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The Effects of Atmospheric Nitrogen Deposition in the Rocky Mountains of Colorado and Southern Wyoming—

a Synthesis and Critical Assessment of Published Results

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U.S. DEPARTMENT OF THE INTERIOR

GAIL A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY

Charles G. Groat, Director

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter (m^2)	10.76	square feet (ft^2)
square meter (m^2)	0.0002471	acre (ac)
hectare (ha)	107600	square feet (ft^2)
hectare (ha)	0.003861	square mile (mi^2)
hectare (ha)	2.471	acre (ac)
Mass		
gram (g)	0.03527	ounce (oz)
kilogram (kg)	35.27	ounce (oz)
kilogram (kg)	2.205	pound (lb)
kilogram (kg)	0.001102	ton, short (t)
ton, short (t)	907.2	kilogram (kg)
Load		
kilogram nitrogen per hectare per year (kgN/ha)/yr	0.8922	(lbN/ac)/yr
milligram nitrogen per square meter per day (mgN/m^2)/d	2.373×10^{-5}	pounds nitrogen per square foot per day (lbN/ft^2)/d
Volume		
liter (L)	0.264	gallon (gal)
liter (L)	0.0353	cubic foot (ft^3)
Temperature		
degrees Celsius (˚C)	(9/5 ˚C) + 32	degree Fahrenheit (˚F)
Concentration		
milligrams per liter NO_3^- (mg/L)	.06201	micromoles per liter (µmol/L)
milligrams per liter NO_3-N (mg/L)	.01401	micromoles per liter (µmol/L)
milligrams per liter NH_4^+ (mg/L)	.01804	micromoles per liter (µmol/L)
milligrams per liter NH_4-N (mg/L)	.01401	micromoles per liter (µmol/L)

Other abbreviations:

kg/ha	kilogram per hectare
(kg/ha)/yr	kilogram per hectare per year
$(mg/m^2)/d$	milligram per square meter per day
μeq/L	microequivalents per liter
μmol/L	micromoles per liter
$\delta^{15}N$	difference between the ratios of isotopes of nitrogen, $^{15}N/^{14}N$, in a sample and atmospheric nitrogen
$\delta^{18}O$	difference between the ratios of isotopes of oxygen, $^{18}O/^{16}O$, in a sample and a standard
pH	A measure of the acid and base properties of a solution that is a number on a scale in which a value of 7 represents neutrality, lower numbers indicate increasing acidity, and higher numbers an increasingly basic solution. Each unit of change represents a tenfold change in acid or base conditions and that is the negative logarithm of the effective hydrogen-ion concentration or hydrogen-ion activity in gram equivalents per liter of the solution (Merriam-Webster, 2002)
ANC	Acid-neutralizing capacity
CASTNET	Clean Air Status and Trends Network
DIN	Dissolved inorganic nitrogen
DON	Dissolved organic nitrogen
GLEES	Glacier Lakes Ecosystem Experiments Site
LTER	Long-Term Ecological Research Program
NADP	National Atmospheric Deposition Program
C	carbon
Ca^{2+}	calcium
$Ca(NO_3)_2$	calcium nitrate
CO_2	carbon dioxide
H^+	hydrogen
H_2SO_4	sulfuric acid
HNO_3	nitric acid
Mg^{2+}	magnesium
N	nitrogen
N_2O	nitrous oxide
NH_3	ammonia
NH_4^+	ammonium
NO_x	nitrogen oxides
NO_3^-	nitrate
P	phosphorus
S	sulfur

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EXECUTIVE SUMMARY

This report provides a synthesis and critical assessment of published results on the effects of atmospheric nitrogen (N) deposition in the Rocky Mountains of Colorado and southern Wyoming. The report includes levels and trends in wet and dry atmospheric deposition of nitrogen, stream and lake nitrogen chemistry, subsurface nitrogen-cycling processes, and effects on terrestrial vegetation, aquatic biota, and amphibians. Key findings are as follows:

Atmospheric N Deposition

- Total N deposition across the region varies from about 1 kilogram per hectare per year at an intermontane area in southern Colorado to 7 kilograms per hectare per year in the Front Range just west of Boulder.
- Nitrogen deposition has increased at only 5 of 15 sites at which atmospheric wet deposition has been monitored for at least 8 years. Thus, these data do not indicate a widespread regional increase in atmospheric wet deposition of N during the past 10 - 17 years.
- All three National Atmospheric Deposition Program (NADP) sites at high elevation (greater than 3000 meters) in the Front Range east of the Continental Divide show trends of increasing N deposition since the 1980s, and thus indicate an increase in wet deposition of N at high elevation in the Front Range.
- Trends of increasing wet deposition of N at Front Range NADP sites at Niwot Saddle and in the

Snowy Range are more than an order of magnitude lower than those previously reported in the literature because the statistical-analysis techniques used in the previous studies are inappropriate for data that are not normally distributed.

- Increases in ammonium concentrations generally have exceeded increases in nitrate concentrations at sites that have shown increasing trends of wet deposition of nitrogen. Therefore, increased attention to sources of atmospheric ammonium is warranted, whereas past research has focused more strongly on nitrate sources.
- No trends in dry deposition of N are evident over the past decade, but only two sites have sufficiently long record (minimum of 8 years) for adequate trend evaluation. Thus, existing dry-deposition measurement sites are of critical importance, and additional sites may be needed in other parts of the region.
- Part of the atmospheric N load originates east of the Front Range, probably from the Denver-Boulder-Fort Collins metropolitan areas and from agricultural areas on the plains. Emissions from eastern sources appear to have greatest effect in summer and least effect in winter. In general, the largest atmospheric N loads are east of the Continental Divide and the lowest are west of the Divide. An exception is the area surrounding the Yampa River Valley, which tends to have greater loads of atmospheric nitrogen than other areas west of the Divide, probably because it is downwind from two major power plants.

Surface Waters

- Surface water nitrate concentrations were greatest at two high elevation watersheds in the Front Range—Loch Vale and the Green Lakes Valley. Nitrate is the dominant N species in these waters, and can range from 30 to 60 micromoles per liter (μmol/L) during early spring snowmelt to 10 to 20 μmol/L during late summer. These watersheds retain only 25 to 50 percent of the N deposited in atmospheric wet deposition because they have a low density of vegetation biomass and a short growing season. These data indicate that high-elevation watersheds in the Front Range are at an advanced stage of nitrogen saturation (stage 1 to 2) comparable to that of watersheds in eastern North America that receive twice as much atmospheric N deposition.
- Watersheds west of the Continental Divide generally have lower surface-water and subsurface-water nitrate concentrations than those east of the Divide; these concentrations are consistent with the patterns in atmospheric N deposition.
- The relative amount of vegetation and soil (or inversely, the relative amount of exposed bedrock and talus) strongly affects the concentration of nitrate in surface waters and may explain much of the variation in nitrate concentrations among watersheds that receive roughly equal amounts of atmospheric N deposition.
- Surface-water nitrate concentrations are highest during the early snowmelt; however, nitrate concentrations are not closely correlated with decreases in surface-water acid-neutralizing capacity during snowmelt. Episodic acidification of these surface waters appears to result mainly from decreased base-cation concentrations through dilution by snowmelt.
- The trend of increasing minimum summer nitrate concentrations at the outlet of Green Lake 4 appears to be an isolated phenomenon and may reflect climatic effects on the flushing rate of the lake. No other monitored surface-water sites in the Front Range showed a similar trend, including other monitored lakes in the Green Lakes Valley. Additionally, the trend in annual minimum nitrate concentrations at Green Lake 4 is of insufficient magnitude to explain the decreasing trend in ANC that has been reported for the lake.

Subsurface N-Cycling Processes

- Results from isotope studies have shown that most of the nitrate in surface water at Loch Vale originates from microbial nitrification, most likely within soil and talus. Atmospheric nitrogen deposition is the source of this nitrogen to the watershed, but physical and biological factors that affect the rates of microbial processes have a more immediate effect on surface water nitrate concentrations.
- The rates of microbial processes such as immobilization, nitrogen mineralization, and nitrification result from complex interactions of soil moisture and soil temperature, and vary according to plant-community type. The duration and date of snowpack development have emerged as major controls on soil freezing and thus, the rates of these microbial processes. Late-developing and (or) thin snow cover are correlated with high nitrate concentrations in surface waters, although one study has disputed that this effect is expressed at the watershed scale.
- Talus contains an active microbial community and is commonly a large ground-water reservoir that provides an important source of surface runoff. Therefore, surface water nitrate concentrations may be controlled by mixing and cycling processes in talus at watersheds that contain abundant talus deposits.

Terrestrial Vegetation

- Growth of vegetation in the alpine tundra and in subalpine forest settings generally is limited by the supply of nitrogen, even at sites in the Front Range that receive the greatest loads of atmospheric N deposition.
- Alpine tundra vegetation at Niwot Ridge responded to an experimental addition of N equivalent to about 4 years of atmospheric N loading through a shift in species composition that favors a grass species with greater subsurface microbial production of nitrate, and consequent greater concentrations of nitrate in soil water.
- Alpine tundra vegetation has responded to recent experimental N additions through an increase in production and a decrease in species richness.

Aquatic Biota and Amphibians

- The effect of atmospheric N deposition on N limitation of phytoplankton growth in high-elevation lakes is unclear because of a limited number of studies that have presented conflicting evidence.
- Diatom populations in two lakes in Rocky Mountain National Park and in Green Lake 4 showed shifts in species composition near the mid-20th century that are consistent with the expected effects of increased N availability in the water column.
- The effects of atmospheric N deposition and episodic acidification of surface waters on amphibian populations are unclear because of limitations in existing studies. Any demonstrated effects on species such as the tiger salamander have been based on laboratory experiments or *in-situ* acidification of enclosures. Mortality within a natural population of tiger salamander in response to episodic acidification under natural conditions has never been demonstrated.

ABSTRACT

The Rocky Mountain region of Colorado and southern Wyoming receives as much as 7 kilograms per hectare per year ((kg/ha)/yr) of atmospheric nitrogen (N) deposition, an amount that may have caused changes in aquatic and terrestrial life in otherwise pristine ecosystems. The Rocky Mountain National Park, in its role of protecting air-quality related values under provisions of the Clean Air Act Amendments of 1977, has provided support for this synthesis and critical assessment of published literature on the effects of atmospheric N deposition. Results from published studies indicate a long-term increase in the rate of atmospheric N deposition during the 20th century, but no region-wide increase during the past 2 decades, although the rate of atmospheric N deposition has increased at three sites east of the Continental Divide in the Front Range region since the mid-1980s. Much of the increase in atmospheric N deposition at all three sites has resulted from an increase in the ammonium concentrations of wet deposition; this suggests an increase in contributions from agricultural areas or from vehicle traffic east of the Rocky Mountains. Lakes at two study sites in the Front Range (Loch Vale and Green Lakes Valley) had NO_3^- concentrations of 30 to 40 micromoles per liter (μmol/L) during early spring snowmelt and remained at 5 to 10 μmol/L during summer. Retention of N in atmospheric wet deposition in some sub-catchments of these lakes was less than 50 percent, which reflects an advanced stage of N saturation. Nitrate concentrations in surface waters west of the Continental Divide were lower—often less than 10 μmol/L during snowmelt and less than 2 μmol/L during summer—than surface waters east of the Divide, except in areas such as the Mt. Zirkel Wilderness that receive elevated amounts of atmospheric N deposition of 4 to 5 (kg/ha)/yr. Atmospheric N deposition in the Front Range east of the Divide may have altered the composition of alpine tundra-plant communities and lake diatoms, but additional studies would be needed to definitively demonstrate the hypothesized cause-and-effect relations. Rates of N-mineralization and nitrification in soils of the Front Range have increased in response to increased atmospheric N deposition. Projected future population growth and energy use in Colorado and the west increase the likelihood that the subtle effects of atmospheric N deposition now evident in the Front Range will become more pronounced and widespread in the future. The likelihood of future increased N emissions along the Front Range warrants a continuation of existing long-term precipitation and surface-water chemistry monitoring programs, and an expansion of the networks into areas that receive large amounts of atmospheric N deposition, but currently lack adequate monitoring. Long-term study and expanded sampling are needed to address uncertainties about the effects of atmospheric N deposition on terrestrial plant communities, nutrient limitation in lake plankton, shifts of dominant species within diatom communities, and on amphibian response to episodic surface-water acidification.

INTRODUCTION

Human activities modify and accelerate the global cycle of nitrogen (N). Fixation of N by humans for energy production, fertilizer production, and crop cultivation now exceeds the amount of biologically fixed N on the continents (Galloway and others, 1995). One aspect of human alteration of the N cycle is the release of NO_x gas from fossil fuel combustion and NH_3 gas from agricultural production to the atmosphere, where they may then be converted to nitrate (NO_3^-) and ammonium (NH_4^+), respectively, and deposited on the land surface as wet and dry deposition (Vitousek and others, 1997). Particulate forms of N originate from precursor emissions resulting from human activities, and are transported through the atmosphere to be deposited as dry deposition. The rate of atmospheric N deposition has increased greatly through human activities such as burning fossil fuels and fertilizer use, and high rates of atmospheric N deposition have been widely documented in Europe as well as in North America (Lovett, 1994; Fenn and others, 1998; Lawrence and others, 2000).

The Rocky Mountain region of Colorado and southern Wyoming receives 2 to 4 (kg/ha)/yr of atmospheric N in wet deposition (National Atmospheric Deposition Program [NADP], 2000), and rates as high as 5.5 (kg/ha)/yr have been reported for the Loch Vale watershed in Rocky Mountain National Park (fig. 1) (Campbell and others, 2000). These rates are lower than those reported for the midwestern, southeastern, and northeastern parts of the United States (NADP, 2000), however, symptoms of advanced stages of N saturation have been reported in alpine ecosystems of the Front Range of the Rocky Mountains (Baron and others, 1994; Williams and others, 1996a; Williams and Tonnessen, 2000). The thin and sparse soil, and the lack of forest vegetation at high elevations in alpine watersheds of the Colorado Rockies result in the export of a large proportion of the N in atmospheric deposition, and the apparent sensitivity of alpine ecosystems to atmospheric N deposition. Retention rates of atmospheric N deposition in subbasins of the Loch Vale watershed range from only 19 to 60 percent (Campbell and others, 2000). Wet deposition of NO_3^- increased from the mid-1980's to the mid-1990's at the Niwot Ridge NADP site (fig. 1), and a similar increase in stream NO_3^- concentrations during the growing season was reported for the outlet of Green Lake 4, near Niwot Ridge (fig. 1) (Williams and others, 1996a). The increased deposition of atmospheric N in the Front Range may adversely affect amphibian populations, and alter terrestrial plant community composition, foliar nitrogen:phosphorus in bristlecone pines, soil-bacteria and fungal communities, and phytoplankton dynamics (Mancinelli, 1986; Morris and Lewis, 1988; Harte and Hoffman, 1989; Bowman and Steltzer, 1998; Williams and others, 1996a).

An increased interest in the effects of atmospheric N deposition in the Colorado and Wyoming Rockies is evident from the large number of publications on the subject during the past decade (Baron, 1992; Baron and others, 1994; Baron and Campbell, 1997; Stottlemyer and others, 1997; Brooks and Williams, 1999, Brooks and others, 1999; Campbell and others, 2000; Meixner and others, 2000, and many others). The Colorado Rockies include the Rocky Mountain National Park and other wilderness areas and wildlife refuges that are protected by law from damage by air pollution under provisions of the Clean Air Act Amendments of 1977. Federal land managers are responsible for protecting air-quality related values (AQRVs) in these Class I wilderness areas. The wealth of published studies on atmospheric N deposition in the Colorado Rocky Mountains has highlighted the spatial and temporal variability of its effects (Clow and Sueker, 2000; Meixner and others, 2000; Sickman and others, 2002), and some studies have produced conflicting conclusions about the ecological effects (Harte and Hoffman, 1989; Corn and Vertucci, 1992). The U.S. Geological Survey, in cooperation with the Rocky Mountain National Park, undertook this synthesis and critical assessment of published studies on the ecological effects of atmospheric N deposition in the Rocky Mountain National Park, and the surrounding region. This report provides a basis for assessing the implications of past research for Park management policy, establishing priorities for future research and monitoring, and developing scientifically based resource-management strategies.

Nitrogen Saturation

The prevailing paradigm until the early 1980s was that vegetation growth in undisturbed terrestrial ecosystems, particularly forested ecosystems, was N limited. This concept was first challenged by researchers in western Europe, who showed

atmospheric N deposition to forests to be in excess of the biological demand, and proposed the variously defined concept of N saturation (Nihlgard, 1985; Skeffington and Wilson, 1988). The N saturation concept was later formalized by Aber and others (1989), who defined four progressive stages of forest-ecosystem response to increasing loads of atmospheric N deposition. They also hypothesized the manner in which the relative rates of biogeochemical processes such as N-mineralization, nitrification, and net primary productivity would be affected at each of these four stages. Stoddard (1994) later related these stages to patterns of NO_3^- concentrations observed in surface waters, but did not provide specific N deposition rates that mark the transition between these stages; subsequent research has shown that N retention within ecosystems is affected by a combination of land-use history, dominant tree species, and soil characteristics, among other factors (Aber and others, 1993; Aber and Driscoll, 1997; Fenn and others, 1998; Lovett and others, 2000). Despite a wide variation in the response of many ecosystems to a given rate of atmospheric N deposition, N-cycling research including N-addition experiments has largely confirmed the 1989 N-saturation model of Aber and colleagues (Aber and others, 1998; Gundersen and others, 1998).

Recent research has shown that the N saturation model, which was originally based largely on data from forested ecosystems, also describes the patterns of NO_3^- leaching observed in alpine ecosystems of the Colorado Rockies (Baron and others, 1994; Williams and others, 1996a; Fenn and others, 1998). If the generally accepted definition is applied that N saturation occurs when the availability of NO_3^- and NH_4^+ exceeds the total combined plant and microbial nutritional demand (Aber and others, 1989), then the evidence indicates that some alpine and subalpine watersheds in the Colorado Rocky Mountains are N saturated (Williams and others, 1996a; Campbell and others, 2000). In apparent contrast, alpine tundra and subalpine forests in the Front Range generally are N-limited ecosystems (Bowman and others, 1993; Campbell and others, 2000). Additionally, NO_3^- concentrations of surface waters in some parts of the Colorado Rockies are low, except early in the snowmelt period, before the onset of the growing season, when elevated NO_3^- concentrations are observed in surface waters (Stottlemyer and others, 1997; Baron and others, 2000). These varying results

provide an important reason for this synthesis and critical assessment of published studies.

As N saturation advances, a series of biogeochemical responses should accompany increased NO_3^- leaching into surface waters, including elevated rates of N-mineralization and nitrification, increased fluxes of nitrous oxide (N_2O) gas from soils, and increased foliar N concentrations (Aber and others, 1989; Aber and others, 1998). The N saturation model does not include the effects of NO_3^- leaching on the distribution and mortality of plankton, fish, amphibians, and vegetation, however, because species viability is dependent on a complex array of physical, chemical, and biological factors that are beyond the scope of such a general nutrient model. Results to date suggest, however, that the atmospheric deposition of N may result in observable changes in plant-community composition (Bowman and Steltzer, 1998; Baron and others, 2000); these results further confirm the need for this synthesis and critical assessment of published studies.

PURPOSE AND SCOPE

In 1999, the U.S. Geological Survey in cooperation with Rocky Mountain National Park began a 1-year study to provide a synthesis and critical assessment of the effects of atmospheric N deposition on ecosystems in the Rocky Mountain National Park and the surrounding Rocky Mountain region based on a comprehensive review of published literature on the topic. This report summarizes the findings of this synthesis and includes mainly literature published from 1980 to 2001, with a few select papers from the 1970s cited where appropriate. The topics addressed are as follows:

1. The rates of wet and dry deposition of NO_3^- and NH_4^+, their historical trends, and the relative effects of N deposition sources east and west of the study area.

2. The concentrations of N compounds (particularly NO_3^-) in stream and lake water, their historical trends, and the relations between atmospheric N deposition and N concentrations and loads in surface waters.

3. The effects of microbial N-cycling processes in soils on the leaching of N from soils to streams and lakes.

4. The effects of atmospheric N deposition on terrestrial vegetation, including alpine tundra and subalpine forest.

5. The effects of atmospheric N deposition on fish, amphibians, and phytoplankton.

For each of these topics, unresolved issues and conflicting evidence from published studies are examined in relation to gaps in current knowledge based on published studies, and the certainty of key conclusions is discussed.

GEOGRAPHIC SCOPE

The principal geographic focus of this synthesis and assessment is the Rocky Mountain National Park and surrounding mountainous region of the Colorado Rocky Mountains; the Glacier Lakes Ecosystem Experiments Site (GLEES) in adjacent southeastern Wyoming (fig. 1) is included because of its geographic proximity, and because several publications based on data collected at this site are available. Most studies of the effects of atmospheric N deposition in this region have been performed at three sites in addition to the GLEES site mentioned above: (1) the Loch Vale Watershed in Rocky Mountain National Park, (2) the Niwot Ridge site and surrounding area northwest of Boulder (funded by the National Science Foundation Long-Term Ecological Research Program [LTER]), and (3) the Fraser Experimental Forest, just west of the Continental Divide (fig. 1). All of these sites contain areas of subalpine forest and alpine tundra, and this report will focus mainly on studies from alpine sites, which are most sensitive to the effects of atmospheric N deposition.

METHODS

Relevant publications were reviewed and are cited in appropriate sections of the report. Original data on wet and dry deposition of N were retrieved and analyzed separately for the section on atmospheric deposition. Time trends in rates and concentrations of atmospheric wet and dry deposition of N were analyzed through the Seasonal Kendall nonparametric statistical test (Helsel and Hirsch, 1992). These atmospheric-deposition data were collected as part of the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNET).

SYNTHESIS RESULTS

The results of this synthesis and assessment are organized into five sections—atmospheric N deposition, stream and lake chemistry, subsurface N-cycling (microbial) processes, terrestrial vegetation, and aquatic biota and amphibians.

Atmospheric Nitrogen Deposition

This section reviews current rates of atmospheric deposition of NO_3^- and NH_4^+, the concentrations of these ions in precipitation, and time trends in concentrations and loads through an examination of data from 15 sites in the region that are part of NADP (fig. 1). The source areas of the N in atmospheric deposition (east or west of the Rockies) also are examined as reported in published studies.

Concentrations and Loads of Dissolved Inorganic Nitrogen (DIN) in Precipitation and Dry Deposition

Wet Deposition

Precipitation samples are collected weekly at 15 NADP sites in the Rocky Mountain region of Colorado and southern Wyoming (fig. 1) (data available at http://nadp.sws.uiuc.edu). The length of data collection at these sites varies from 8 to 21 years, and 10 sites have a data record of between 12 and 17 years. During 1998, the chemistry of bulk deposition in and around Rocky Mountain National Park was monitored at 15 additional sites (Ingersoll and others, 2000).

Loads. The mean annual load (1995-99) of inorganic N in wet deposition at the 15 NADP sites ranged from 0.7 (kg/ha)/yr at the Alamosa site to 6.8 (kg/ha)/yr at the Niwot Saddle site (table 1). The precipitation collector at Niwot Saddle catches blowing snow in excess of the amount deposited, however, necessitating a 32 percent downward correction in annual inorganic N loads for 1986-95 (Williams and others, 1998a). If the 1995-99 mean for this site is adjusted similarly, the resulting mean load of 4.6 (kg N/ha)/yr is still the highest in the region, and close to the values of 3.0 to 3.7 calculated for the Buffalo Pass, Loch Vale, Snowy Range, and Wolf Creek Pass sites (table 1). All NADP sites with mean annual wet deposition loads of less than 2.0 (kg N/ha)/ yr are below elevations of 3000 m or are west of the

Figure 1. Location of the Fraser Experimental Forest, Niwot Ridge, Loch Vale Watershed, and Glacier Lakes Ecosystem Experiments Site in Colorado and southern Wyoming.
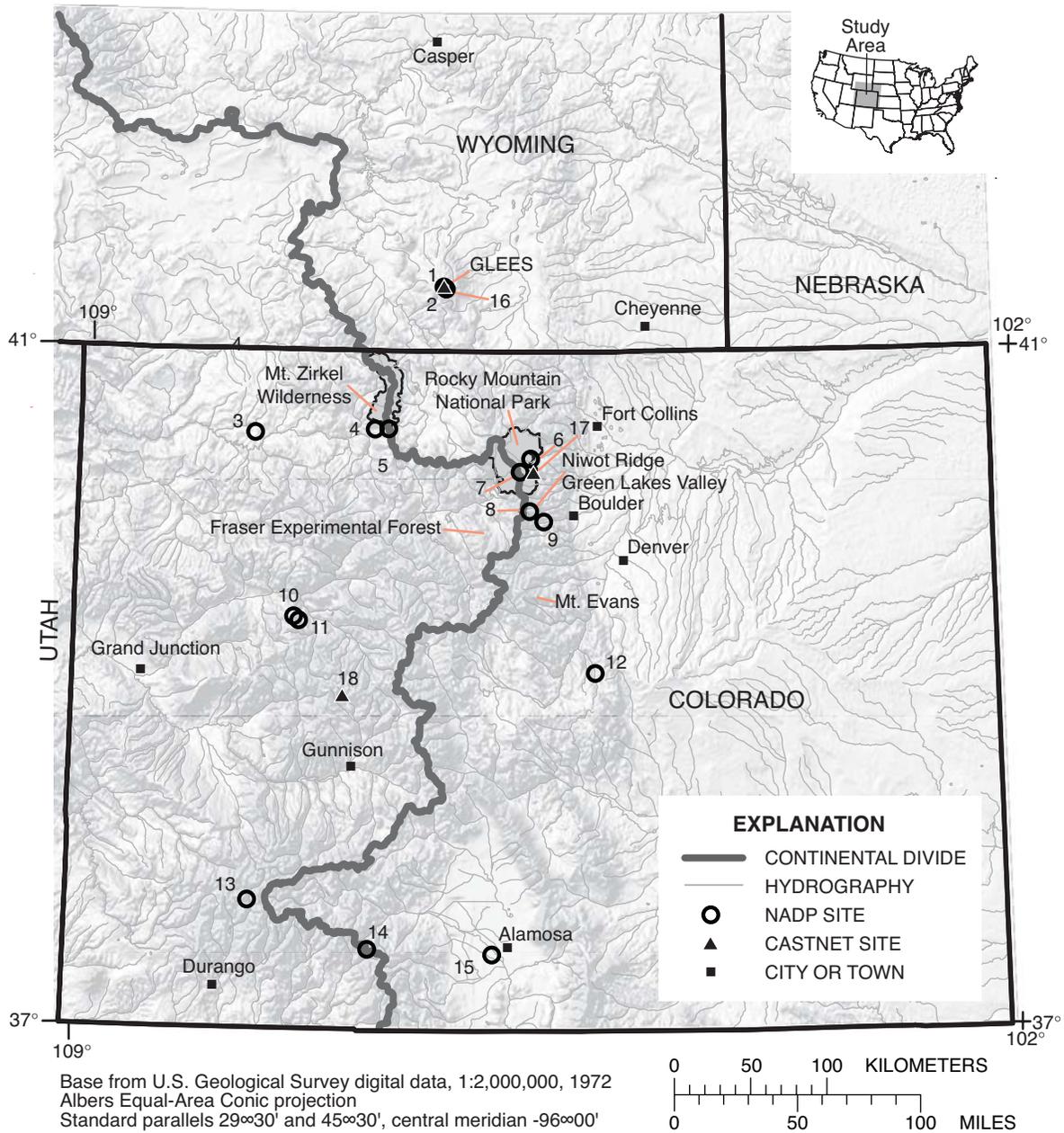
NADP SITES

1 Snowy Range	2 Brooklyn Lake	3 Sand Spring
4 Dry Lake	5 Buffalo Pass	6 Beaver Meadow
7 Loch Vale	8 Niwot Saddle	9 Sugarloaf
10 Sunlight Peak	11 Four Mile Park	12 Manitou
13 Molas Pass	14 Wolf Creek Pass	15 Alamosa

CASTNET SITES

16 Centennial	17 Rocky Mountain National Park	18 Gothic

Table 1. Mean annual wet deposition of N, precipitation amount, NO_3^- concentration, and NH_4^+ concentrations for 1995-99 at 15 NADP sites in the Rocky Mountains of Colorado and southern Wyoming. Standard deviation of the mean is in parentheses.

Site Name	Elev. (m)	N Deposition ((kg/ha)/yr)	Precipitation (cm)	NO_3^- (µmol/L)	NH_4^+ (µmol/L)
Alamosa	2298	0.7 (0.06)	16.8 (2.1)	13.7 (1.5)	16.9 (4.3)
Beaver Meadows	2490	2.0 (0.3)	47.4 (7.3)	16.9 (1.3)	14.0 (1.9)
Brooklyn Lake	3212	2.7 (0.3)	131.2 (10.7)	9.7 (1.1)	4.7 (0.5)
Buffalo Pass	3234	3.3 (0.5)	134.4 (22.4)	11.4 (1.4)	6.1 (1.0)
Dry Lake	2527	2.5 (0.4)	93.3 (14.2)	13.2 (1.5)	6.1 (1.2)
Four Mile Park	2502	1.5 (0.3)	61.5 (13.3)	11.1 (1.9)	6.3 (1.0)
Loch Vale	3159	3.0 (0.3)	120.7 (21.4)	11.7 (2.4)	6.7 (0.8)
Manitou	2362	2.1 (0.1)	45.4 (7.1)	21.1 (3.0)	12.5 (2.4)
Molas Pass	3249	1.8 (0.2)	85.5 (5.9)	10.9 (2.4)	4.2 (0.8)
Niwot Saddle	3520	4.6* (1.3)	157.8 (42.0)	14.0 (0.2)	7.0 (1.3)
Sand Spring	1998	1.2 (0.2)	36.3 (6.7)	15.3 (2.7)	7.8 (1.5)
Snowy Range	3286	3.7 (0.5)	134.4 (22.4)	12.2 (1.4)	6.8 (1.1)
Sugarloaf	2524	2.8 (0.5)	57.8 (8.3)	18.3 (2.4)	16.0 (3.5)
Sunlight Peak	3206	1.6 (0.2)	73.6 (8.7)	10.6 (1.7)	5.6 (0.8)
Wolf Creek Pass	3292	3.3 (0.5)	143.7 (10.0)	11.4 (1.0)	5.0 (1.0)

* - corrected by subtracting 32% of the measured total according to Williams et al., 1998a

Continental Divide. The mean annual inorganic N load in wet deposition at the 15 NADP sites is highly correlated with precipitation amount ($r^2 = 0.59$, $p = 0.003$, as indicated by least-squares linear regression), but is not correlated with the mean annual DIN concentration ($p = 0.77$); this indicates that DIN loads are controlled mainly by climatic and orographic factors that affect the precipitation amount.

Concentrations. Mean annual NO_3^- concentrations in precipitation ranged about two-fold, from 9.7 µmol/L at Brooklyn Lake to 21.1 µmol/L at Manitou (table 1), whereas mean annual NH_4^+ concentrations ranged more than those of NO_3^-; from 4.2 µmol/L at Molas Pass to 16.9 µmol/L at Alamosa. The four sites with the highest NH_4^+ concentrations were among the six easternmost sites, which are closest to agricultural sources on the plains and to transportation sources in the Denver-Boulder-Fort Collins urban corridor. The percentage of wet N deposition that consisted of NH_4^+ (on a molar basis) at these 15 sites, ranged from 28 percent at Molas Pass to 55 percent at Alamosa. The mean annual value for all 15 NADP sites was 37 percent.

Dry Deposition

Dry deposition generally is more difficult and expensive to measure than wet deposition and thus, is measured less commonly and at fewer locations. Three such sites—two in the Colorado Rockies and one in southern Wyoming are part of CASTNET (data available at http://www.epa.gov/castnet/data.html), a network of dry-deposition sites at which concentrations of gases and particulates are measured weekly and combined with meteorological data to calculate dry-deposition rates. Of the first two sites, one is at 2743 m elevation in Rocky Mountain National Park; the second is at 2926 m near Gunnison, Colo. (Gothic site), and the third is at 3178 m in the GLEES (Centennial site) in Wyoming. The mean annual N loads at these sites ranged from 0.5 (kg/ha)/yr at the Gothic site to 1.4 (kg/ha)/yr at the Rocky Mountain National Park site (table 2). Comparison of these values with those at nearby NADP wet-deposition sites indicates that dry deposition generally constitutes 25 to 30 percent of total atmospheric N deposition at these three sites. Zeller and others (2000) similarly found that dry deposition of N averaged 30 percent of total atmospheric N deposition at the GLEES during 1989-94.

Sievering and others (1989) used an incident throughfall approach to estimate a dry-deposition rate of 1 to 2 (mg N/m^2)/d during the 1987-88 growing season in a lodgepole pine canopy at 3100 m near Niwot Ridge. This range is equivalent to a load of 3.6 to 7.2 (kg N/ha)/yr if distributed over the entire year, but subsequent studies (Sievering and others, 1992; Sievering and others, 1996) found growing-season rates of dry deposition of N to be more than twice

Table 2. Mean annual dry deposition of N at three CASTNET sites in the Rocky Mountains of Colorado and southern Wyoming.

Site	Years	Mean Dry Deposition ((kg N/ha)/yr)	Std. Deviation
Gothic	1991-99	0.5	0.09
Rocky Mountain National Park	1995-98	1.4	0.11
Centennial	1992-99	1.1	0.09

those of the dormant season in this area. Sievering and others (1992) estimated a dry-deposition rate of 0.7 to 0.9 (kg N/ha)/yr at this site for 1979-84, based on previously reported ambient air concentrations of NO_x, HNO_3, particulateNO_3, NH_3, and particulateNH_4 (Fahey and others, 1986; Parrish and others, 1986; Roberts and others, 1988; Langford and Fehsenfeld, 1992). Later, Sievering and others (1996) reported a mean annual dry deposition rate of 2.8 (kg N/ha)/yr for 1993-94 at this site; this rate is the highest reported for the Colorado Rockies. The mean annual-adjusted (Williams and others, 1998a) wet-deposition rate for the same 2 years at the nearby Niwot Saddle NADP site was 3.2 (kg N/ha)/yr; therefore, Sievering and others (1996) mean annual dry-deposition estimate represented 47 percent of total N deposition, a value considerably greater than the percent of total N deposition that consists of dry deposition at the CASTNET sites. Part of the difference in dry-deposition loads between the 1992 and 1996 studies can be attributed to the difference in elevation between the two sites; the Niwot Ridge site at 3540 m is exposed to greater wind velocity, and therefore, greater rates of dry deposition than at the Niwot Saddle NADP site at 3100 m. Additionally, Sievering and others (1996) show that ambient concentrations of N-species in air at Niwot Ridge doubled from the mid-1980s to the mid-1990s; therefore, dry-deposition rates of N also may have increased from 1992 to 1996.

Arthur and Fahey (1993a) used throughfall measurements in a subalpine spruce-fir forest at the Loch Vale watershed to estimate that 56 percent of total atmospheric N deposition consisted of dry deposition during May through October 1986-87. Annual loads of N in dry deposition in this subalpine forest are likely to constitute less than 56 percent of total N deposition, however, considering the previously discussed finding from Niwot Ridge that dry deposition in the growing season is about twice that during the dormant season.

Together, the data from the NADP and CASTNET networks and from the published studies discussed previously indicate that the total rate of atmospheric DIN deposition to the Colorado Rocky Mountains ranges from about 1 (kg/ha)/yr in dry intermontane areas in southern Colorado (Alamosa) to about 7 (kg/ha)/yr in high elevation areas of the Front Range east of the Continental Divide (Niwot Ridge). Total DIN deposition averages about 4.4 (kg/ha)/yr at Loch Vale. Cloud and fog deposition in the Colorado Rocky Mountains have generally not been measured, but might enhance these reported rates of atmospheric N deposition. Sievering and others (1989), however, noted that dew-wetted alpine tundra occasionally is observed at Niwot Ridge, but in a later study recorded no cloud or fog deposition events at the Ridge during 1993-94 (Sievering and others, 1996). Thus, the estimates of total inorganic N deposition reported herein probably are only slightly low.

Organic N is not measured in wet deposition at the NADP sites, nor in dry deposition at the CASTNET sites, but the relative contribution of organic N to total N loads in atmospheric wet deposition at the Green Lakes Valley in the Front Range during 1996-98 was 16 percent (Williams and others, 2001). Data from the Sierra Nevada suggest that organic N loads in wet deposition from drier regions of the west, such as central and western Colorado, may represent as much as 25 percent of the total N load (Sickman and others, 2001). Thus, the estimated total atmospheric N loads are probably 15 to 25 percent higher than the inorganic N loads throughout the Rocky Mountain region of Colorado and southern Wyoming.

Trends in Concentration of DIN and Rates of Atmospheric Deposition

Wet Deposition

Time trends in wet deposition of N were identified through Seasonal Kendall analyses of volume-

Table 3. NADP sites in the Rocky Mountains of Colorado and southern Wyoming that have statistically significant trends (p < 0.05) of increasing NO_3^- or NH_4^+ concentrations, or increasing wet deposition of N as determined by Seasonal Kendall analysis.

[NS-not statistically significant at p = 0.05 level.]

| Site	Length of Record	NO_3^- Conc. (µmol/L)/yr		NH_4^+ Conc. (µmol/L)/yr		N Load (kg/ha)/yr	
		Trend	p	Trend	p	Trend	p
Buffalo Pass	16 yr, 9 mo	0.37	<0.001	0.28	<0.001	0.010	<0.001
Four Mile Park	13 yr, 0 mo	NS	NS	0.26	0.021	0.004	0.004
Loch Vale	17 yr, 4 mo	NS	NS	0.13	0.006	0.0044	0.018
Niwot Saddle	16 yr, 6 mo	0.32	0.025	0.32	0.002	0.013	0.001
Snowy Range	14 yr, 8 mo	NS	NS	NS	NS	0.0059	0.004

NS - not statistically significant at p = 0.05 level.

weighted mean monthly concentrations and loads in weekly samples as reported on the NADP Web site (http://nadp.sws.uiuc.edu) from the beginning of the record at each site through December 2000. Correlation of concentration or load with precipitation amount was accounted for in the analysis through linear regression; therefore, only the residuals of these relations were used to identify time trends. Most of the records from the 15 NADP sites extend back to the mid-1980s, but two—Brooklyn Lake and Wolf Creek Pass—began in 1992. An analysis of trends in mean annual N loads in wet deposition at these 15 sites indicates statistically significant (p < 0.05) trends of increasing N deposition at 5 of the sites—Buffalo Pass, Four Mile Park, Loch Vale, Niwot Saddle, and Snowy Range (table 3). All five of these sites have data since 1983-87, and four of the sites are at high elevation (> 3000 m); the fifth (Four Mile Park) is at 2502 m. The slopes of the regression relations for these five sties indicate an annual increase in wet deposition that ranges from about 0.004 (kg N/ha)/yr at Four Mile Park to 0.013 (kg N/ha)/yr at Niwot Saddle. Four of the five sites (except Snowy Range) also showed significant increasing trends in NH_4^+ concentrations, but only two of these sites—Buffalo Pass and Niwot Saddle—had significantly increasing NO_3^- concentrations. These two sites also were the only ones with increasing trends in precipitation amount (data not shown). This suggests that the increasing N loads in wet deposition at Buffalo Pass and Niwot Saddle result from increasing NO_3^- and NH_4^+ concentrations as well as increasing precipitation amount, whereas the increasing N loads in wet deposition at Four Mile Park and Loch Vale result primarily from increasing NH_4^+ concentrations. The trend of increasing N loads at the Snowy Range site is attributed to a combination of nearly-significant

increases in NO_3^- and NH_4^+ concentrations in wet deposition (p = 0.06 and 0.08, respectively).

A significant increasing trend in wet deposition of 0.32 (kg N/ha)/yr at the Niwot Saddle site previously was reported for 1984-96 (Williams and Tonnessen, 2000), and a similar trend of increasing wet deposition of 0.35 (kg/ha)/yr was reported at the Snowy Range site for 1986-90 (Williams and others, 1996a). About half of the 1984-93 increase at Niwot Saddle was attributed to an increase in the amount of precipitation, and about half to an increase in the volume-weighted concentration of NO_3^- (Williams and others, 1996a). The results reported here for Niwot Saddle and Snowy Range generally are consistent with those of Williams and others (1996a) and Williams and Tonnessen (2000), except that: (1) the trends reported here are more than an order of magnitude lower (fig. 2, table 3), and (2) the increasing NH_4^+ concentrations noted here contributed significantly to the increasing N loads. One likely reason for these differences in the slope of trends is that Williams and Tonnessen (2000) used linear regression analysis of annual N loads, whereas the present study used Seasonal Kendall analysis of monthly weighted mean values. The nonparametric analysis used here is preferred to linear regression because these chemical data fail the standard Wilk-Shapiro test (Shapiro and Wilk, 1965) for normality; therefore, linear regression is not considered a valid approach to identify monotonic time trends (Helsel and Hirsch, 1992). The trend of increasing N loads in wet deposition at Niwot Saddle identified by Seasonal Kendall analysis indicates that about 50 percent of the increase results from increasing precipitation, about 25 percent from increasing NO_3^- concentrations, and about 25 percent from increasing NH_4^+ concentrations.
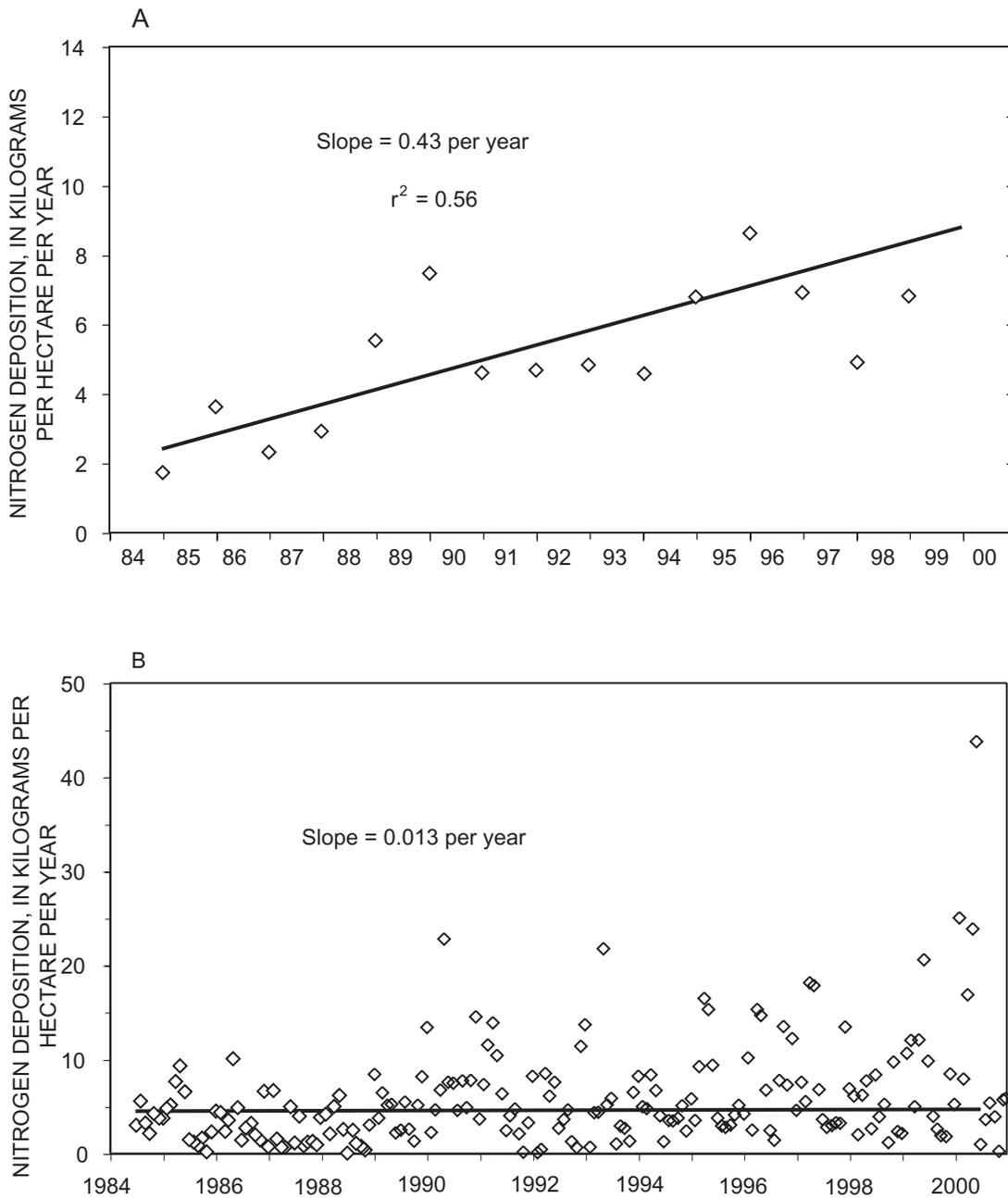
Figure 2. Trends in wet deposition of N at Niwot Saddle NADP site. A. Linear regression based on annual volume-weighted mean values. B. Seasonal Kendall trend line fit to monthly volume-weighted mean values.

The Niwot Ridge site showed an increase in annual precipitation amount and a decrease in mean annual air temperature from 1951-95 (Williams and others, 1996b). The results obtained here concur that precipitation amount at Niwot Saddle increased significantly from 1984 to 2000, but only one other NADP site in the region had an increasing trend, suggesting the lack of a region-wide increase in precipitation. The decrease in air temperature is counter to the general predicted effects of climatic warming driven by increasing concentrations of CO_2 in the atmosphere, and no consensus has been reached that colder and snowier conditions should be expected at high elevations in the Rockies in the future as a result of predicted climate change (Hauer and others, 1997).

Dry Deposition

The Gothic and Centennial CASTNET sites show no statistically significant trend in annual dry N deposition over their periods of record, which extend back to the early 1990s. The site at Rocky Mountain National Park was not analyzed for time trends because the record was shorter than the 8-year minimum considered necessary for Seasonal Kendall analysis (Helsel and Hirsch, 1992). The Niwot Ridge site shows a 30-fold increase in atmospheric concentrations of N species since pre-industrial times (Fahey and others, 1986; Sievering and others, 1992), and a more recent study has shown that the air concentration of N species at Niwot Ridge during the growing season more than doubled from the mid-1980s to the mid-1990s (Sievering and others, 1996).

Surprisingly, the monthly mean concentration and monthly flux of particulate NO_3^- and NH_4^+ in dry deposition have decreased significantly through the 1990s at the Gothic and Centennal CASTNET sites (the decreased NO_3^- flux at the Centennial site was of marginal statistical significance, p = 0.10). These data are inconsistent with the observations from Niwot Ridge, but the difference probably can be attributed to the different sampling location and collection periods at these sites.

In conclusion, the rate of wet deposition of N increased from the 1980s through 2000 at 5 of 15 NADP sites across the Colorado and southern Wyoming Rockies, but no change in N deposition is evident at the 10 other NADP sites in this region. Additionally, no significant trend in dry deposition of N since the early 1990s is supported by data from two CASTNET sites, although the paucity of data on dry deposition make a regional trend difficult to recognize.

Data from Niwot Ridge support an increasing trend of N species concentrations in air from the 1980s to the 1990s, but rates of dry deposition have not been estimated from these data. The Niwot Ridge site also had the greatest increase in wet deposition of N from the mid-1980s through 2000. All three high-elevation (> 3000m) NADP sites in the Front Range with data since the 1980s show significant increases in N loads in wet deposition. The two NADP sites (Beaver Meadows and Sugarloaf) at lower elevations (about 2500 m) in the Front Range, however, showed no significant trend in wet deposition of N during a similar time interval. Overall, these data do not indicate a widespread increase in atmospheric N deposition throughout the Colorado Rockies from the mid-1980s through the 1990s, but imply such an increase at high elevation in the Front Range. These data also suggest a need to re-calculate these trends periodically because two sites that did not show a significant trend in wet deposition of N show an increasing trend of borderline statistical significance (0.05 < p < 0.10); this indicates that a continuation of present patterns may result in significant increasing trends within the next 5 to 10 years.

Origin of N in Atmospheric Deposition – East or West?

The Colorado Rocky Mountains are in an area of predominantly west wind; this suggests that most sources of airborne N should originate from west of the Rocky Mountains (Hansen and others, 1978; Sievering and others, 1996). Investigators have reported, however, that significant amounts of atmospheric N deposition—especially in the Front Range—originate from the east (Langford and Fehsenfeld, 1992; Baron and Denning, 1993; Heuer and others, 2000). Additionally, Parrish and others (1990) inferred from N species concentrations and source patterns in air at Niwot Ridge that N from sources to the east can become mixed into higher level flow from the west, and later be deposited from these eastward flowing air masses.

The relative amount of atmospheric N deposition that originates from east of the Front Range in the Denver-Boulder-Fort Collins urban corridor varies with season. Precipitation samples collected at NADP sites west of the Continental Divide during 1992-97 had lower mean annual volume-weighted

concentrations of NO_3^- and NH_4^+ than samples collected east of the divide, and precipitation samples collected during the summer (May - September) of those years showed a similar pattern (Heuer and others, 2000). In contrast, snow samples collected west of the Continental Divide during winter-pack surveys had higher NO_3^- concentrations than samples from east of the Divide, but NH_4^+ concentrations showed no east-west difference. These results are consistent with a large summer N contribution to atmospheric deposition from the Denver-Boulder-Fort Collins urban corridor; this process is associated with differential heating of air at low elevations that then moves upvalley toward the mountains. These upslope events commonly are associated with convective thunderstorms (Toth and Johnson, 1985). Baron and Denning (1993) found that a significant amount of the NO_3^- and NH_4^+ measured in precipitation samples at the Beaver Meadows and Loch Vale NADP sites in the Rocky Mountain National Park originated east of the mountains. The lower elevation Beaver Meadows site received N deposition from the east throughout the year, whereas the higher elevation Loch Vale site received N deposition from the east only during summer.

One region, the Yampa River Valley, whose headwaters are in the Mt. Zirkel wilderness (fig. 1), does not follow the typical east-west deposition pattern observed in the Colorado Rockies. The concentrations of NO_3^- in winter snowpack samples from the Yampa River Valley are among the highest measured anywhere in the Colorado Rocky Mountain region (Turk and others, 1992). This observation is consistent with the moderately high mean annual wet-deposition loads (1995-99) of 2.5 (kg/ha)/yr at Dry Lake and 3.3 (kg/ha)/yr at Buffalo Pass in this valley (table 1). This region is downwind (east) of two large power plants in northwestern Colorado whose emissions exceed 5000 t/yr of NO_x (Dickson and others, 1994). The large annual N loads in wet deposition at Dry Lake and Buffalo Pass, which are unusual for mountainous areas west of the Continental Divide in Colorado, have been attributed to emissions from the power plant (Turk and Campbell, 1997).

Stream and Lake Chemistry

Concentrations and loads of NO_3^- and NH_4^+ (mainly NO_3^-) in surface waters have been measured on a routine basis at a few intensive-study sites in the Rocky Mountain study region, and at several other sites, primarily through surface water-chemistry surveys. Some of these measurements have been made during periods of episodic water chemistry changes that occur during snowmelt, and to a lesser extent, during rainstorms. Only a few sites have sufficient data for analyses of historic trends in surface-water NO_3^- concentrations, however. Much of the variation in NO_3^- concentrations and loads in surface waters in the study region have been attributed to variations in atmospheric N deposition, and load data from two lakes in the Front Range provide some of the strongest evidence that high-elevation ecosystems are at an advanced stage (1-2) of N saturation.

Concentrations of N Species in Surface Waters at Four Intensively Studied Sites

Dissolved inorganic N

DIN concentrations in surface waters of the Rocky Mountains of Colorado and southern Wyoming show wide spatial and temporal variability. Snowmelt dominates the annual hydrograph in high-elevation watersheds, and the highest NO_3^- and NH_4^+ concentrations in surface waters commonly occur early in the snowmelt (Campbell and others, 1995; Williams and Tonnessen, 2000). Most of the sites at which surface-water chemistry is frequently monitored are in alpine or mixed alpine-subalpine watersheds; thus, little information is available from exclusively subalpine watersheds.

Surface-water DIN concentrations have been measured routinely year-round at four locations during the 1980s and 90s and reported in the peer-reviewed literature; these are Loch Vale in Rocky Mountain National Park, Green Lakes Valley near the Niwot Ridge LTER site, Glacier Lakes at GLEES in southern Wyoming at the northernmost extent of the Front Range, and at three stream watersheds in the Fraser Experimental Forest (fig. 1). The first three of these sites are in the Front Range; only Fraser Forest is west of the Continental Divide; therefore, results based on data collected at these locations reflect this limited geographic representation.

DIN in surface waters of the Colorado Rockies consists mostly of NO_3^-, as reported in other mountainous regions of North America and Europe. The NH_4^+ concentrations in most surface waters are < 1 μmol/L (Ruess and others, 1995; Campbell and others, 2000; Williams and others, 2001).

Dissolved (or particulate) organic N

Few measurements of dissolved (or particulate) organic N (DON) concentrations in surface waters of the Colorado Rockies are available, but a recent study found that mean total N during 1996-98 at Green Lake 4, near Niwot Ridge, was about 15 percent DON, 7 percent particulate organic N (PON), 5 percent NH_4^+, and 73 percent NO_3^- (Williams and others, 2001). DON concentrations at Green Lake 4 never rose above 10 µmol/L, but those in a stream draining a nearby tundra landscape were higher than those measured in a stream draining mainly talus. Campbell and others (2000) and Williams and others (2001) both emphasize that more measurements of DON in surface waters of the Rockies are needed to improve understanding of the N cycle.

Nitrate at Loch Vale, Green Lakes Valley, Glacier Lakes, and Fraser Forest

Tributaries to Loch Vale generally have the highest reported surface-water NO_3^- concentrations in the Colorado Rocky Mountains. Two of these—Andrews Creek and Icy Brook, had mean volume-weighted NO_3^- concentrations of 18 to 25 µmol/L during 1992-97 (Campbell and others, 1995; Campbell and others, 2000), higher than the mean concentrations of about 16 µmol/L at the outlet of Loch Vale during the 1980s and early 1990s (table 4) (Baron, 1992; Baron and Campbell, 1997). These tributary NO_3^- concentrations typically increase to about 40 µmol/L during early snowmelt, then decrease from the time of peak snowmelt through late summer before rising again to about 20 µmol/L by late September (Campbell and

Table 4. Nitrate concentrations at intensive study sites in the Rocky Mountains of Colorado and southern Wyoming. All concentrations are reported in µmol/L.

Study Site/Watershed	Area (ha)	Elev. (m)	Reference	Year(s)	Mean	Max.	Min.
Loch Vale							
Icy Bk.	326	3159	Campbell *et al.*, 2000	1992-97	18-22	30-40	10-15
Andrews Ck.	183	3100	Campbell *et al.*, 2000	1992-97	22-25	40-50	10-15
Loch Vale	660	3120	Baron & Campbell, 1997	1982-93	16	20-25	10-12
Green Lakes Valley							
Arikaree	9	3785	Williams & Tonnessen, 2000	1994	15-20	50	5
Martinelli	8	3415	Caine, 1995	1985-94	15-20	35-45	5
Navajo	42	3700	Williams & Tonnessen, 2000	1994	20-25	50	15
Green Lake 4	220	3550	Williams & Tonnessen, 2000	1984-96	10-15	25-35	1-9
Lake Albion	700	3250	Caine, 1995	1985-94	8	20-25	0-5
GLEES							
East Glacier Lake	29	3282	Reuss *et al.*, 1995	1988-90	0.6		
West Glacier Lake	61	3276	Reuss *et al.*, 1995	1988-90	4.9		
Fraser Forest							
Fool Ck.	67	3180	Stottlemyer & Troendle, 1992	1987-88	2.0		
East St. Louis Ck.	803	2880	Stottlemyer & Troendle, 1992	1987	1.0		
Lexen Ck.	124	2985	Stottlemyer *et al.*, 1997	1990	2.5	5	0

others, 2000). Nitrate concentrations in these tributaries rarely fall below 10 µmol/L, even far downstream at the outlet of Loch Vale (Baron, 1992).

Nitrate concentrations at the outlet of Green Lake 4, near Niwot Ridge, generally range from about 20 µmol/L during winter baseflow to 30 µmol/L during early snowmelt, and then decrease to less than 5 µmol/L in late summer (table 4) (Williams and others, 1996a; Williams and Tonnessen, 2000; Williams and others, 2001). The drainage area above the Green Lake 4 outlet is 220 ha—about one-third the size of the drainage area above the Loch Vale outlet; thus, these two sites may not be comparable. The outlet of Lake Albion in the Green Lakes Valley drains an area of about 700 ha, however, which is comparable to that of the Loch Vale drainage. The NO_3^- concentrations at the Lake Albion outlet increase to only about 20 µmol/L during snowmelt and decline to near 0 by August (Caine, 1995). Water samples are routinely collected for measurement of inorganic N species at the 42 ha drainage area scale and at three watersheds of < 10 ha in the Green Lakes Valley. In general, NO_3^- concentrations increase upvalley at smaller drainage basins, except for some variation that reflects the geomorphology and vegetation drained at the smallest basin scale (Caine and Thurman, 1990; Williams and Tonnessen, 2000; Williams and others, 2001).

The outlets of East and West Glacier Lakes (GLEES) have been sampled for DIN species since the late 1980s. The mean NO_3^- concentration at the East Glacier Lake outlet (29 ha drainage area) was about 1 µmol/L during 1988-90, and about 5 µmol/L at the West Glacier Lake outlet (61 ha drainage area) during the same period (table 4) (Ruess and others, 1995). The NO_3^- concentrations here, as at Loch Vale and Green Lakes Valley, increase with decreasing drainage area and increasing elevation; mean NO_3^- concentrations at the two principal inlets to West Glacier Lake were about 10 µmol/L, and were about 60 µmol/L at the Cascade tributary stream during snowmelt in 1991-93 (Williams and others, 1996a).

Streams at the Fraser Experimental Forest have the lowest NO_3^- concentrations of any of the four intensive study locations. Mean NO_3^- concentrations at East St. Louis Creek (803 ha drainage area) in subalpine forest, were about 2 µmol/L during 1987-88, and those of Fool Creek (67 ha drainage area) in the alpine zone were only 1 µmol/L during 1987 (table 4) (Stottlemyer and Troendle, 1992). A small seasonal increase in NO_3^- concentrations from 6 µmol/L at

baseflow to 10 µmol/L during snowmelt was evident at an elevation of 3415 m in Lexen Creek (124 ha drainage area) during 1990, and increases with increasing elevation also were noted (Stottlemyer and others, 1997). Nitrate concentrations at the base of this watershed (2985 m) peaked at only 5 µmol/L during early snowmelt in April 1990, however, then decreased to below detection limits by the beginning of June (Stottlemyer and others, 1997).

Nitrate at Other Locations

Nitrate concentrations in surface waters at a few additional sites in the Colorado Rockies during a few short periods of data collection are available. Lewis and Grant (1979, 1980) measured DIN species at Como Creek, in a mostly sub-alpine 664-ha watershed just east of the Continental Divide near Niwot Ridge during 1975-78 and found a peak NO_3^- concentration of about 6 µmol/L during late winter of 1977, but peak values of only about 1 to 2 µmol/L during 1976 and 1978. They attributed the higher values of 1977 to soil freezing in the absence of thick snow cover. Nitrate concentrations during the summer and fall of 1975-78 were mainly between 0 and 1 µmol/L.

Heuer and others (1999) monitored NO_3^- concentrations during the 1996 snowmelt in Deer Creek and Snake River, two mainly alpine watersheds (about 1000 ha drainage area each) west of the Continental Divide near Dillon, Colo. Nitrate concentrations in Deer Creek reached a maximum of about 16 µmol/L during early spring and declined to about 3 µmol/L by late summer, and those at a site on this stream that drained alpine terrain were higher than those at a site that drained subalpine terrain. In contrast, NO_3^- concentrations in the Snake River ranged narrowly between 3 and 7 µmol/L over the same period, and concentrations at alpine sites were indistinguishable from those at subalpine sites.

Stednick (1989, 1995) measured NO_3^- concentrations at sites in an alpine watershed (99 ha drainage area) and a subalpine watershed (924 ha drainage area) on Hourglass Creek, a tributary of the Cache la Poudre River in north-central Colorado. Mean annual NO_3^- concentrations at the alpine site were 11 µmol/L, and those at the subalpine site were 5 to 6 µmol/L during 1984-85.

Table 5. Concentrations of NO_3^- from lake and stream surveys in the Colorado Rocky Mountains.

Reference	Sampling Months	n	Complete Survey	n	East of Divide	n	West of Divide
		Mean or median NO_3^- concentration µmol/L					
Gibson et al., 1983	Summer	127	8.5	90	9.8	37	5.4
Eilers et al., 1987[*]	Sept – Oct.	44	4.6	33	5.8	11	0.9
Turk and Spahr, 1991	Summer	50	0.2				
Newell, 1993	July – Sept.	10	1.0			10	1.0
Musselman et al., 1996	July – Oct.	267	6.4				
Baron et al., 2000	July – Sept.	44	8.5	30	10.5	14	6.6
Williams et al., 2000	July – Aug.	54	5.3	35	7.1	19	1.9
Clow et al., in press	Sept. – Oct.	22	4.3				

* Front range lakes above 3,000 m as described by Baron and others, 2000

Nitrate Concentrations in Lake Surveys

Seven surveys that included NO_3^- concentrations in alpine and subalpine lakes in the Colorado Rockies (table 5) have assessed regional N status with respect to atmospheric N deposition (Gibson and others, 1983; Eilers and others, 1987; Turk and Spahr, 1991; Newell, 1993; Musselman and others, 1996; Baron and others, 2000; Williams and Tonnessen, 2000). In all of these surveys, samples were collected during late summer and fall, when the remote high-elevation terrain is accessible, but NO_3^- concentrations tend to be at or near their annual minimum values. Therefore, NO_3^- concentrations reported from these surveys tend to be lower than the mean volume-weighted values reported for the four intensive study sites described previously for which samples were collected year round. A recent study by Inyan and others (1998) observed that NO_3^- concentrations in surface waters west of the Continental Divide were several-fold higher early in the spring than when they were near 0 in the late summer.

Nitrate concentrations reported from the seven lake surveys range from 0.2 to 8.5 µmol/L (table 5). Data from four of these surveys can be separated into lakes east and west of the Continental Divide. All four of the surveys whose data can be separated in this manner indicate that NO_3^- concentrations in lakes east of the Divide are about two to six times higher than in lakes west of the Divide (Gibson and others, 1983; Eilers and others, 1987; Baron and others, 2000; Williams and Tonnessen, 2000). All four of these studies included only lakes in the Front Range.

Causes of Variation in NO_3^- Concentrations

Seasonal Variation

Surface-water data collected at the four intensive study locations indicate a several-fold increase in NO_3^- concentrations from late summer to early spring snowmelt (Campbell and others, 2000; Williams and Tonnessen, 2000). This seasonal pattern is typical of that observed in upland surface waters of northeastern North America (Murdoch and Stoddard, 1992) and Europe (Peters and others, 1998). Nitrate concentrations in alpine ecosystems decrease in late spring as biological demand for N increases, then increase as the short growing season ends late in the summer. The highest NO_3^- concentrations typically occur from late April to mid-May, well before peak snowmelt runoff in mid-June to early July (Campbell and others, 2000; Williams and Tonnessen, 2000). The maximum NO_3^- concentrations in surface waters at sites with high rates of NO_3^- leaching, such as Loch Vale and Green Lakes Valley, exceed those measured in the snowpack, even if the potential addition of NO_3^- from NH_4^+ oxidation is included. Additions of $^{15}NH_4^+$ to snow at Niwot Ridge indicate, however, that little nitrification occurs in the snowpack prior to melt (Williams and others, 1996b).

Measurements of $\delta^{18}O\text{-}NO_3^-$ indicate that even during snowmelt, much of the NO_3^- in tributaries of Loch Vale originates from nitrification in soils (Kendall and others, 1995; Campbell and others, 2002). This is consistent with a build-up of NO_3^- in the soil and talus under the snowpack through

nitrification, followed by its flushing into surface waters during snowmelt (Brooks and others, 1996; Brooks and others, 1998). Annual variations in the thickness of alpine snow cover in the Colorado Rockies in part, controls seasonal and annual variations in NO_3^- concentrations in surface waters (Brooks and others, 1999), although the importance of this control has been disputed (Sickman and others, 2001).

Spatial Variation

Much of the spatial variation in NO_3^- concentrations among surface waters of the Colorado Rockies can be attributed to two factors. First, rates of atmospheric N deposition east of the Continental Divide tend to be greater than west of the Divide, as discussed previously. This factor alone may explain much of the east-west difference in surface-water NO_3^- concentrations observed among the four intensive study sites and the seven lake surveys. The second factor is land cover type. Recent studies have shown that local variations in land cover explain a significant amount of the variation in surface-water NO_3^- concentrations in high elevation watersheds of Colorado (Clow and Sueker, 2002; Sueker and others, 2001; Sickman and others, 2002). The land-cover types that explain the greatest amount of variation in NO_3^- leaching rates among watersheds is the proportion of the watershed that consists of: (1) vegetation and soil cover, and (2) bedrock and steep talus slopes; these land-cover types are inversely related (Clow and Sueker, 2000). Other land-cover types such as wetlands, which can promote N uptake, immobilization, and denitrification, appear to have only a minor affect on the N cycle in the Colorado Rockies (Baron and Campbell, 1997). Vegetation and soil cover promotes retention of N, and therefore, lower NO_3^- concentrations in surface waters, whereas bedrock and talus slopes allow the rapid movement of infiltrating precipitation to surface waters, have little vegetation to take up N, and are therefore, associated with higher NO_3^- concentrations in surface waters. Talus slopes often contain small patches of soil-like material that are sometimes covered by vegetation; however, these patches can have high rates of nitrification and high NO_3^- concentrations in waters draining through the talus (Bieber and others, 1998). Thus, detailed spatial modeling of talus areas within a watershed could result in improved spatial models of surface-water NO_3^- concentrations in alpine environments.

Relation of NO_3^- Concentrations to Acid-Neutralizing Capacity

Nitrate and Watershed Acidification

The loss of NO_3^- from upland watersheds that contain surface waters with low acid-neutralizing capacity (ANC) (< 100 µeq/L) is typically viewed as an acidifying process, because of the association of NO_3^- with H^+ in atmospheric deposition. The internal cycle of N within watersheds also produces H^+ to accompany NO_3^- in drainage waters—nitrification of 1 mole of NH_4^+ produces 2 moles of H^+ (Stoddard, 1994). Although some of the NO_3^- in surface waters is associated with base cations such as Ca^{2+} and Mg^{2+}, the increased leaching of NO_3^- generally results in an increase in H^+ concentrations and a decrease in the ANC of such waters. Decreased ANC (particularly to values < 0 µeq/L) is associated with changes in aquatic species and biodiversity (Schindler and others, 1989; Baker and others, 1993), and is therefore, of concern. Additionally, acidification of soil by atmospheric deposition presumably has resulted in increased mortality of red spruce and sugar maple at some sensitive stands in the northeastern United States (DeHayes and others, 1999; Horsley and others, 2000); this suggests that persistent acidification of soil eventually may affect growth and biodiversity in subalpine forests of the Colorado Front Range (Williams and Tonnessen, 2000). For these reasons, the relation between stream ANC and NO_3^- in surface waters of the Colorado Rockies is examined here.

Chronic surface water acidification, as indicated by persistent values of ANC < 0 µeq/L, has not been reported at high-elevation sites of the Colorado Rockies except where the waters have been affected by acidic mine drainage (Turk and Spahr, 1991; Newell, 1993), but many surface waters in the region have ANC values < 200 µeq/L, which indicates possible susceptibility to future chronic acidification (Kling and Grant, 1984). The pH and ANC of some of these surface waters may have already declined since the 1930s (Lewis, 1982). Indeed, Green Lake 4 shows a significant trend of decreasing ANC since the 1980s or earlier (Caine, 1995; Williams and Tonnessen, 2000).

The effect of NO_3^- on spatial and temporal patterns of ANC that have been measured in surface waters of the Colorado Rockies is not clear. Waters

with low ANC tend to have high NO_3^- concentrations, but quantitative modeling has not established the relative contributions of NO_3^-, SO_4^{2-}, organic acids, and aluminum to observed ANC patterns. For example, ANC at Green Lake 4 has declined by more than 30 μeq/L since 1984, but the annual minimum NO_3^- concentrations increased by only 3 to 4 μeq/L during that time (Williams and Tonnessen, 2000). This implies that increased concentrations of nitric acid are not the principal cause of the ANC trend. Similarly, two nearby streams in smaller watersheds that do not drain lakes in the Green Lakes Valley show significant downward trends in ANC values, but no trend in the annual minimum NO_3^- concentration (Caine, 1995). The trend at Green Lake 4 may be driven in part by year-to-year variation in the flushing time of the lake and its effect on biological uptake of NO_3^-, but no clear relation between trends in ANC and NO_3^- concentrations at the Green Lakes Valley has been demonstrated.

Nitrate and Episodic Decreases in ANC

Episodic decreases in surface water ANC typically are associated with snowmelt and have been widely observed in the Front Range (Denning and others, 1991; Campbell and others, 1995). The lowest recorded values during snowmelt were at two tributaries (9 and 42 ha drainage areas) in the Green Lakes Valley, which had ANC values < 0 μeq/L for a 3-week period during the 1994 snowmelt (Williams and Tonnessen, 2000). Similar to the long-term trends described above, however, episodic decreases in ANC that occur during snowmelt in surface waters of the Green Lakes Valley and the Loch Vale watershed are not strongly related to the pattern of NO_3^- concentrations, nor are they symmetrical opposites, as would be expected if NO_3^- were the primary cause of episodic acidification. Decreased ANC during snowmelt at Loch Vale appears more closely related to DOC and Al concentrations than to NO_3^- and SO_4^{2-} concentrations; this suggests much of the episodic acidification is due to natural organic acidity (Denning and others, 1991). Nitrate concentrations at Loch Vale increase and reach their annual maximum values in May, whereas ANC values do not reach their annual minimum until late June (Campbell and others, 1995). The data collected at these and other sites in the western United States suggest that instead of increasing NO_3^- concentrations, the primary cause of episodic ANC decline in Rocky Mountain surface

waters is the lowering of base-cation concentrations through dilution (Leydecker and others, 1999). Clearly, additional detailed quantitative analysis and modeling of the causes of episodic acidification in acid-sensitive Rocky Mountain watersheds is warranted.

Trends in NO_3^- Concentrations

The only sites from which surface-water chemistry data are sufficient for evaluation of trends in NO_3^- concentrations are the Loch Vale and Green Lakes Valley sites. Surface waters at the Loch Vale watershed show no significant trends in NO_3^- concentrations, but Green Lake 4 site shows a trend of increasing annual minimum NO_3^- concentrations from 1984-93 (Williams and others 1996a) and from 1985 to 1997 (Williams and Tonnessen, 2000) as discussed above. The entire NO_3^- record at this lake shows no significant trend, however, and the annual minimum NO_3^- concentrations at two small-watersheds without lakes, and at the lake that drains the entire 700-ha Green Lakes Valley, show no trend (Caine, 1995). The trend at Green Lake 4 is not consistent across the Green Lakes Valley; this suggests that some factor other than increasing N deposition (as recorded at the nearby Niwot Saddle) may be causing the upward trend in the annual minimum NO_3^- concentration at the Green Lake 4 outlet.

N Budgets and N Saturation

As indicated previously, the elevated NO_3^- concentrations in streams and lakes of the Colorado Rockies are probably a direct result of atmospheric N deposition, particularly in the Front Range. These elevated NO_3^- concentrations, which average as high as 15 to 25 μmol/L in the Loch Vale and Green Lakes Valley watersheds (Campbell and others, 2000; Williams and Tonnessen, 2000), however, are relatively low compared to values of 50 to 200 μmol/L in watersheds of eastern North America and Europe that have been affected by atmospheric N deposition (Hauhs, 1989; Peterjohn and others, 1996). The relatively low NO_3^- concentrations in surface waters of the Front Range warrant evaluation of these ecosystems in terms of the N saturation model discussed previously. The proportion of atmospheric N deposition retained by the ecosystem may provide a more representative N status measurement than NO_3^- concentrations in surface waters, because retention

accounts for the low biological activity and high runoff at high-elevation Rockies watersheds.

Accurate measurement of atmospheric inputs to mountainous watersheds in the Colorado Rockies is difficult and commonly requires estimation techniques because of inputs of blowing snow from outside the watershed (Baron, 1992; Williams and others, 1998a), but reasonably accurate N budgets have been calculated for the four intensive study locations described previously (Stottlemyer and Troendle, 1992; Reuss and others, 1995; Baron and Campbell, 1997; Campbell and others, 2000; Williams and others, 2001). These N budgets indicate that retention of inorganic N from atmospheric wet deposition ranges from 25 to 50 percent in the Loch Vale and Green Lakes Valley watersheds to 68 to 95 percent in the GLEES and Fraser Forest watersheds (table 6). If N in dry deposition were included, the percent retention would be even greater. For example, the estimated N retention at Loch Vale was 57 percent when dry deposition was included as opposed to only 25 percent when only wet deposition was used (Baron and Campbell, 1997). The spatial retention patterns among these sites are broadly consistent with the patterns observed in NO_3^- concentrations in their surface waters.

Watersheds in eastern North America that receive 50 to 100 percent more N in wet deposition than Loch Vale and the Green Lakes Valley have retention values of 50 to 80 percent (Driscoll and others, 1989)—a range comparable to that of Green Lake 4, and less than that of Loch Vale. The percent retention of DIN in wet deposition at Loch Vale is comparable to values observed at Fernow Watershed 4 in West Virginia, a site considered to be at an advanced stage (2) of N saturation (Peterjohn and others, 1996; Fenn and others, 1998). These comparisons indicate that alpine watersheds in the Front Range of Colorado that receive only 3 to 4 (kg N/ha)/yr in wet deposition are at a stage of N saturation comparable to that of watersheds in eastern North America that receive 6 to 8 (kg N/ha)/yr in wet deposition (stage 1 to 2; Aber and others, 1989; Stoddard, 1994). This similarity is attributed to the low biomass and short growing season in alpine watersheds of the Front Range.

Subsurface N-Cycling Processes

Recent studies of the $\delta^{15}N$ and $\delta^{18}O$ composition of surface water NO_3^- at the Loch Vale watershed indicate that, even in an alpine watershed with relatively low biomass, most of the NO_3^- in surface water originates from nitrification in the soil and talus (Kendall and others, 1995; Campbell and others, 2002). Atmospheric deposition is the source of the N in soil and talus, but microbial processes in the soil, the interaction of soil microorganisms with vegetation, and the flushing of soils by rain and snowmelt are the dominant short-term controls on NO_3^- and NH_4^+ concentrations in surface waters.

Table 6. Percent input of N in wet atmospheric deposition that was retained in watersheds in the Rocky Mountains of Colorado and southern Wyoming.

Site	Reference	Years	Retention of DIN Input (%)
Green Lakes Valley			
Green Lake 4	Williams et al., 2001	1996-98	49*
Loch Vale			
Andrews Creek	Campbell et al., 2000	1992-97	29
Icy Brook	Campbell et al., 2000	1992-97	46
Loch Vale	Baron and Campbell, 1997	1984-93	25
Fraser Forest			
East St. Louis Creek	Stottlemyer and Troendle, 1992	1987-88	95
Fool Creek	Stottlemyer and Troendle, 1992	1987	96
GLEES			
East Glacier Lake	Reuss et al., 1995	1988-90	96*
West Glacier Lake	Reuss et al., 1995	1988-90	68*

* - includes snow inputs from pits or lysimeters

N-Mineralization, Nitrification, and Immobilization

Several major advances toward understanding of microbial cycling of N in alpine environments of the Colorado Rocky Mountains have been made in the past decade. Most of this research has been done in an alpine-tundra environment at the Niwot Ridge LTER site (see review in Fisk and others, 2001).

Tundra

Nitrogen storage in tundra at Niwot Ridge ranges from 7000 to 8000 kg/ha, and 85 to 95 percent of this N is stored in soil organic matter (Fisk and others, 1998). Microbial biomass accounts for < 1 percent of N storage in the tundra ecosystem but accounts for a majority of the actively cycled N. As much as 5 percent of the microbial N turns over daily (Fisk and others, 1998), and large temporal variation in the amount of N in this pool has been noted (Fisk and Schmidt, 1995; Brooks and others, 1998; Jaeger and others, 1999). The seasonal dynamics of the microbial N pool in the tundra during the fall and winter appear to be controlled by prolonged periods with temperatures > 0ºC and carbon availability (Lipson and others, 2000). Microbial N pools and associated microbial N-cycling processes also are spatially heterogeneous within the alpine tundra and seem to be controlled by complex relations among soil moisture, plant community type, soil temperature, and snow cover thickness (Brooks and others, 1995; Fisk and Schmidt, 1995; Fisk and others, 1998). Results of a fertilization experiment indicate that microbial biomass may provide an important short-term sink for N should rates of atmospheric N deposition at Niwot Ridge continue to increase (Fisk and Schmidt, 1996).

Microbial N-Cycling Processes beneath Snow Cover. Nitrogen cycling processes under snow cover provide a key to understanding seasonal and annual dynamics of NO_3^- concentrations and export in soil water and surface water (Williams and others, 1998b; Brooks and Williams, 1999; Brooks and others, 1999). Soil in areas that develop consistent snow cover early in the season remain thawed throughout the winter; thus, they have high rates of microbial immobilization of N and do not release much NO_3^- during snowmelt. In contrast, soil in areas with inconsistent snow cover become frozen, and thus have low rates of microbial N immobilization and release large amounts of NO_3^- during snowmelt (Brooks and others, 1998). Rates of N-mineralization as high as 75 (kg/ha)/yr have been measured in alpine tundra, and

changes in microbial biomass N under snow cover can exceed those of the snow-free season (Brooks and others, 1995; Brooks and others, 1996; Lipson and others, 1999). Export of NO_3^- at a stream site near Niwot Ridge and at Loch Vale generally was greater in years of thin snow cover than in years with thick snow cover; this is consistent with recent findings of subnivian N-cycling dynamics (Lewis and Grant, 1980; Brooks and others, 1999). In contrast, a recent study at Loch Vale that included a greater number of years than were considered by Brooks and others (1999), found no relation between NO_3^- export and annual precipitation (assumed to be a proxy for snow-cover duration) (Sickman and others, 2001). This more recent study found that export of NO_3^- increased as snow-cover duration increased at Emerald Lake watershed (in the Sierra Nevada), and the authors hypothesized that duration of the vegetation growing season may be the principal control on NO_3^- export (Sickman and others, 2001). The effect of snow cover on NO_3^- export in the Sierra Nevada may differ from that in the Colorado Front Range, however, because in the Sierra Nevada, the soils generally do not freeze in the absence of snow cover.

Microbial N-Cycling Processes beneath Talus. One concern in relating results based on data collected in mountainous alpine tundra to concentrations and loads of N species in downstream surface waters is that the tundra commonly occurs on flat ridgetop areas that may be hydrologically isolated from the surface-water flow system in the surrounding alpine watershed (Clow and Sueker, 2000). The steep, rocky talus slopes that often extend from below these flat alpine ridgetops down to the valley floor have been less frequently studied because they were formerly assumed to be inert piles of rocks and sand with little capability to actively cycle N. These talus slopes are well connected to the streamflow system, however, and recent studies have revealed that they can contain areas of sand, clay, and organic material, some of which support patches of tundra-like vegetation, and have a dynamic N cycle (Williams and others, 1997; Bieber and others, 1998). Inorganic N pools and rates of N-mineralization and nitrification in soil below these vegetation patches are comparable to those measured in alpine tundra, although the microbial biomass N and total N pools are about an order of magnitude lower than in the tundra (Williams and others, 1997; Bieber and others, 1998). Even barren patches of talus soil without much vegetation contain

wind-deposited organic matter and measurable microbial biomass (Ley and others, 2001). The direct hydrologic connection between talus slopes and surface waters probably makes these areas a major source of NO_3^- found in surface waters, especially during the growing season. Areas classified as bedrock (including talus slopes) are the dominant source of NO_3^- to surface waters in the Loch Vale watershed (Baron and Campbell, 1997). Given the potential importance of talus, additional studies of N cycling in talus and N contributions from talus to surface water NO_3^- are warranted.

Subalpine Forest

Nitrification and N-mineralization rates also have been measured in several studies of subalpine forests in the Rocky Mountains of Colorado and southeastern Wyoming. Rueth and Baron (2002) measured net N-mineralization and nitrification rates in laboratory incubations of organic-horizon soil from Englemann spruce stands. The mean net N-mineralization rate for sites east of the Front Range (4300 (kg/ha)/yr) was significantly greater than the mean for sites west of the Front Range (860 (kg/ha)/yr), but the mean net nitrification rate for sites east of the Front Range (710 (kg/ha)/yr) was not significantly greater than the mean for sites west of the Front Range (75 (kg/ha)/yr). Stump and Binkley (1993) reported net N-mineralization rates from *in-situ* incubations of organic-horizon soil from several subalpine sites west of the Front Range to range from -5 to 52 (kg/ha)/yr. These values varied with the type of forest cover, and decreased in the order aspen > spruce-fir > lodgepole pine. The N-mineralization rates for lodgepole pine stands were similar to those reported for this species in southeastern Wyoming (Fahey and others, 1985; Binkley and others, 1990), whereas the values for spruce-fir stands were notably lower than the mean value of 27 (kg/ha)/yr reported for spruce-fir stands in Rocky Mountain National Park (Arthur and Fahey, 1992). The data reported thus far from subalpine forests are broadly consistent with the hypothesis that N-mineralization rates east of the Front Range are higher than those west of the Front Range because the eastern area receives higher rates of atmospheric N deposition.

DIN Concentrations in Soil Water and Ground Water

Data on DIN species in subsurface waters are needed to identify the hydrologic sources of surface water and the biogeochemical processes that may transform N during its movement through watersheds. Concentrations of NO_3^- and NH_4^+ in water from zero-tension lysimeters, tension lysimeters, and wells and springs have been measured at various sites in the Colorado Rocky Mountain region (Arthur and Fahey, 1993b; Stottlemyer and others, 1997; Williams and others, 1997; Campbell and others, 2000).

Soil Water

Generally, the spatial pattern of NO_3^- concentrations in soil water is similar to that observed in surface waters—the highest concentrations are in watersheds east of the Continental Divide (Arthur and Fahey, 1993b; Campbell and others, 2000), and the lowest concentrations are in watersheds west of the divide (Stottlemyer and others, 1997; Heuer and others, 1999)—except that the east-west differences in soil waters generally have been less than those in surface waters.

Collection of soil water—even with tension lysimeters—generally is limited to late April through July in high-elevation watersheds because little snow melts before late April and soils become too dry to provide samples by August. The highest NO_3^- concentrations in soil water (10 to 20 µmol/L) typically occur during early snowmelt and undergo gradual dilution through the summer; a similar seasonal pattern has been observed in ground water (Arthur and Fahey, 1993b; Peters and Leavesley, 1995; Stottlemyer and others, 1997). The high NO_3^- concentrations in soil water during the early snowmelt period have been hypothesized to originate from the flushing of 8 to 9 months accumulation of the products of N-mineralization and nitrification (Fahey and Yavitt, 1988; Arthur and Fahey, 1993b).

Nitrate concentrations in soil water from subalpine forest at Loch Vale generally are lower than those of stream water, except at the start of snowmelt; this suggests that soil water is not the dominant source of stream runoff in this watershed (Arthur and Fahey, 1993b; Campbell and others, 2000). Soil water from the forest floor and rooting zone of subalpine forest at Loch Vale had relatively high NH_4^+ concentrations (10 to 20 µmol/L) (Arthur and Fahey, 1993b), whereas stream water at this site contains little NH_4^+. The lack

of NH_4^+ in stream water could be interpreted as additional evidence that soil water is not a major source of stream water or, alternatively, that NH_4^+ is adsorbed or nitrified along soil-water flow paths before reaching the stream.

Nitrate concentrations in alpine soil water have been studied less than those of subalpine soil water, but the data suggest that NO_3^- concentrations in alpine soil waters tend to be greater (Stottlemyer and others, 1997; Bowman and Steltzer, 1998; Campbell and others, 2000). This difference could result from a lower density of above-ground biomass and a shorter growing season in alpine than in subalpine ecosystems, but the data are insufficient to confirm the cause of these differences. Bowman and Steltzer (1998) found that soil water from lysimeters installed beneath *Dechampsia* (an alpine graminoid or grass plant) had higher NO_3^- concentrations than soil water from beneath *Acomastylis* (a forb or low broad-leaved plant), and attributed the difference to higher nitrification rates in soils under *Dechampsia*. The alpine zone at Loch Vale and, probably, at other high-elevation watersheds of the Colorado Rockies, is not hydrologically well connected to the ground-water flow system that provides streamflow (Clow and Sueker, 2000); therefore, alpine soil water with elevated NO_3^- concentrations may not reach local sources of stream water.

Ground Water

Nitrate concentrations in ground water that drains talus fields and slopes at Loch Vale and Green Lakes Valley can range from 5 to 88 µmol/L (Williams and others, 1997; Campbell and others, 2000). In general, NO_3^- concentrations in talus ground water are higher than those of subalpine and alpine soil water, and talus ground waters have been hypothesized to be a major source of NO_3^- found in surface waters during snowmelt. Similar to the NO_3^- that is flushed from the soil during early snowmelt, much of the NO_3^- found in talus water has been hypothesized to originate from the flushing of N-mineralization and nitrification by-products and not directly from melting snow (Williams and others, 1997).

Chemical and isotope analyses of soil water and ground water have been used to develop quantitative multi-component mass-balance models of streamflow during snowmelt at watersheds in eastern North America (Wels and others, 1991; Burns and McDonnell, 1998), but few such models have been developed for watersheds of the Colorado Rockies, partly because many of these watersheds are inaccessible for sampling during early snowmelt. The sources and sinks of nitrogen during snowmelt in the Rockies warrant further study including the development of multi-component runoff models that incorporate solute and isotope data from the various source waters.

Terrestrial Vegetation

Changes in plant-community composition, individual species growth rates, and species diversity result from changes in many interdependent factors that include climate, nutrient availability, competition, disease, and degree of disturbance. The effect of atmospheric N deposition in plant-community changes is difficult to define and isolate from these factors, but one approach is to study historical changes by establishing vegetation plots, then periodically documenting changes within the plots as rates of atmospheric N deposition change. Another common approach is to make measurements of the plant community over a spatial gradient of atmospheric N deposition, then use time-for-space substitution to draw inferences. A third approach is to simulate additions of N to represent past or future projected increases in atmospheric N deposition. All of these approaches have been used in studies of the subalpine and alpine terrestrial-plant community in the Colorado Rockies. Some of these studies have examined the alpine tundra-plant community at Niwot Ridge, and much has been learned about the effects of atmospheric N deposition on this community.

Acomastylis vosii, a common flowering plant found in alpine tundra (Photograph courtesy of William Bowman.)

Alpine Tundra

The alpine tundra of Colorado has lower rates of primary production than ecosystems at lower elevations in the region because of its short growing season, low temperatures, and seasonal extremes of moisture (Bowman and Fisk, 2001). Another result of the harsh climate is that only 1 to 2 percent of N storage is in living plant biomass, most living biomass is stored in roots, and the majority of N use for production is by the roots (Fisk and others, 1998).

Investigators at Niwot Ridge have categorized tundra plant communities as dry meadow, moist meadow, or wet meadow; results indicate large differences in the rates of N-cycling processes among these communities (Bowman and others, 1993; Bowman, 1994; Fisk and others, 1998). The moisture regimes in these tundra communities are driven by a combination of landscape position, aspect, and wind-driven snow accumulation that results in a seasonal snowpack that lingers longest in the wet meadows and shortest in the dry meadows (Bowman, 1992). Thus, the wet meadow snowpack provides more nitrogen and moisture to the underlying soils than the shorter lived dry meadow snowpack, which results in higher rates of N-mineralization and higher concentrations of NO_3^- and NH_4^+ in wet meadow soil (Bowman and others, 1993; Fisk and others, 1998).

Experiments entailing the addition of N and P at the rate of 25 (kg/ha)/yr to 4-m^2 plots in wet and dry alpine meadow at Niwot Ridge indicated that the dry-meadow vegetation was N-limited and responded by a shift in community structure, whereas the wet meadow vegetation was N- and P-limited and responded by a shift from nutrient limitation to light limitation (Bowman and others, 1993; Bowman, 1994). Because tundra plants only have a limited capacity to increase growth or N content as soil N increases, much of the observed increase in plant N uptake during the experimental N additions occurred through changes in species composition (Bowman and others, 1995; Theodose and Bowman, 1997). Results of the N-addition experiments support a hypothesized shift in wet-meadow community dominance from *Acomastylis* to *Deschampsia* in response to increasing atmospheric N deposition (Bowman and others, 1995), which may lead to increased leaching of NO_3^- from soils because *Deschampsia* has several-fold greater rates of N-mineralization and nitrification than *Acomastylis* (Bowman and Steltzer, 1998; Steltzer and Bowman, 1998). This hypothesis is further supported by soil-water samples from a wet meadow in which *Deschampsia*-dominated locations had higher NO_3^- concentrations than *Acomastylis*-dominated locations (Bowman and Steltzer, 1998).

Other recent plot scale experiments at Niwot Ridge have shown an increase in production and a decrease in species richness in response to N additions across a variety of alpine tundra plant communities (Gough and others, 2000; Seastedt and Vaccaro, 2001). Seastedt and Vaccaro (2001) attributed a decrease in plant species richness to an increase in soil acidity in response to increased nitrification rates in plots to which N was added. They also found that addition of P to tundra plots increased foliar production, and indicate, as Williams and others (1996a) have noted previously, that one probable result of long-term increases in atmospheric N deposition is a shift in terrestrial-plant productivity from N-limitation to P-limitation.

Future changes in alpine vegetation if atmospheric N deposition increases in the Colorado Rockies defy simple predictions because future climate change may induce unforeseen complications. For example, snowfall increased at Niwot Ridge from 1951 to 1994 (Williams and others, 1996c), and a snow-fence experiment to simulate a possible increased snowpack in the future resulted in the loss of *Cobras myosuroides* (a sedge) and replacement by *Acomastylis rossii* and *Deschampsia caespitosa* at dry and moist meadow sites (Bowman, 2000; Seastedt and Vaccaro, 2001). In general, species richness declined at sites that were manipulated to receive increased snow cover (Seastedt and Vaccaro, 2001), a finding consistent with that found for natural snow gradients in the Rocky Mountains of Colorado (Stanton and others, 1994). The change in snowpack thickness and duration, whether induced by the snow fence or by future changes in snowfall amount, is likely to mask any changes that may result from atmospheric N deposition alone.

Interpretation of nutrient-addition results where the N additions represent from 3 to 35 years of average atmospheric N deposition (Bowman and others, 1993; Seastedt and Vaccaro, 2001) requires caution because plant-community responses to a gradual, long-term increase in atmospheric N deposition may differ from responses projected from short-term experimental data. At least one study examined natural long-term (1953-96) changes in alpine plant communities at the plot scale and showed that graminoids increased

relative to forbs (Korb, 1997), as they did in N-addition experiments (Theodose and Bowman, 1997). Of the shared species in the long-term plots of Korb (1997), 55 percent showed a response over 43 years that was similar to the response observed 5 years after N additions by Theodose and Bowman (1997). These long-term changes in the alpine-plant community also could be explained by other factors, however, such as increased snowpack and herbivory by voles (Korb, 1997). Studies of long-term plant-community changes in response to changing rates of atmospheric N deposition in the Colorado Rockies are lacking at present, and the long-term data from the plot studies cited above are difficult to interpret because of the many factors that may affect plant communities. Nevertheless, these data may at least reveal whether observed long-term changes are consistent with the expected effects of atmospheric N deposition, and may help to distinguish the effects of N deposition from the effects of climate and herbivores.

Alpine and Subalpine Forest

Alpine and subalpine forests in the Rocky Mountains of Colorado and southeastern Wyoming generally are limited by the availability of N and several other factors (Fahey and others, 1985; Prescott and others, 1992; Ryan and Waring, 1992). Two recently published studies suggest, however, that N limitation may not apply in forested areas east of the Continental Divide that receive the highest rates of atmospheric N deposition (Williams and others, 1996a; Rueth and Baron, 2002). The first of these studies found higher foliar N:P ratios in Bristlecone pine at 3650 m on Mt. Evans (in the Front Range) than at two other sites on Mt. Evans at 3550 m and 3450 m (Williams and others, 1996a). They assumed that atmospheric N deposition is greater at the highest site but obtained no data to support this assumption, nor do they report the variation among their measurements of five trees at each elevation; thus, the significance of the reported values is difficult to evaluate. The second study reports higher percentages of foliar N and organic soil N, and lower C:N ratios, in foliage and organic soil samples from six stands of Englemann spruce east of the Continental Divide than in samples from six comparison sites west of the Divide, and attribute these differences to the greater atmospheric N deposition east of the divide (Rueth and Baron, 2002). The Bristlecone pine and Englemann spruce data are within the N limitation range of forest productivity,

however (Barrick and Schoettle, 1996). Nitrogen limitation in subalpine forest also is generally indicated by the reported absence or miniscule presence of NO_3^- in subalpine soil waters at the Loch Vale watershed (Campbell and others, 2000).

No published studies have reported on potential detrimental effects of current rates of atmospheric N deposition on tree growth, nor on species diversity, in the subalpine forest of the Colorado Rockies. At present, atmospheric N deposition seems likely to primarily enhance subalpine forest growth rates, but additional and continued studies are needed to examine the effects in areas furthest east in the Front Range that have the highest rates of N deposition. The early signs of changes in nutrient content of foliage and forest floor may continue, given current patterns of atmospheric N deposition.

Aquatic Biota and Amphibians

The principal aquatic biota studied in the Colorado Rocky Mountain region in relation to acid precipitation and atmospheric N deposition are algae and amphibians. Little is known about the effects of atmospheric deposition on fish because many of the lakes most sensitive to acidification are fishless or have a history of stocking with non-native species (Peterson and others, 1998). Adverse effects on fish populations in high-elevation lakes and streams in the Colorado Rockies probably are minimal, however, because these waters have not been chronically acidified by atmospheric deposition.

Algae

Three major areas of study regarding the effects of atmospheric N deposition on algae and in the Colorado Rockies are addressed in this section, whether (1) algae are important in the N cycle of alpine/subalpine watersheds, (2) algal production is limited by N in lakes and streams, (3) algal populations have been affected by atmospheric N deposition.

Role in N Cycle

Baron and Campbell (1997) found that algae form a significant pool of N in the Loch Vale watershed, and that phytoplankton are the largest biological consumer of N in the watershed, exceeding the N uptake of alpine tundra and subalpine forest vegetation on an annual basis. McKnight and others (1990) found that

the population of the diatom *Asterionella formosa* increased by 34 percent/d during the peak snowmelt in Loch Vale; this indicates relatively large N uptake even during this period of rapid hydrologic flushing. Although the load of organic N from Loch Vale is less than that of DIN, as much as 18 percent of the particulate organic N load from Loch Vale may be phytoplankton (Baron and Campbell, 1997). No other studies published to date have described the relative importance of plankton in the N cycle at other watersheds in the Colorado Rockies; but their role may be even greater at other high-elevation watersheds because Loch Vale has among the highest loads of NO_3^- in the Colorado Rockies.

N as a Limiting Nutrient

One likely outcome of increasing N saturation in an ecosystem is a shift in nutrient limitation of terrestrial and aquatic biota from N to other nutrients such as P (Jassby and others, 1994; Williams and others, 1996a). Morris and Lewis (1988) studied nutrient limitation in phytoplankton at eight Colorado mountain lakes that are located mostly west of the Continental Divide, and found examples of N limitation, P limitation, concurrent N and P limitation, reciprocal N and P limitation, and neither N nor P limitation. The potential role of atmospheric N deposition in this aspect of phytoplankton growth cannot be easily ascertained, however, because some of the lakes are affected by human development and its associated nutrient runoff. The only lake that did not show N (nor N and P) limitation of phytoplankton production was Brainard Lake, east of the Continental Divide. Toetz (1999) found N and P co-limitation in periphytic epilithon at subalpine North Boulder Creek in the Green Lakes Valley. McKnight and others (1990) measured the response of phytoplankton photosynthesis rates to additions of either $Ca(NO_3)_2$ or H_2SO_4 and concluded that growth stimulation by NO_3^- could not be conclusively demonstrated. To date, neither the number of aquatic nutrient studies, nor the spatial extent of such studies in the Colorado Rockies, has been great enough to provide general conclusions about spatial patterns of nutrient limitation among phytoplankton species. Additional research is needed at previously studied sites that encompasses a significant temporal change in atmospheric N deposition.

Effects of Increased N Deposition on Diatoms

Algal species observed in lakes at Rocky Mountain National Park and in Green Lakes Valley in the 1980s were those generally associated with circum-neutral waters (McKnight and others, 1986; Baron and others, 1986; Toetz and Windell, 1993). Baron and others (1986) found no effect of atmospheric deposition on historical pH inferred from diatom species at four subalpine lakes in Rocky Mountain National Park, but recently collected sediment cores from three Front Range lakes indicate long-term shifts in diatom populations that are consistent with increased atmospheric N deposition rates since the mid-20th century (Wolfe and others, 2001; Waters and others, in press). Sediment cores from Sky Pond and Lake Louise, east of the Continental Divide in Rocky Mountain National Park, showed increasing amounts of the diatom species *Asterionella formosa* and *Fragilaria crotonensis* in sediment from 1900 to 1950 and eventual dominance of *A. formosa* between 1950 and 1970 (Wolfe and others, 2001). Both species are correlated with agricultural effects (Anderson and others, 1995) and respond quickly to N additions (McKnight and others, 1990). Wolfe and others (2001) also found a 2 - 3 permil increase in $\delta^{15}N$ at Sky Pond and Lake Louise after 1950 that paralleled the changes in species composition, and attributed these changes to the effects of increasing atmospheric N deposition to these lakes from the east. Waters and others (in press) found changes in the diatom community at Green Lake 4 that began about 1939 including (1) increased *Fragilaria* species, (2) increased abundance of microbial and algal humic substances, and (3) decreased species diversity. They attributed these changes to the long-term effects of increased atmospheric N deposition from increased use of ammonia-based fertilizer in the west since 1939. One puzzling aspect of these data is why the shifts indicative of N enrichment began in 1939 in Green Lake 4, and not until 1950 in the two lakes in Rocky Mountain National Park. The long-term changes in the diatom community are noteworthy, however; but additional sediment studies are necessary to discern whether the changes are widespread across the Front Range, and whether the differences in atmospheric N deposition east and west of the Continental Divide are reflected in sediment cores.

Amphibians

Populations of several amphibian species have declined in the Colorado Rocky Mountain region and worldwide in recent decades (Wyman, 1990). Many species are sensitive to acidity during their aquatic stages (Pierce, 1985), and episodic acidification of small vernal pools has been suggested as a possible explanation for declines in populations of tiger salamander (*Abystoma tigrinum*), boreal toad (*Bufo boreas boreas*), and chorus frog (*Pseudacris triseriata*) (Harte and Hoffman, 1989; Carey, 1993; Kiesecker, 1996). Other studies, however, indicate that episodic acidification generally occurs before amphibian species lay their eggs in the spring, and therefore, does not affect the aquatic stages (Corn and Vertucci, 1992; Wissinger and Whiteman, 1992; Vertucci and Corn, 1996). Atmospheric N deposition is a possible threat to amphibians because of its potential, though uncertain effect (as discussed previously) on episodic acidification of surface waters in the Colorado Rockies.

Most of the evidence supporting acidification of habitat as a cause of amphibian-population declines in the Colorado Rockies comes from laboratory experiments or circumstantial evidence, but no field evidence currently is available to unequivocally attribute population declines to acidification (Vertucci and Corn, 1996). Perhaps the strongest evidence of the effects of acidification on amphibian decline comes from a study in which tiger salamander eggs were exposed to varying pH conditions within *in situ* microcosms in a lake in the Elk Mountains (Mexican Cut Nature Reserve) of west-central Colorado, where surface waters are known to become episodically acidic in the early spring, and where tiger salamander populations were declining through the 1980s (Harte and Hoffman, 1989). An LD-50 pH (value at which 50 percent mortality occurs) of 5.6 was obtained from the experiments, and 100 percent mortality of the zooplankton *Diaptomus coloradensis* (a major component of the aquatic food web) at pH 5.0 was observed. No egg or larval mortality was observed in the ponds under natural conditions, but the pH of some of the ponds in the area decreased to values < 5.0 during early spring snowmelt, when tiger salamander eggs were assumed to have been present in pond waters. Wissinger and Whiteman (1992) monitored the demographics of tiger salamander in the same region and found that episodic acidification associated with snowmelt occurred only before the

eggs were laid in ponds, and they also found no correlation between the ANC of ponds and embryonic survival. Their observations support pond drying as a greater source of tiger salamander mortality than episodic acidification.

Kiesecker (1996) examined potential competitive interactions between tiger salamander and chorus frog as a function of pH in laboratory experiments. Decreasing pH resulted in reduced growth and increased development time for tiger salamander larvae, which led to their decreased predation on chorus frog larvae. These results indicate that simply measuring the rate of egg and larvae mortality is not sufficient to assess the cause of amphibian population declines—a broad array of ecosystem interactions should be evaluated as well.

Turk and Campbell (1997) hypothesized that the pH of ponds in the Mt. Zirkel Wilderness area (fig. 1) downwind from two large power plants in northwestern Colorado, would probably decline during early snowmelt to levels that would be toxic to tiger salamander eggs, but neither this study, nor any others in the Colorado Rockies, reported observations of tiger salamander egg mortality that could be directly related to episodic acidification. Tiger salamanders have shown sensitivity to low pH conditions, but studies are needed to document the timing of egg laying and larval development relative to the acid pulse in the early spring. Continued monitoring and study of tiger salamander populations in ponds of the Mexican Cut Nature Reserve in the Elk Mountains of west-central Colorado is warranted.

SUMMARY

Atmospheric N deposition in the Rocky Mountain Region of Colorado and southern Wyoming ranges from 1 to 7 (kg/ha)/yr, and may be even greater at high elevations (> 3500 m) in the Front Range. From 25 to 30 percent of total N deposition consists of dry deposition, but these values are less certain than for those of wet deposition because fewer measurements are available. Atmospheric N deposition generally is greater east of the Continental Divide than west of the Divide in the Front Range, except in areas that are directly downwind of large power plants, such as the Buffalo Pass NADP site. Despite the prevailing west winds at this latitude, westward upslope movement of air masses with elevated concentrations of nitrogen from the Denver-Boulder-Fort Collins metropolitan

area appears to be contributing to atmospheric deposition of N east of the Divide, particularly during summer. A tendency toward higher NH_4^+ concentrations in wet deposition at NADP sites east of the Divide than those west of the Divide is evident and probably reflects agricultural and vehicle sources and of atmospheric NH_4^+ from east of the Rockies.

Five of 15 NADP sites show trends of increasing wet deposition of N from the mid-1980s through 2000. A region-wide trend of increasing wet deposition of N is not evident, however, three of the five sites with increasing trends, Loch Vale, Niwot Saddle, and Snowy Range, are at high elevations east of the Divide in the Front Range. No trend of increasing wet deposition of N has previously been reported at the Loch Vale site, and this recent trend is attributed mainly to increasing NH_4^+ concentrations in precipitation, whereas the trend at the Niwot Saddle site results equally from increasing precipitation and increasing concentrations of NO_3^- and NH_4^+ in precipitation. The increasing trends of wet deposition of N at the Niwot Saddle and the Snowy Range sites are more than an order of magnitude less than reported in earlier studies, because those studies erroneously used linear regression to examine trends in data that are not normally distributed.

Despite levels of atmospheric N deposition that are no more than half those reported in eastern North America, the Loch Vale and Green Lakes Valley watersheds are at similar advanced stages of N saturation; some tributary watersheds retain less than half of their annual wet deposition of N. Surface-water NO_3^- concentrations at these sites range from 30 to 40 µmol/L during early spring snowmelt and remain above 5 to 10 µmol/L during summer. An increasing amount of data indicates that surface water and ground water east of the Divide in the Front Range generally have higher NO_3^- concentrations than surface and ground water west of the Divide. This spatial pattern is attributed largely to higher rates of atmospheric N deposition east of the Divide than west of the Divide, but differences in the relative amounts of vegetation and exposed rock probably also affect the spatial pattern.

An increasing trend in the annual minimum NO_3^- concentration at Green Lake 4 from 1985 to 1997 has been reported, but this trend is not evident at other watersheds in the Green Lakes Valley, nor in other lakes east of the Divide in the Front Range. Whether the reported trend is the result of increasing N

deposition or results from changes in the hydrologic flushing time of the lake is uncertain. No other time trends in NO_3^- concentrations in surface water, soil water, or ground water have been reported for the Colorado Rockies.

Storage and cycling of N by roots and microorganisms in alpine zones of the Colorado Rockies is relatively greater than in forested regions of the world because the amount of N stored in above-ground vegetation in tundra is low. Variations in the thickness and duration of the alpine snowpack affects the rates of N-mineralization and nitrification, and thereby, affects the release of NO_3^- to subsurface and surface waters. Active microbial N-cycling processes in talus also affect the release of NO_3^- to alpine/subalpine surface waters in the region.

Increases in atmospheric N deposition may cause long-term changes in the alpine and subalpine vegetation communities in the Front Range, but few data on these effects are available. Nitrogen addition experiments have indicated, however, that N applications at rates 3 to 4 times greater than present rates of N deposition can alter the species composition of alpine plant communities. Subalpine forest vegetation generally is N-limited, even at Front Range sites that receive the highest rates of atmospheric N deposition in the region.

The amounts of N stored in alpine vegetation are relatively low; therefore, plankton in high-elevation lakes can store and cycle a significant proportion of the total N in alpine/subalpine watersheds. Nutrient-limitation studies have not been sufficient in number nor widespread enough to indicate whether plankton in lakes that receive the highest rates of atmospheric N deposition have shifted from N-limitation to limitation by other nutrients such as P. Two recent studies of diatoms in sediment from three Front Range lakes indicate changes in diatom species composition that may result from increased atmospheric N deposition since the mid-20th century. One of these studies indicated that diatom species changes have been accompanied by changes in $\delta^{15}N$ of lake sediment that are consistent with the effects of the long-term increase in atmospheric N deposition.

The effect of atmospheric deposition on populations of amphibians in the Colorado Rockies is uncertain, and an insufficient number of field studies have been completed to indicate whether habitat acidification by atmospheric deposition has affected amphibian populations. Some circumstantial evidence

of detrimental effects on tiger salamander has been reported for a location in north-central Colorado that receives high rates of atmospheric N and S deposition. The effects of atmospheric acid deposition on competition and predation in amphibians have not been addressed in many studies; therefore, some subtle effects may previously have been overlooked.

Atmospheric deposition of N in the Colorado Rocky Mountains is a subtle environmental perturbation whose effects have been difficult to quantify, given the variety of climatic and human disturbance factors that can affect nutrient-cycling processes in alpine and subalpine ecosystems. Nonetheless, atmospheric deposition of N is increasing in high-elevation locations east of the Front Range, and alpine regions there are receiving N in excess of the ecosystem demand. Current rates of atmospheric N deposition east of the Divide in the Front Range have undoubtedly caused increased rates of N-mineralization and nitrification in alpine soils, and consequently, increased concentrations of NO_3^- in surface waters. Additionally, inferred increases in atmospheric deposition of N since the mid-20th century appear to have caused a shift in the species composition of the diatom community at some high-elevation lakes in the Front Range. The effects of current rates of atmospheric N deposition on amphibians and alpine vegetation are uncertain, but continued increases in N-deposition rates may result in measurable changes in the future.

SUGGESTIONS FOR FUTURE RESEARCH

1. **Continue monitoring at existing long-term study sites.** The current trends in population growth and energy use in Colorado and the west indicate that long-term monitoring of the chemistry of atmospheric deposition, surface-water chemistry, and nutrient-cycling processes in alpine/subalpine ecosystems is needed to provide continued assessments of the effects of atmospheric N deposition. Monitoring sites at high elevation (> 3000 m) in the Front Range require the highest priority. Data from long-term study sites such as those at Loch Vale, Niwot Ridge and Green Lakes Valley, Glacier Lakes, and Fraser Forest are particularly valuable in assessing trends and warrant the highest priority for funding.

2. **Increase monitoring of surface water chemistry at locations with high rates of atmospheric N deposition that are not sampled regularly at present.** Few data on surface-water chemistry or rates of nutrient cycling processes are available from areas that surround some NADP sites such as Buffalo Pass and Wolf Creek Pass, that receive atmospheric N deposition at rates that are among the highest in Colorado. Additional surveys of lake-water chemistry that encompass the areas of greatest atmospheric N deposition are needed to provide a complete regional analysis of patterns in NO_3^- chemistry.

3. **Identify the cause of the trend of increased NO_3^- concentrations in late summer at Green Lake 4.** A thorough investigation is needed to (1) determine why Green Lake 4 shows a long-term increase in minimum NO_3^- concentration, whereas other monitored lakes east of the Continental Divide do not show a similar trend, and (2) ascertain whether this trend can be attributed unequivocally to atmospheric N deposition.

4. **Develop improved models to investigate the role of NO_3^- in episodic decreases in surface water ANC.** Quantitative multi-component runoff modeling techniques that include end-member mixing analysis will be necessary to link atmospheric N deposition to surface-water chemistry and to provide a basis for sound long-term predictions of future water chemistry. Models are needed particularly to determine the relative contributions of changes in NO_3^-, SO_4^{2-}, base cation, and organic acid concentrations in episodic decreases in the ANC of surface waters during spring snowmelt.

5. **Obtain more dissolved organic nitrogen data from surface waters.** The role of DON in alpine plant nutrition in the Colorado Rockies has been studied (Raab and others, 1996; Lipson and Monson, 1998), but few data on DON in surface waters are presently available, and little is known of the availability of DON for biological cycling in high-elevation aquatic ecosystems. This lack of data suggests a need for additional studies of the N cycle that include measurements of DON.

6. **Investigate the role of talus in the watershed N cycle**. Information on the long-term effect of talus areas in the N cycle of alpine/subalpine watersheds is needed, as are data on the amount of N stored in talus, the residence time of N in talus, talus hydrology, and the effect of talus on long-term trends in surface-water chemistry.

7. **Create index sites for monitoring changes in plant-community composition as a function of spatial and temporal changes in the rates of atmospheric N deposition.** Data on long-term changes in plant-community composition, and the potential role of atmospheric N deposition in such changes, are needed. The interpretation of changes in species composition and growth rates in long-term vegetation plots is complicated by climatic and human disturbance factors that may affect the data. Repeated sampling over many years may reveal whether the effects of atmospheric N deposition can be distinguished from the effects of these other factors.

8. **Obtain data on how nutrient limitation in plankton changes as N saturation increases.** Long-term nutrient-limitation studies of plankton in high-elevation lakes are needed to provide data on their response to changing rates of atmospheric N deposition. Repeated monitoring of previously studied lakes could reveal long-term changes in nutrient status. Collection of sediment cores from a regionally extensive set of lakes throughout the Colorado Rockies would provide data on diatom-inferred pH and nutrient status, and on temporal changes in species with different nutrient tolerance ranges and $\delta^{15}N$ content.

9. **Obtain additional data on historic changes in diatom populations and N isotope composition.** Analyses of diatoms from a wide variety of lakes over a gradient of atmospheric N deposition are needed to evaluate whether changes in species and N isotopes are consistent with the hypothesis that atmospheric N deposition is the principal cause of such changes.

10. **Establish field studies of amphibian survival during acidic episodes during spring snowmelt.** Field studies in surface waters that are prone to acidification could discern whether atmospheric deposition of acids increases the mortality of amphibian eggs in the spring. These studies also could examine mortality in terms of interactions between predator and prey.

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