., Gunderson, L.H., Levinson, B.M., Palmer, M.A., Paerl, H.W., Peterson, G.D., Reynolds, J.F., Turner, M.G., Weathers, K.C., Weins, J., 2006. Ecological thresholds: the key to successful environmental management or an important concept with no practical application. Ecosystems 9, 1–13.
- Heer, C., Körner, C., 2002. High elevation pioneer plants are sensitive to mineral nutrient addition. Basic Appl. Ecol. 3, 39–47.
- Högberg, P., Fan, H., Quist, M., Binkley, D., Tamm, C.O., 2006. Tree growth and soil acidification in response to 30 years of experimental nitrogen loading on boreal forest. Global Change Biol. 12, 489–499.
- Komárková, V., 1979. Alpine Vegetation of the Indian Peaks Area, Front Range, Colorado Rocky Mountains. Flora et Vegetatio Mundi, Bd VII. J Cramer, Vaduz.
- Lieb, A.M., Darrouzet-Nardi, A., Bowman, W.D., 2011. Nitrogen deposition decreases acid buffering capacity of alpine soils in the southern Rocky Mountains. Geoderma 164, 220–224.
- Loreau, M., Naeem, S., Inchausti, P. (Eds.), 2002. Biodiversity and Ecosystem Functioning: Synthesis and Perspectives. Oxford University Press, Oxford.
- Molau, U., Alatalo, J.M., 1998. Responses of subarctic-alpine plant communities to simulated environmental change: biodiversity of bryophytes, lichens, and vascular plants. Ambio 27, 322–329.
- Nilsson, I., Grennfelt, P., 1988. Critical Loads for Sulfur and Nitrogen. Report from a Workshop Held at Stokhoster, Sweden, March 19–24, 1988. Miljo Rapport 1988: 15. Nordic Council of Ministers, Copenhagen, Denmark.
- NPS ARD [National Park Service, Air Resources Division], 2002. Air Quality in the National Parks, second ed. U.S. Department of Interior, Washington, DC.
- Olofsson, J., Shams, H., 2007. Determinants of plant species richness in an alpine meadow. J. Ecol. 95, 916–925.
- Pepin, N.C., Losleben, M.L., 2002. Climate change in the Colorado Rocky Mountains: free-air versus surface temperature trends. Int. J. Climatol. 22, 311–329.
- Porter, E., Blett, T., 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.

- Rao, L.E., Allen, E.B., 2010. Combined effects of precipitation and nitrogen deposition on native and invasive winter annual production in California deserts. Oecologia 162, 1035–1046.
- Stevens, C.J., Dise, N.B., Mountford, J.O., Gowing, D.J., 2004. Impact of nitrogen deposition on the species richness of grasslands. Science 303, 1876–1879.
- Stoddard, J.L., Jeffries, D.S., Lukewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kamp, A., Mannio, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Weiting, J., Wilander, A., 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401, 575–578.
- Suding, K.N., Collins, S.L., Gough, L., et al., 2005. Functional and abundance-based mechanisms explain diversity loss due to N fertilization. Proc. Natl. Acad. Sci. USA 102, 4387–4392.
- Theodose, T.A., Bowman, W.D., 1997. Nutrient availability, plant abundance, and species diversity in two alpine tundra communities. Ecology 78, 1861–1872.

- Thomas, R.Q., Canham, C.D., Weathers, K.C., Goodale, C.L., 2010. Increased tree carbon storage in response to nitrogen deposition in the US. Nat. Geosci. 3, 13–17.
- van Breemen, N., Mulder, J., Driscoll, C.T., 1983. Acidification and alkalinization of soils. Plant Soil 75, 283–308.
- Warby, A.F., Johnson, C.E., Driscoll, C.T., 2009. Continuing acidification of organic soils across the Northeastern USA: 1984–2001. Soil Sci. Soc. Am. J. 73, 274–284.
- 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.
   Webber, P.J., May, D.E., 1977. The magnitude and distribution of below ground plant structures in the alpine tundra of Niwot Ridge, Colorado. Arct. Alp. Res. 9,
- 157–174. Williams, M.W., Tonnessen, K.A., 2000. Critical loads for inorganic nitrogen depo-
- sition in the Colorado Front Range, USA. Ecol. Applic. 10, 1648–1665.
  Yoshida, L.C., Allen, E.B., 2004. <sup>15</sup>N uptake by mycorrhizal Artemisia californica and the invasive Bromus madritensis of a N-eutrophied shrubland. Biol. Fert. Soils 39, 243–248.