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A slide down a slippery slope – alpine ecosystem responses to nitrogen deposition

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Background: Nitrogen (N) deposition in the Front Range of the southern Rocky Mountains has been increasing for several decades, and has exceeded the critical load for several ecological metrics.
Aims: Our objective was to predict potential future ecological changes in alpine zones in response to anthropogenic N deposition based on a review of research from Niwot Ridge, Colorado.
Results: Empirical observations and experimental studies indicate that plant, algal and soil microbe species compositions are changing in response to N deposition, with nitrophilic species increasing in abundance. Biotic sequestration of N deposition is insufficient to compensate for greater nitrate production, leading to the potential for acidification and base cation loss.
Conclusions: Changes in biotic composition in both terrestrial and aquatic ecosystems have important impacts on ecosystem functioning, including a lower capacity to take up and neutralise the acidifying effect of anthropogenic N, increasing phosphorus limitation of production in terrestrial and aquatic systems, and shifts in rates of N and carbon cycling. Continued elevated N deposition rates coupled with ongoing climate change, including warmer summer temperatures and lower snow cover of shorter duration, will influence the ecological thresholds for biotic and functional changes. We suggest that these thresholds will occur at lower inputs of N deposition under future climate change, meriting reconsideration of current N critical loads to protect sensitive alpine ecosystems.

Keywords: acidification; alpine; biotic response; ecosystem function; nitrogen deposition; soil response

Introduction

Anthropogenic emissions of reactive nitrogen (N) and subsequent deposition have resulted in a multitude of environmental changes worldwide, contributing to a loss of plant diversity (Stevens et al. 2004; Dupré et al. 2010; Bobbink et al. 2010), enhancement (Thomas et al. 2010) as well as decline (Likens et al. 1996) of forest growth, and acidification of soils and surface waters (Aber et al. 1998; Driscoll et al. 2001). The sensitivity of ecosystems to the impacts of N deposition varies in association with the capacity of the system to take up and neutralise deposited reactive N and the background N cycling rates and associated adaptations of the organisms to N supply (Bobbink et al. 2010). Alpine ecosystems are particularly sensitive to N deposition due to low background rates of N cycling, low biomass and production of plants and soil microbes, and elevated rates of deposition due to greater precipitation rates relative to surrounding lowlands in most mountain ranges (Williams and Tonnessen 2000; Weathers et al. 2006).

Research on the impacts of N carried out in the 1990s at Niwot Ridge, a long-term ecological research site located in the Front Range of the southern Rocky Mountains, focused on its role in controlling primary production and plant species composition (Bowman et al. 1993, 1995; Theodose and Bowman 1997; Seastedt and Vaccaro 2001), abiotic drivers of N cycling in soils (Fisk et al. 1998) and the temporal variation of N concentrations in surface waters draining the ridge (Caine 1995; Williams et al. 1996). While concern had been raised about the potential environmental impacts of N deposition (Lewis and Grant 1980; Williams et al. 1996; Burns 2003), experimental approaches and observational research were limited in predicting the expected specific trajectory of biotic and abiotic impacts. Over the past 15 years, studies on Niwot Ridge and the Green Lakes Valley have led to a greater understanding of the changes in plant, algal and microbial composition, soil responses and impacts on surface waters due to N deposition. Here we review this work to better predict how this and other alpine geo-ecological systems will respond to continued elevated inputs of N deposition. The review is organised according to the biotic and functional responses of the system (Figure 1), emphasising the work at the Niwot Ridge research site, but where appropriate using related research carried out at other alpine sites. We show that gradual changes in the abundance and numbers of plant and microbial (including algae) species are ongoing, and that the potential exists

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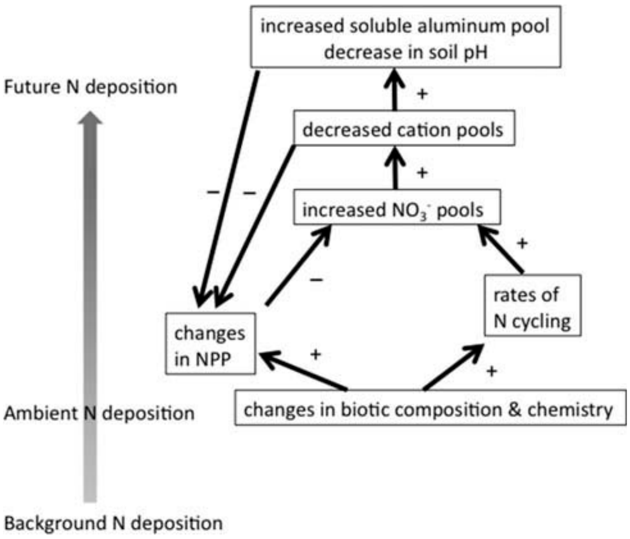

Figure 1. Conceptual model of progressive impacts of increasing N deposition on selected biotic composition, pools and processes in an ecosystem, and their positive and negative interactions. As deposition rates and N pools increase from pre-anthropogenic (background) to current ambient conditions, changes in community composition of primary producers and their chemistry (lower C:N ratio) result in feedbacks that enhance rates of N cycling and net primary production (NPP). These biotic changes can offset (greater NPP) or accentuate (higher N cycling rates) the increase in pools of NO_3^-, which in turn influences losses of base cations and increases in soluble aluminium. Loss of nutrient base cations and increased aluminium negatively influence the abundance and functioning of organisms, decreasing NPP. The timing and magnitude of changes in ecological processes are dependent on the biotic composition and their feedbacks, which have been the subject of research during the past two decades at the Niwot Ridge research site.

for increased nitrate in surface and groundwaters, depletion of base cations, acidification of soils and surface waters and loss of ecosystem services in the alpine zone/belt if N inputs into the system continue unabated.

Biotic responses

Vegetation

Plant community responses to experimental N inputs vary across the alpine landscape on Niwot Ridge. Experimental additions of N and phosphorus (P) at high amounts suggested that N supply had a strong influence on diversity in dry and moist meadow alpine communities, while wet meadow communities were more responsive to P additions or a combination of N and P (Bowman et al. 1993, 1995; Theodose and Bowman 1997; Seastedt and Vaccaro 2001). Diversity responses were driven by increases in the abundance of nitrophilic species, primarily graminoids, and the decreasing abundance of dominant species in nutrient-poor communities and rarer species in more fertile communities (Theodose and Bowman 1997). No significant changes in species richness were observed in any of these fertilisation experiments, a result that contrasts with the response of many other ecosystems to N fertilisation where diversity is associated with both gains and losses of species (Bobbink et al. 2010).

Changes in plant abundance were linked with the sensitivity to responses in production. The majority of the growth responses to N fertilisation were driven by changes in plant species composition, rather than by stimulation of growth of the dominant species. Thus the constraint of N on primary production is partially biotic, resulting from adaptations of the dominant species to low N supply (Bowman and Bilbrough 2001). However the amount (30–70 times that of ambient deposition) and chemical form (urea or ammonium sulphate) of N added in these earlier experiments did not closely mimic the chemistry and input rate of N deposition (primarily as ammonium and nitrate), complicating the interpretation of these results. Thus, to better understand the effects of future changes in N deposition, an experiment was initiated in a dry meadow on Niwot Ridge in 1997, using ammonium nitrate in a range of concentrations that simulated 3×, 6× or 9× (20, 40 or 60 kg N ha^{-1} $year^{-1}$) the ambient deposition rate (Bowman et al. 2006). Similar experiments were also run in a dry meadow in nearby Rocky Mountain National Park (Bowman et al. 2012) and in the Western Tatra Mountains of Slovakia (Bowman et al. 2008), providing a coarse comparison from lightly to heavily impacted alpine vegetation.

Changes in plant species composition and diversity were smaller when lower amounts of N were added (Bowman et al. 2006, 2012) relative to earlier experiments. Diversity increased initially due to changes in evenness, but species richness was not affected by N deposition (Bowman et al. 2006). The diversity response had declined by year 8 of the experiment, and no differences in diversity were found after 17 years of treatment (W.D. Bowman, unpublished data). Individual species showed dose-dependent increases in cover, providing a tool for determining the thresholds at which plant responses to N deposition would occur (Figure 2). At both Niwot Ridge and Chapin Pass in Rocky Mountain National Park, increases in the cover of common sedge (*Carex rupestris*) were detected over four years at all N input rates and the control plots, suggesting that ambient rates of N deposition are altering plant species composition in alpine dry meadow communities. Critical loads (the rate of input of a pollutant below which there are no impacts on sensitive environmental elements such as plant composition or soil aluminium concentrations; Nilsson and Grennfelt 1988; Porter et al. 2005) for N were established at 3 kg N ha^{-1} $year^{-1}$ for Rocky Mountain National Park and 4 kg N ha^{-1} $year^{-1}$ for Niwot Ridge (Bowman et al. 2006, 2012). Ambient deposition at both sites exceeds this critical load, and thus we concluded that changes in vegetation are ongoing in Colorado Front Range due to N deposition. Changes in whole-community assemblages were estimated to occur at 10 kg N ha^{-1} $year^{-1}$ at Niwot Ridge (Bowman et al. 2006).

Nitrogen fertilisation at rates equal to or under 60 kg N ha^{-1} $year^{-1}$ generally had little effect on whole-community biomass production in dry meadows (Bowman

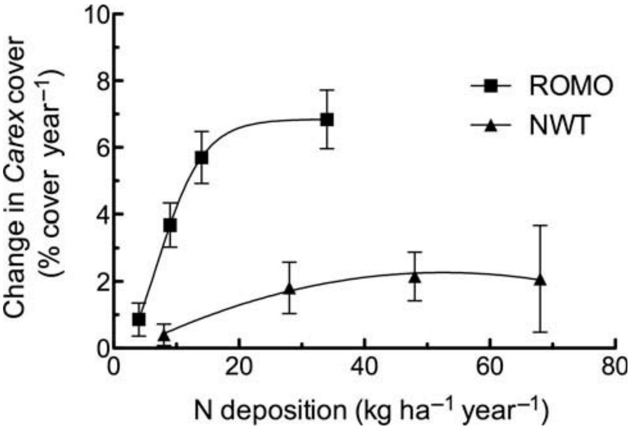

Figure 2. Rate of change in projected cover of the sedge, *Carex rupestris* with ambient and experimentally increased N deposition in alpine dry meadows at Niwot Ridge (NWT) and Rocky Mountain National Park (ROMO). Data were obtained in the first four years of manipulation at the ROMO site and after seven years at the Niwot site, explaining some of the differences in the calculated rates of cover change. Extrapolation of response curves (fitted using non-linear sigmoidal dose response function) to the N deposition axis provided estimates of N critical loads, which were 3 kg N ha^{-1} year^{-1} for ROMO and 4 kg N ha^{-1} year^{-1} for Niwot. Whole-community changes, as noted by significant changes in ordination scores, occurred at 10 kg N ha^{-1} year^{-1} at Niwot. Symbols are means, error bars are ±SE ($n = 5$). (Modified from Bowman et al. 2006, 2012.)

et al. 2006, 2012). While there were significant biomass increases in one out of the three years measured at Niwot Ridge, the inter-annual variability in production was greater than any stimulation due to N addition. A lack of biomass increase to N addition was also noted in moist meadows (Suding et al. 2008), although earlier results showed an increase in moist meadow biomass with N fertilisation (Bowman et al. 1995). While the total community biomass increase in dry meadows was small, the contribution to the total biomass by different species shifted with greater N inputs, due to an increase in biomass of the more responsive graminoid species (principally *C. rupestris*) and a decrease in the biomass of the dominant sedge, *Kobresia myosuroides*. Conceptual models (Aber et al. 1998) and empirical observations suggest that as N inputs increase, production should become insensitive and eventually inhibited by the deposition of N. Nitrogen additions at an alpine site with a legacy of high anthropogenic N inputs in the Western Tatra Mountains, Slovakia decreased biomass production, due probably to loss of nutrient base cations and increases in soluble toxic metals (Bowman et al. 2008). Thus we can anticipate little or no increase in biomass production with increasing N deposition for the alpine ecosystems on Niwot Ridge, supporting the notion that alpine vegetation has a very low capacity to buffer N deposition impacts on soils. The more responsive species had higher tissue N concentrations, indicating that as plant communities change, their ability to take up N will increase somewhat, although in our experiments it was not sufficient to compensate for the greater N inputs, as less than 50% of the applied N was taken up. Such has evidently been the case in more heavily impacted alpine areas in the Tatra Mountains (Bowman et al. 2008). The higher tissue N concentrations may provide a positive feedback to soil N cycling that could influence soil responses (discussed under *Ecosystem function responses*).

Soil microorganisms

Multiple studies in alpine and other ecosystems have shown that bacterial community composition correlates with the size of N pools. Across natural N gradients (e.g. Nemergut et al. 2010; Legg et al. 2012) and fertilised gradients (Ramirez et al. 2010), soils and sediments higher in N often harbour communities with higher relative abundances of taxa that are considered copiotrophic (fast-growing species adapted to high-resource environments). The abundance of bacteria relative to Archaea has been shown to be positively correlated with soil C:N ratios both within (e.g. Nemergut et al. 2010) and among ecosystems (Bates et al. 2011). Finally, correlations between soil C:N ratios and fungal–bacterial ratios have also been observed (e.g. Eskelinen et al. 2009). These results strongly indicate that N deposition is likely to cause shifts in soil microbial community structure and function. Predicting those changes presents a challenge addressed here based on field observations and experiments.

At Niwot Ridge, Nemergut et al. (2008) examined the effects of chronic N additions over 10 years on soil microbial community structure. Marked changes in the phylogenetic structure of fertilised bacterial communities were observed, including increases in the relative abundance of Bacteroidetes and Gemmatimonadetes and a decrease in the relative abundance of Verrucomicrobia. This work also showed that while the abundance of fungi relative to bacteria did not change in response to the treatment, N amendments resulted in a large increase in the relative abundance of Ascomycota and a decrease in Basidiomycota.

The above study used molecular phylogenetic approaches and thus the functional implications of these observed changes in microbial community structure are unknown, but hypotheses can be generated using comparisons to known organisms in culture. For example, Basidiomycota often possess lignin oxidase enzymes (Hammel 1997). As the degradation of N-rich recalcitrant compounds, including lignin, may be less favourable under N-rich conditions (Fog 1988), it is possible that Basidiomycota are outcompeted in fertilised soils by fungal groups less reliant on lignin as a N source. Alternatively, as Basidiomycota often form ectomycorrhizal associations with plants (prostrate willows and some sedges), the decrease in their relative abundance may be due to the decrease in demand for mycorrhizal infections that can enhance plant N acquisition (Mullen and Schmidt 1993) due to the enhanced N availability. Loss of fungal mutualists was suggested as contributing to the decline in abundance of *Geum rossii* following N deposition in moist meadows (Dean et al. 2014), although a loss of ectomycorrhizal associations was not associated with declines in the abundance of *K. myosuroides* in dry meadows (T. Potter, unpublished data).

The shift toward a higher relative abundance of Bacteriodetes could represent a change to a community that is more capable of degrading recalcitrant carbon (C) compounds (Zhang et al. 2003), possibly due to the enhanced N availability. Finally, the shift toward a community with a lower relative abundance of Archaea in fertilised soils is unexplained given the previously mentioned negative relationship between C:N ratios and Archaea both within and among ecosystems (e.g. Nemergut et al. 2010; Bates et al. 2011). However, other work has documented similar decreases in the abundance (He et al. 2007) and diversity (Gattinger et al. 2007) of Archaea in response to N amendments. Thus, it is possible that Archaea may be outcompeted in more nutrient-rich systems. Indeed, more recent work has demonstrated that archaeal nitrifiers, which can represent major portions of soil archaeal communities (Leininger et al. 2006), thrive under low available N conditions (Martens-Habbena et al. 2009; Verhamme et al. 2011).

The mechanisms driving the observed shifts in microbial community structure in response to increases in N are poorly understood. For example, it is unclear to what degree the changes in communities are due to the direct effects of increases in N availability as opposed to the indirect effects of changes in plant community composition, increases in plant productivity and/or changes in pH. However, preliminary work on Niwot Ridge as well as experiments from other ecosystems suggests that changes may be due to direct effects on the soil microbial community, at least to some degree. For example, an incubation experiment using unvegetated talus soils also revealed a decrease in the relative abundance of Archaea in response to N amendments (D.R. Nemergut and S. Schmidt, unpublished data). Likewise, a cross-ecosystem study that used incubation approaches to examine the response of soil community composition to N amendments resulted in similar shifts in bacterial taxa (Ramirez et al. 2012). As such, incubation experiments are plant free, these results indicating a direct effect of N availability on microbial community structure. Furthermore, Acidobacteria, taxa that are typically more abundant under low pH (Lauber et al. 2009), tend to decrease in relative abundance in response to N fertilisation treatments (Ramirez et al. 2010, 2012). This supports the hypothesis that the observed shifts are not due to the decreases in pH that typically accompany fertilisation with ammonium nitrate, and further support the role of direct effects of N amendments on the soil microbial community. Thus, fertilisation may lead to a shift toward taxa with lower C:N ratios and with higher C assimilation and growth rate efficiencies (Fierer et al. 2012), which may also explain the commonly observed decreases in respiration and biomass in response to fertilisation treatments (Treseder 2008). Indeed, metagenomic studies have shown shifts in the genomic complement of microbial communities in fertilised soils toward genes that are likely to be key for rapid growth, including genes involved in RNA synthesis, electron transport and protein metabolism (Fierer et al. 2012). While the functional implications are somewhat uncertain, it is clear that N deposition has the potential to alter soil microbial composition in alpine ecosystems, which, in turn, will influence rates of nutrient cycling and plant–microbial interactions.

Lake phytoplankton

The previous sections indicate that terrestrial alpine ecosystems offer limited buffering of N deposition to coupled aquatic ecosystems due to limited biological uptake of inorganic N by terrestrial vegetation–microbial systems. High-elevation alpine lakes are largely surrounded by unvegetated slopes, providing very little biological buffering; thus these lakes and associated streams are episodically subjected to elevated N concentrations (Caine 1995; Williams et al. 1995). Based on these and similar results from other locations, Williams et al. (1996) suggested that increasing concentrations of nitrate in the surface waters of at Niwot Ridge indicated the possibility that these systems were switching from N limitation to N saturation because of increasing amounts of N in wet deposition. Phytoplankton communities in the lakes responded rapidly to environmental change, such as increasing N deposition that caused long-term sustained biotic response (Moraska Lafrancois et al. 2003; Anneville et al. 2005; Flanagan et al. 2009). Elser et al. (2009) compared phytoplankton biomass, the absolute and relative abundance of limiting nutrients (N and P) and phytoplankton nutrient limitation in alpine lakes of the Rocky Mountains that receive elevated rates of atmospheric N deposition. Their results indicated that elevated atmospheric N deposition caused a shift in nutrient supply from a relatively balanced but predominantly N-deficient regime to a more consistently P-limited regime in alpine lakes receiving higher N deposition, consistent with a switch from N-limited ecosystems to N-saturated ecosystems. The study by Elser et al. (2009) included lakes in the Green Lakes Valley, which were in the high-N deposition category. Concentrations of chlorophyll and seston (live and dead particulate matter) C were 2–2.5 times higher in high-deposition lakes relative to low-deposition lakes, while high-deposition lakes also had higher seston C:N and C:P ratios. This study places the long-term results of monitoring nutrients and phytoplankton in Green Lake 4 in the broad context of changes occurring in alpine lakes experiencing both a dynamic climate and sustained increases in N deposition.

Analysis of the influence of N deposition on present-day phytoplankton communities has been estimated using a retrospective analysis of diatom frustules preserved in lake sediments, which provide insight into the past and ongoing changes in phytoplankton communities, and the potential drivers of ecosystem change on algal communities. Wolfe et al. (2001) interpreted historical increases in two diatom species sensitive to N status, *Asterionella formosa* and *Fragilaria crotonensis*, and concomitant decreases in δ^{15}N values in sediment cores from lakes in Rocky Mountain National Park. Their results indicated that diatom assemblages had responded to increases in N deposition associated with agricultural and industrial development in the region. Similarly, decreases in *Aulacoseira* spp. and increases in *Fragilaria* spp. in a Green Lake 4 sediment core were observed at a depth concurrent with the initiation of commercial fertiliser manufacture in the 1930s and subsequent increase in reactive N emissions (Miller and McKnight Forthcoming 2014).

The influence of N deposition on the composition and abundance of lake phytoplankton is dynamic and is influenced by climate. Experimental additions of N and P in microcosms in Green Lake 4 during the summer of 2002, which was one of the driest years on record, showed that algal biomass increased in response to P and N + P additions, but not in response to the addition of N alone (Gardner et al. 2008). Increases in the abundance of *Chlamydomonas* sp. and *Scenedesmus* sp. in response to P additions indicate that the phytoplankton response to nutrient additions was taxon specific. These findings suggest that the phytoplankton community in Green Lake 4 was N insensitive and P limited during 2002. In a multi-year study of phytoplankton response to climate, physical habitat and water quality conditions in Green Lake 4, it was demonstrated that phytoplankton abundance during the 2002 drought was not correlated with nitrate concentrations, but rather correlated with acid-neutralising capacity and concentrations of sulphate, chloride and potassium (Flanagan et al. 2009).

Taken as a whole, the work on high-elevation lakes in the Green Lakes Valley and other nearby lakes indicates that the phytoplankton community has been impacted by N deposition for at least 40 years. Future impacts of N deposition on phytoplankton composition and biomass will depend on the ability of the terrestrial system to sequester incoming N, the accumulation of N in the terrestrial ecosystem and climate change.

Ecosystem function responses

Soil responses

A key to understanding the impacts of N deposition on the functioning of terrestrial and aquatic ecosystems is the rate of nitrate (NO_3^-) production through nitrification and leaching (Binkley and Richter 1987; Aber et al. 1998). Nitrate leaching results in a progressive loss of base cations from the soil, which can induce nutrient deficiencies in plants, loss of soil buffering capacity and eventually to increases in toxic soluble aluminium (Van Breemen et al. 1983; Driscoll et al. 2001; Bouwman et al. 2002). Thus the inability of plants and soil microbes to take up soluble N from deposition can lead to acidification of soils and surface waters and cause ecosystem degradation.

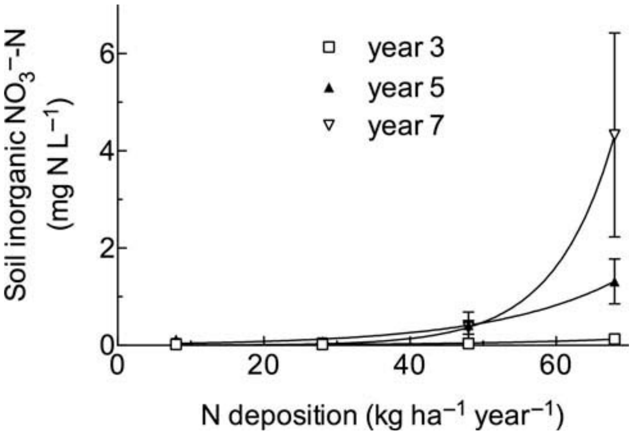

Figure 3. Progressive build-up of soil solution NO_3^-, measured using soil solution collected from microlysimeters prior to initiating the year's fertilisation, over seven years in plots on Niwot Ridge receiving ambient and elevated inputs of N deposition. The critical load for increases in soil solution NO_3^- by year 7 was estimated to be around 20 kg N ha^{-1} year^{-1}. Symbols are means, error bars are ± SE (n = 5). (Modified from Bowman et al. 2006.)

Changes in alpine soil N cycling and enhanced NO_3^- leaching occur at levels of N input lower than in most other ecosystems (Bowman et al. 2006, 2012; Bobbink et al. 2010). Low rates of N uptake and stimulation of N cycling rates due to changes in plant tissue chemistry (lower C:N ratios and higher tissue turnover rates) and species composition (Bowman and Steltzer 1998) contribute to the low threshold of N deposition rates that elicit NO_3^- leaching. Enhanced nitrate leaching occurred at input rates of 10–20 kg N ha^{-1} year^{-1} in dry meadows on Niwot Ridge and Rocky Mountain National Park, and soil solution nitrate increased over time (Figure 3). Nitrification rates increased at input rates between 20 and 40 kg N ha^{-1} year^{-1} (Bowman et al. 2006). These thresholds are sensitive to the accumulated N in the system, such that over time, lower input rates of N deposition will elicit enhanced NO_3^- leaching (Dupré et al. 2010).

Loss of base cations occurred after seven years of experimental N addition above 28 kg N ha^{-1} year^{-1} in alpine dry meadow soils at Niwot Ridge, and was associated with lower acid-neutralising capacity and a drop in pH (Figure 4, Lieb et al. 2011). Loss of base cations has been linked to forest decline and increased susceptibility to low-temperature stress in plants (Mohamed et al. 1997; DeHayes et al. 1999; Juice et al. 2006). In addition, increases in extractable aluminium and manganese occurred in alpine soils on Niwot Ridge with experimental N additions. These metal cations are toxic to plant roots, aquatic organisms and soil microbes (Delhaize and Ryan 1995), and were implicated in the majority of the damage associated with acid rain in the latter half of the twentieth century (Jacobson 2002). The progression of dominant soil cations transitioning away from the base cations, such as calcium, magnesium and potassium, towards an aluminium-dominated system has been observed in forest

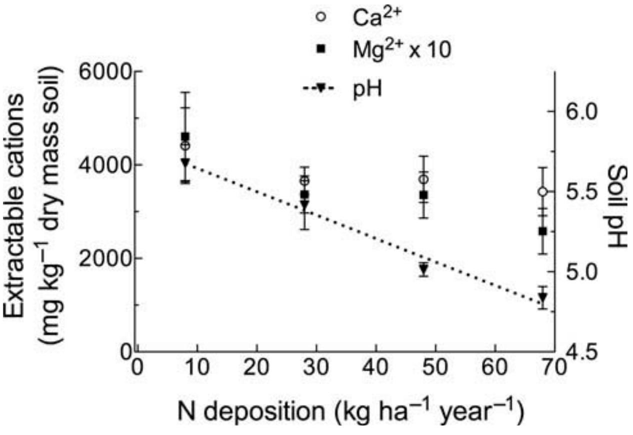

Figure 4. Changes in soil pH and soil extractable base cations Ca^{2+} and Mg^{2+} in plots on Niwot Ridge receiving ambient and elevated N deposition. Corresponding to these changes, significant losses of acid-neutralising capacity were measured in soils from these plots (Lieb et al. 2011). Symbols are means, error bars are ±SE (n = 5). (Data from Lieb et al. 2011.)

ecosystems as a result of acid rain (both N and S deposition) (Johnson et al. 1994; Driscoll et al. 2001; Högberg et al. 2006). Alpine soils can, and have, experienced the same transition towards an aluminium-dominated chemistry. A heavily impacted alpine site in the Western Tatra Mountains of Slovakia exhibited an even more extreme response to N inputs, with a loss of extractable aluminium and an increase in extractable iron, marking a transition between soil buffering systems observed only in the most heavily acidified soils such as acid mine drainage sites (Bowman et al. 2008). Soil pH values at this site were between 3.4 and 3.2, whereas alpine soils in the Colorado Front Range are generally between 5 and 6. However, simulated N deposition resulted in lower pH values in soils on Niwot Ridge (Lieb et al. 2011).

Soil parent material, clay minerals, amount of soil organic matter (humus) and the dominant plant species and the chemical properties of their litter influence the sensitivity of soils to N deposition across the alpine landscape. Soils on Niwot Ridge are more depleted in base cations than those at the Chapin Pass research site in Rocky Mountain National Park, probably associated with differences in parent material chemistry (Lieb et al. 2011; Bowman et al. 2012). Depletion of base cations and decreases in soil pH have not been recorded in N-addition experiments at the Chapin Pass site. In addition, the plant community, winter snow depth and soil disturbance can influence soil characteristics that determine its buffering capacity (Litaor et al. 2002). Conifers have a pronounced influence on soil-buffering capacity and soil pH by producing acidic litter that depletes base cations and creates acidic soils (Liptzin and Seastedt 2009; A. Lieb and A. Darrouzet-Nardi, unpublished data). Thus alpine soils may be somewhat less sensitive than surrounding subalpine forests to N deposition. Baron et al. (2000) found lower magnesium in soils of old-growth forests on the eastern side of the Continental Divide relative to the western side, consistent with N deposition leading to more base cation depletion and coinciding with observed losses of extractable magnesium in N-fertilised alpine soils (Lieb et al. 2011).

A wild card that could greatly influence soil biogeochemical sensitivity to N deposition in the southern Rocky Mountains is the deposition of base cation-laden dust from the Colorado Plateau (Litaor 1987; Ley et al. 2004; Muhs and Benedict 2006; Lawrence et al. 2010). Fine soil particles are carried on south-westerly winds and subsequently deposited at high elevations in the Rockies, providing a substantial source of acid-neutralising capacity for alpine soils (Lawrence et al. 2010) and potentially offsetting the acidifying effects of N deposition and losses of nutrient base cations. Dust inputs increased with the introduction of cattle to the south-western USA in the late nineteenth century (Neff et al. 2008) and have remained elevated, due possibly to drought and land-use change in the Colorado Plateau. The accumulation of this dust in the already acidic granite-derived soils of Niwot Ridge and other sites in the southern Rocky Mountains has most likely prevented the onset of soil and surface water acidification due to N deposition. If increases in N deposition and associated NO_3^- leaching alter the soil buffering system, soil acidification will occur along with losses of nutrient base cations. Soil acidification could have long-lasting impacts on soil biogeochemistry, diversity and plant production (Bowman et al. 2008; Lieb et al. 2011).

Impacts on aquatic ecosystems

The impact of N deposition on the functioning of aquatic ecosystems is associated with its influence on shifts in resource limitations of NPP, and subsequent influence on N fluxes downstream. While the historic response of lake diatoms to N deposition and the evidence for present-day P limitation of the phytoplankton community support the idea of a historic shift from N to P limitation, P-limited algal communities have the potential to influence downstream N flux in alpine freshwater ecosystems. Hood et al. (2003) demonstrated that nitrate concentrations increased from the Arikaree Glacier, at the top of the Green Lakes Valley watershed above the six lakes found in the valley, and then decreased by a factor of five below the lowest alpine lake in the catchment. These results suggest that different biogeochemical processes influence nitrate transport in surface waters along an elevation gradient.

Reactive transport modelling indicates that the increase in nitrate concentrations below the headwater portions of the Arikaree Glacier are due, in part, to transport of ammonium from the hyporheic zone to the stream, where it is rapidly oxidised to nitrate (Miller et al. 2006). Because the residence time of water in lakes increases during the summer while the algal populations are increasing, there is a potential for significant in-lake (autochthonous) N uptake to occur. A reactive transport model developed by Miller, McKnight, Chapra, et al. (2009) was used to quantify the reactivity of dissolved organic

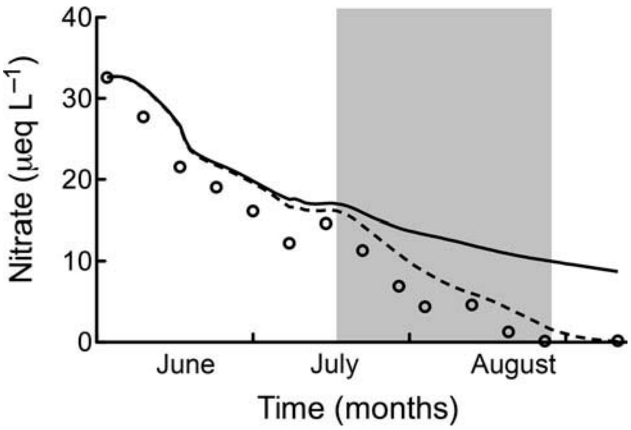

Figure 5. Measured nitrate concentrations (points), conservative estimate of nitrate concentrations (solid line), and reactive transport estimate of nitrate concentrations assuming first-order decay dependent on chlorophyll *a* concentrations (dashed line) at the outlet of Green Lake 4 during the summer of 2006. The shaded area represents the timing of the peak in chlorophyll *a*.

matter in Green Lake 4 over the course of the run-off season, (Appendix). The conservative estimate of nitrate concentrations in the epilimnion of Green Lake 4, assuming no N uptake (decay rate of 0), consistently overestimated the measured concentrations at the outlet to the lake during the 2006 growing season (Figure 5). The largest deviation between conservative estimates and measured nitrate concentrations occurred during the late summer when chlorophyll *a* concentrations, which serve as a proxy for algal biomass, peaked. The addition of a first-order nitrate decay rate, dependent on chlorophyll *a* concentration, resulted in an improved fit between the measured nitrate concentrations and those estimated using the reactive transport model. This fit was most improved at peak chlorophyll *a* concentrations. The conservative and reactive transport estimates suggest that Green Lake 4 serves as a seasonal sink for nitrate in the watershed. Moreover, the largest losses of nitrate in the lake occur during the peak in algal productivity.

Further improvement in the reactive transport model could be attained when a time-variable nitrate decay rate is used. Given the seasonal shifts in phytoplankton community composition observed by Gardner et al. (2008), it is possible that, in addition to being dependent on total algal biomass, nitrate uptake rates may also be dependent on the relative abundance of phytoplankton species in the lake at any given time. For example, the simulation with a constant value for the N decay rate overestimates the nitrate concentration in mid-July when chlorophyll *a* concentrations began to increase and the phytoplankton community was dominated by the chlorophyte *Chlamydomonas* sp., which was less abundant later in the summer (Miller, McKnight, Chapra 2009). Furthermore, it would be necessary to develop a complete data set for the downstream lakes to evaluate whether the values for N decay rate would be similar in the subalpine lakes found in the lower reaches of the Green Lakes Valley, which have greater residence times and different phytoplankton communities. Taken together, the modelling results suggest that, although nitrate is not currently limiting NPP in Green Lake 4, in-lake consumption of nitrate is an important processes determining downstream nitrate transport and, subsequently, the patterns seen at the catchment scale.

Catchment responses to and snowpack controls on N fluxes

The previous sections indicate that uptake of N occurs as it passes through terrestrial and aquatic systems in the alpine belt/zone of Niwot Ridge, augmented by shifts toward nitrophilic species of plants and phytoplankton. However sequestration is limited due to low abundances of organisms and strong seasonality in biological activity. Previous research indicated that N saturation occurs in the highest reaches of the Green Lakes Valley and is associated with episodic acidification of surface waters (Caine 1995; Williams and Caine 2001). Prior to the occurrence of N saturation, nitrate concentrations in Green Lake 4 during the summers of 1985 and 1986 were near or below detection limits. Biota apparently had the ability to utilise all available N from atmospheric deposition and were N limited during the growing season. Starting in 1987, nitrate began to leak out of the basin in surface waters during the growing season, reaching annual minimum concentrations of about 10 μeq L^{-1} in 1990. This increase in annual minimum concentrations of NO_3^- in surface waters paralleled the large increase in NO_3^- loading from wet deposition in the late 1980s (Williams et al. 1996), and is consistent with a switch from N-limited ecosystems to N-saturated ecosystems.

As noted earlier, alpine ecosystems exhibit low N-critical loads due to low rates of biological activity. Williams and Tonnessen (2000) used an empirical approach to estimate catchment-level critical loads for N in wet deposition to the southern Rocky Mountains. They showed that high-elevation sites (>2500 m) had higher wet deposition rates between 1992 and 1996 (2.5–3.5 kg N ha^{-1} $year^{-1}$) than low-elevation sites (<2500 m, <2.5 kg N ha^{-1} $year^{-1}$). Furthermore, a synoptic survey in 1995 of 91 high-elevation lakes in the southern Rocky Mountains suggested that water quality was being affected by inorganic N in wet deposition throughout the region (Williams and Tonnessen 2000). Williams and Tonnessen (2000) suggested that critical loads of inorganic N in wet deposition to Class 1 areas in the southern Rocky Mountains be set at 4 kg N ha^{-1} $year^{-1}$ (wet only), based on patterns of NO_3^- loss from the catchment and associated patterns of wet deposition. This critical load matches the value found for vegetation responses (Bowman et al. 2006), but is higher than critical loads set for lake algal responses (Baron 2006).

Our ability to understand N fluxes and effectively manage high-elevation catchments is constrained by the lack of process-level understanding of the N cycle (Williams and Caine 2001). At present, we do not fully know the source of NO_3^- in surface waters of the Colorado Front Range and other high-elevation catchments in the western USA. Snowmelt run-off is the dominant hydrologic event in these catchments. Nitrate concentrations in surface waters are generally consistent with the release of NO_3^- from storage in the seasonal snowpack in the form of an ionic pulse (Williams et al. 1995), and the NO_3^- in stream waters is often assumed to be from deposition (Williams et al. 1996). As noted earlier, some of the NO_3^- inputs are derived from nitrified NH_4^+ in the hyperheic zone. Additional work in the alpineat Niwot Ridge has shown that microbial activity in snow-covered soils plays a key role in N cycling in alpine ecosystems prior to snowmelt run-off, with winter net mineralisation rates similar to or greater than those during the summer (Brooks et al. 1996). Microbial communities have the capacity to adjust rapidly to the seasonal dynamics of soil environment-associated changes in snow cover (Schmidt et al. 2007). Brooks et al. (1997) found that winter CO_2 and N_2O fluxes were strongly related to snow cover depth and snow duration. Consistent snow cover insulated the soil surface from extreme air temperatures and allowed heterotrophic activity to continue through much of the winter. In contrast, soil remained frozen at sites with inconsistent snow cover and microbial growth did not begin until snowmelt. Over-winter heterotrophic activity in snow-covered soil has the potential to mineralise from <1% to >25% of the C fixed in above-ground NPP, while over-winter N_2O fluxes ranged from less than half to an order of magnitude higher than growing season fluxes. The variability in these fluxes suggests that small changes in climate that affect the timing of seasonal snow cover may have a large effect on C and N cycling in these environments.

Brooks et al. (1998) conducted a series of experiments on the dynamics of microbial activity under the seasonal snowpack and resulting export of NO_3^- to surface waters. Soil under early-accumulating, consistent snow cover remained thawed during most of the winter, and both microbial biomass and soil inorganic N pools gradually increased under the snowpack. At the initiation of snowmelt, microbial biomass N pools increased concurrent with a decrease in soil inorganic N pools. During the latter stages of snowmelt, microbial biomass N pools decreased sharply with no concurrent increase in inorganic N pools or significant leaching losses. In contrast, soil under inconsistent snow cover remained frozen during most of the winter. During snowmelt, microbial biomass initially increased and then decreased as sites became snow free, and NO_3^- export from these areas of inconsistent snow cover sites was greater than from sites with consistent snow cover. These results suggest that microbial activity, growth and turnover in consistently snow-covered soil provide a significant buffer, limiting the export of inorganic N to surface water during snowmelt. However, this buffer is very sensitive to changes in snowpack regime. This work helps inform the link between inter-annual variability in the timing and depth of snowpack accumulation and loss of inorganic N concentrations in surface water.

A model of snowpack control on soil N dynamics developed by Brooks and Williams (1999) was evaluated using soil measurements from ongoing snow fence and N-fertilisation experiments (Freppaz et al. 2012). After 16 years of manipulated snow cover, soil properties correlated with the amount, timing, and duration of snow cover. Under moderate snow cover and without N addition, the total soil organic C (TOC) and total N (TN) were significantly greater than in soils under both deep and shallow snow. Nitrogen amendments in general worked in the opposite direction to snowpack controls on soil processes. The addition of N caused a significant increase in TOC and TN under the shallow snow treatments, while there was a significant decrease in these properties under the moderate snow treatment. In the latter case, the addition of N did not significantly influence the soil-extractable dissolved inorganic N pools, but was correlated with a decline in soil pH and a consequent increase in exchangeable Al and reduction in exchangeable base cations, which may have influenced soil microbial biomass, and as discussed earlier, the composition and functional attributes of microbes as well. These results demonstrate how long-term changes in snow properties and N deposition may interact in affecting alpine soil chemistry.

Conclusions and future research

Research over the past two decades has led to a better understanding of the controls on N cycling and the potential impacts of N deposition on alpine ecosystem functioning and plant and microbial species composition. The potentials for loss of biotic diversity, greater plant susceptibility to water and temperature stress, and soil and surface water acidification are very real in the alpine of the southern Rocky Mountains, and in some cases these are already occurring (Figure 6). Although the rates of N deposition did not increase markedly over the first decade of the twenty-first century, this trend is due primarily to low precipitation during this period as atmospheric concentrations of NH_4^+ and NO_3^- tended to increase (based on National Atmospheric Deposition Program-National Trends Network monitoring; http://nadp.sws.uiuc.edu/). Furthermore the more N that accumulates in an ecosystem, the more sensitive it is to further impacts of N deposition (Dupré et al. 2010), so even if rates of N deposition level off or decrease, alpine ecosystems will remain susceptible to harmful environmental effects. Thus it is likely that over the next few decades, plant and algal species composition will continue to change with increases in nitrophilic species, potentially leading to losses of diversity of more rare species and possibly an increase in invasive species. If rates of N deposition increase, soils will become susceptible to losses of base cations, and acidification of soils and surface waters will become a serious concern.

Climate change will influence the impacts of N deposition, potentially exacerbating decreases in biodiversity (evenness but not in species richness) and alterations of ecosystem function (Baron et al. 2013; Porter et al. 2013). Climate change impacts on snow cover and duration will affect N cycling and the capacity of alpine ecosystems to

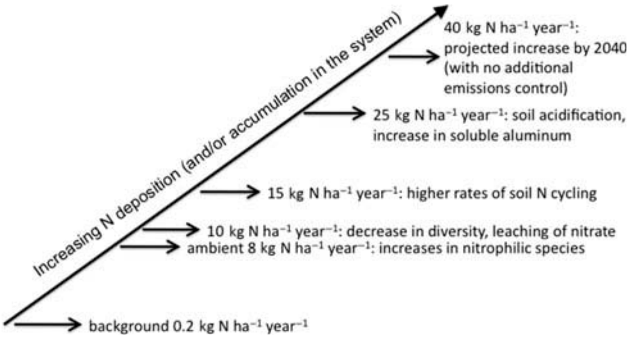

Figure 6. Predicted trajectory of ecosystem change in alpine ecosystems of the southern Rocky Mountains under elevated and accumulating N deposition. Under current conditions, nitrophilic/copiotrophic plant, algal and microbial species are increasing in abundance. A short-lived increase in diversity noted in past experiments would be followed by a decrease in diversity at ca. 10 kg N ha^{-1} year^{-1} as more rare species are excluded by nitrophiles. Higher concentrations of N in plants and soil organic matter enhance rates of N cycling, accelerating the leaching of NO_3^- and loss of base cations. Eventually with sufficient build-up of N in the system, or elevated N deposition rates of 25 kgN ha^{-1} year^{-1}, leaching of base cations leads to decreases in soil pH and increases in soluble Al. Worst case projections for N deposition increases suggest these levels will be surpassed by 2050 (Dentener et al. 2006).

retain N in stable organic forms. Climate change will also directly affect the capacity of vegetation to take up N inputs from deposition. Greater frequency of droughts and early-season frost (Inouye 2008) will lower the biotic uptake of N, increasing the potential for loss of soil base cations and acid-neutralising capacity.

Understanding the ecological thresholds associated with N deposition is key to preventing further detrimental impacts on alpine ecosystem composition and functioning. Additionally, knowledge of the reversibility of these impacts is important to setting management goals in relation to N emission rates. We believe there is a substantial system inertia that would limit reversibility of ecological changes even if rates of N deposition were substantially lowered. Factors influencing the recovery of ecosystems include the dominance exerted by nitrophilic species once they are established, biogeochemical feedbacks to the system associated with the establishment of these nitrophilic species that enhance rates of N cycling, and slow rates of geochemical change in soils that will limit their recovery from acidification.

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Appendix. Mass balance model for nitrate export in alpine lakes

Mass balance equations for the epilimnion (upper layer of the lake during thermal stratification) and hypolimnion (lower layer of the lake during stratification) are:

$$\begin{aligned} V_e dN/dt = {} & Q_{in}(t)N_{in} + Q_p(t)N_p \\ & - \big(Q_{in}(t) + Q_p(t)\big)N_e \\ & + E't(t)(N_h - N_e) \\ & - \lambda N 1.07^{(T-20)} r_{ca} chla V_e \end{aligned} \tag{1}$$

$$\begin{aligned} V_h dN_h/d_t = {} & E'(t)(N_e - N_h) \\ & - \lambda N 1.07^{(T-20)} r_{ca} chla V_h \end{aligned} \tag{2}$$

where V is volume, N is nitrate concentration, t is time, Q is volumetric flow rate, E'_t is thermocline mixing rate, T is the temperature of the layer in question, λ is the first-order nitrate decay rate and r_{ca} is the ratio of carbon to chlorophyll *a* (Chla) in the algae. The subscripts indicate epilimnion (e), hypolimnion (h), inflow stream (in) and precipitation (p). Conservative estimates of nitrate concentration were estimated by setting λ_N to zero. For reactive estimates of nitrate concentrations, λ_N was determined by calibration to fit the measured data.