Chapter 8- Headwater Catchments of North Boulder Creek, Colorado

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Abstract

Streamflows from the Colorado alpine are an important contribution to the water resources of the Boulder Creek Watershed and are generated almost entirely by melting of seasonal snow cover. Water quality in this high-elevation ecosystem is relatively sensitive to changes in the flux of energy, chemicals, and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils, and short growing seasons. With specific conductance values below 10 microsiemens per centimeter, surface waters in North Boulder Creek are among the most sensitive to perturbation in the world. Alkalinity values below 3 milligrams per liter show that these surface waters are extremely sensitive and that even small increases in the atmospheric deposition of sulfate and nitrate may cause acidification, particularly during snowmelt runoff. High nitrate concentrations in these headwater basins relative to more pristine areas on the western slope of the Rocky Mountains and other high elevation mountain ranges suggest that atmospheric deposition of nitrogen is causing changes in ecosystem function within the headwater catchments of North Boulder Creek. These results suggest that water quality in North Boulder Creek is being degraded at present levels of nitrogen deposition in wetfall, and may serve as an early warning system for other high-elevation catchments in the Colorado Front Range and for downstream ecosystems within the North Boulder Creek drainage.

INTRODUCTION

Streamflows generated in the Colorado alpine are an important contribution to the flow of Boulder Creek. Discharge in headwater catchments of the Boulder Creek Watershed are generated almost entirely by melting of seasonal snow cover. As such, they are remarkably predictable, following the temporal patterns of solar radiation, which drives snowmelt. Within the Green Lakes Valley, the diurnal flow cycle is most consistently developed in headwater subbasins and is superimposed upon the predominant annual cycle. Together, these snowmelt-driven cycles account for up to 90 percent of the variability in streamflow. Summer rainfall, though occasionally intense, has relatively little hydrologic influence (Williams and Caine, 2001).

The quantity and quality of stream waters in the headwaters of Boulder Creek are protected by a variety of administrative actions. The city of Boulder owns the upper reaches of North Boulder Creek and limits access by the public. Much of the high-elevation area is encompassed by the Indian Peaks Wilderness Area. Nonetheless, these protected, high-elevation areas are within the "airshed" of the greater Denver Metropolitan area. The airshed connection means that the chemical and nutrient content of this headwater region can be changed by downstream activities resulting in the emission of pollutants which are then transported to this area. Many high-elevation ecosystems are relatively sensitive to changes in the flux of energy, chemicals and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils,

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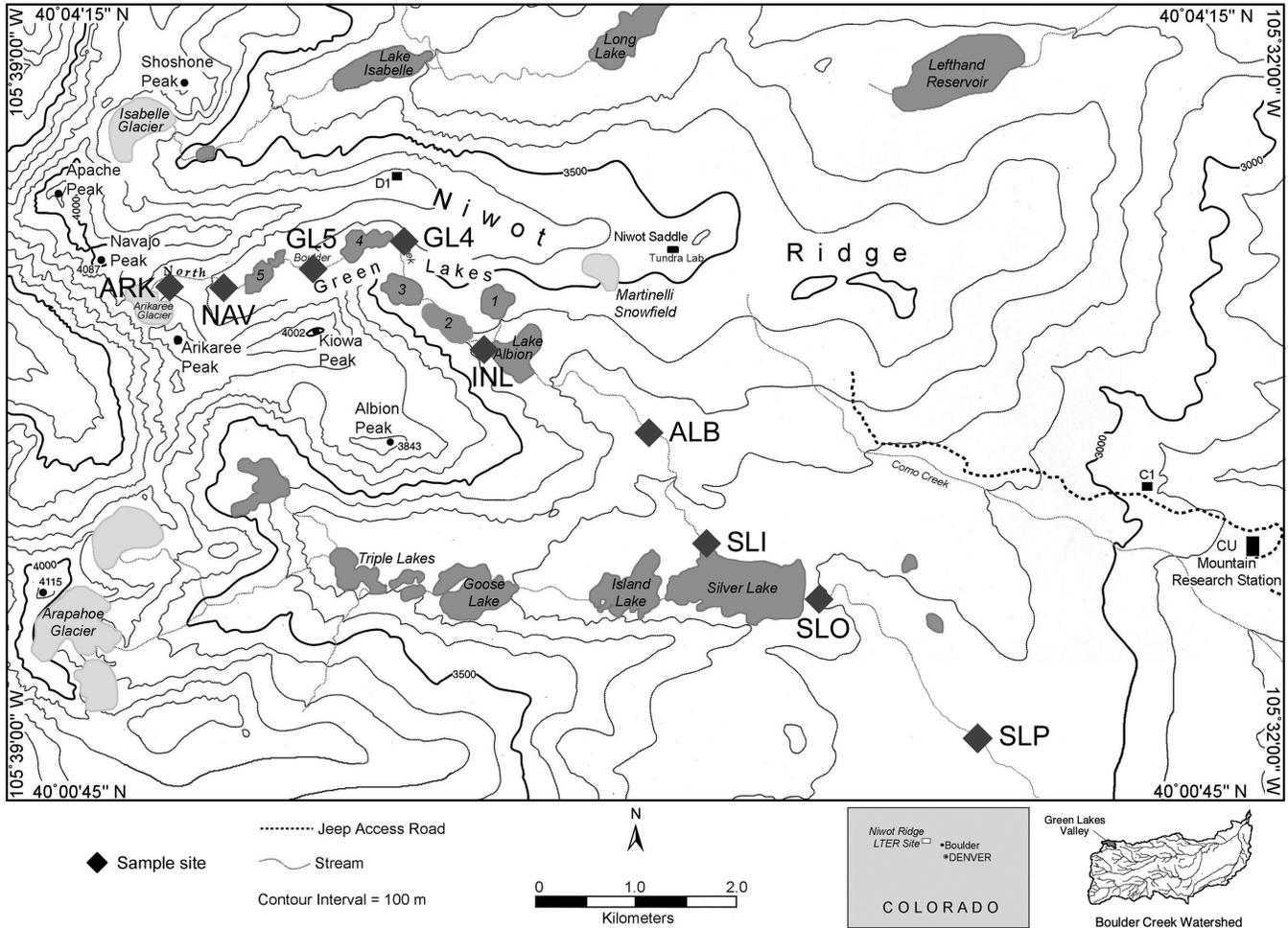
Figure 8.1. Map of study area.

and short growing seasons. Small changes in atmospheric deposition can cause large changes in ecosystem dynamics and water quality. Furthermore, these ecosystem changes may occur in alpine areas before they occur in downstream ecosystems.

STUDY SITE

Green Lakes Valley is an east-facing headwater catchment, 27 km^2 in area, extending from Silver Lake (elevation 2963 m) to the crest of the Continental Divide (over 4000 m) in the Colorado Front Range (fig. 8.1).

The Green Lakes Valley is characterized by a continental climate, with a mean annual temperature of -3.8°C and an average annual precipitation of 1000 mm (Williams, Losleben,

and others, 1996), 80 percent of which is in the form of snow (Caine, 1996). The valley is located within a protected area owned by the city of Boulder (Murphy and others, 2003) and public access has been restricted since the 1930s. As a result, the hydrologic and biogeochemical systems are protected from recreational and commercial perturbations.

The 5 km^2 of the catchment above Lake Albion is unforested and alpine in nature, and is underlain by crystalline bedrock. Steep rock walls and talus slopes are the dominant landforms and vegetation is sparse. In the upper valley, soils are limited in extent, depth, and development as a result of late-Pleistocene glaciation (Madole, 1982). Catchment soils are a mixture of Cryic Inceptisols and Entisols with Histosols in wetter areas on the valley floor (Burns, 1980).

Below Lake Albion, the catchment is dominated by a mixed conifer forest composed primarily of subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*), with some limber pine (*Pinus flexilis*) at treeline and regrowth lodgepole pine (*Pinus contorta*) lower in the basin. This portion of the catchment is typified by extensive vegetative cover and developed soils on glacial till and moraine deposits. Watershed soils overlie granitic and metamorphic parent material. Soils are Inceptisols and intermixed Alfisols with Histosols in wet meadow areas. Soil depths range from 30 to 100 cm with the deeper soils located on well-drained glacial moraines. Soil pH values range from 4.5 to 6.0.

Above Silver Lake, the Green Lakes Valley consists of a linear cascade of 5 lakes (fig. 8.1). There are 5 alpine sample sites (ARK, NAV, GL5, GL4, and INL) which range in elevation from 3345 to 3785 m and in catchment area from 0.9 to 3.5 km^2. There are 4 forested sample sites (ALB, SLI, SLO, and SLP) ranging in elevation from 2963 to 3250 m and in basin area from 7 to 27 km^2. The highest site sampled (ARK) was outflow from the Arikaree Glacier at 3785 m. The ALB site, located at treeline, represents the transition from an alpine ecosystem to a forested subalpine ecosystem. The lowest-elevation (2963 m) sampling site (SLP) was located 3 kilometers downstream from the outflow of Silver Lake at the intake for the Silver Lake Pipeline. This pipeline diverts water from North Boulder Creek to the Lakewood Reservoir. The Lakewood Pipeline then diverts water to the city of Boulder's Betasso Water Treatment Plant (Murphy and others, 2003). The North Boulder Creek watershed provides about 40 percent of the city of Boulder's water supply (City of Boulder, 2001).

METHODS

Stream samples were collected as grab samples following the protocol of Williams, Brooks, and others (1996). Polyethylene bottles were soaked with deionized water overnight and then rinsed copiously with deionized water. Bottles were further rinsed three times with sample water at the time of collection. Samples were transported within a few hours of collection to a wet chemistry laboratory located at the University of Colorado's Mountain Research Station. Subsamples were immediately filtered through glass fiber filters with a nominal pore size of 1.0 µm and stored in the dark at 4°C for subsequent analysis. Samples for dissolved organic carbon (DOC) analysis were collected in precombusted amber glass bottles. DOC samples were filtered (at the time of collection) through precombusted Gelman A/F glass fiber filters with an approximate pore size of 1.0 µm.

All water samples were analyzed for pH, alkalinity, specific conductance, and major ions. The pH measurements were made with combination electrodes suitable for use in dilute waters (Sargent Welch S-30072-15 or Ross 8104) and a Fisher Acumet 805 pH meter. For each series of measurements the electrode was calibrated with pH 7.00 and pH 4.00 reference buffers and washed twice for 3 minutes with stirred deionized water. The pH calibration was then verified with low ionic strength solutions of hydrochloric acid (HCl; 10^{-5} and 10^{-4} N); calibration was repeated if the measured pH values of these solutions differed from the expected values by more than 0.1 units. The electrode was rinsed with an aliquot of sample, and the temperature-compensated pH determination made on a fresh, quiescent sample after five minutes. Specific conductance was measured with a Yellow Springs Instruments Model 32 and a glass electrode with a 0.1 cell constant. Simultaneous temperature measurements were made, and conductivity was standardized to 25°C using a coefficient of 2 percent per degree C. The conductivity cell was calibrated with dilute solutions of potassium chloride. Alkalinity was measured as acid neutralizing capacity (ANC) and is considered to equal bicarbonate (HCO_3^-) for these dilute waters.

Subsets of all samples were immediately filtered through pre-rinsed (300 mL) 47-mm Gelman A/E glass fiber filters with a nominal pore size of 1.0 μm. Nitrate was analyzed using a Dionex DX 500 ion chromatograph with an IonPac AS4A-SC Analytical Column. The detection limit was 0.00042 mg/L and precision was 1.1 percent. Ammonium was measured on a Lachat QuikChem 4000 Flow Injection Analyzer using a method based on the Berthelot reaction. The detection limit was 0.00462 μg/L and precision was 0.91 percent. Total N (TN) concentrations were determined by using potassium persulfate digestion to oxidize all forms of N into NO_3-N on both unfiltered and filtered samples. Nitrate was then measured on a Lachat QuikChem 4000 Flow Injection Analyzer as described above. Detection limits for TN were 0.0098 mg/L and precision was 1.62 percent. DON was calculated by subtracting measured inorganic N from total N on filtered samples. DOC was analyzed at the Institute of Arctic and Alpine Research (INSTAAR) in Boulder using a Dohrman high-temperature combustion instrument. Three replicate DOC analyses were done for each sample. The standard deviation for these analyses was typically 0.05 mg/L with a range of 0.01 to 0.12 mg/L.

RESULTS

Specific conductance provides an estimate of the amount of dissolved solutes in stream waters and hence the magnitude of geochemical weathering in a catchment. In June, specific conductance more than doubled from about 7 microsiemens per centimeter (μS/cm) near the Continental Divide to about 20 μS/cm at the lowest-elevation site, SLP (table 8.1 and fig. 8.2a). The increase in specific conductance with distance downstream reflects longer residence time in ground-water reservoirs and enhanced geochemical weathering.

Specific conductance values measured in October were much higher than in June above Lake Albion (table 8.1 and fig. 8.2a). These higher specific conductance values in October reflect longer residence times in ground-water reservoirs and increased geochemical weathering before waters contribute to stream flow. Below Lake Albion there was little difference in specific conductance between June and October values. Most likely the similarity in values between June and October is because of the storage and release of water from reservoirs on North Boulder Creek.

Calcium concentrations mirror specific conductance values (fig. 8.2b). The correlation between measurements of calcium and specific conductance suggest that specific conductance values are dominated by the amount of base cations in solution. In turn, concentrations of base cations in stream flow are primarily driven by residence time and geochemical weathering processes in subsurface reservoirs before water contributes to stream flow. As residence time in the subsurface decreases during snow melt runoff, base cation concentrations in surface waters are diluted and concentrations decrease.

Alkalinity values during snowmelt runoff were as low as 1.5 mg/L at the highest elevation sites closest to the Continental Divide, such as Arikaree (table 8.1 and fig. 8.2c). The low values of alkalinity at this time are driven in part by dilution of geochemical weathering products with snowmelt runoff. Values of alkalinity then increased downstream to about 9.15 mg/L at the lowest elevation site. In October, alkalinity values increased by 0.6 to 1.2 mg/L compared to values during snowmelt runoff. The higher values in the autumn sampling are the result of both the lack of dilute snowmelt runoff and increased residence time before contributing to stream flow.

The value of pH during the June synoptic survey was about 5.4 at Arikaree near the Continental Divide and then increased downstream to values near 7.0 (table 8.1 and fig. 8.3a). The pH values were greater in October compared to June values in the upper end of North Boulder Creek. To illustrate, the lowest pH values of 6.0 at the high-elevation Arikaree site was more than one-half of a pH unit greater than June. The low pH values during June may be due

Table 8.1. Results of water quality analyses for headwaters of North Boulder Creek, June and October 2000

[S/cm, microsiemens per centimeter; mg/L, milligrams per liter; N, nitrogen; C, carbon; --, not analyzed; all inorganic samples analyzed at Kiowa Environmental Chemistry Laboratory, Mountain Research Station, University of Colorado; organic samples (dissolved organic N and dissolved organic C) analyzed at the Institute of Arctic and Alpine Research]

Site	Site description	Elevation (meters)	Date	Time	Specific conductance (S/cm)	pH (units)	Alkalinity* (mg/L)	Calcium (mg/L)	Ammonium (mg/L as N)	Nitrate (mg/L as N)	Dissolved organic nitrogen (mg/L as N)	Dissolved organic carbon (mg/L as C)
JUNE 2000												
ARK	Arikaree glacier outflow	3785	6/15/00	1125	7.11	5.34	1.39	0.50	0.147	1.37	0.031	--
NAV	Navajo site	3720	6/15/00	1210	7.92	5.78	1.47	0.83	0.004	1.87	0.027	--
GL5	Green Lake 5	3620	6/15/00	1330	9.37	6.09	2.74	1.20	0.005	1.13	0.022	--
GL4	Green Lake 4	3550	6/15/00	0945	12.7	6.30	3.93	1.74	0.005	0.90	0.000	0.55
INL	Inlet to Lake Albion	3400	6/15/00	0900	17.9	6.56	4.99	2.33	0.007	0.81	0.036	1.45
ALB	Downstream of Lake Albion	3250	6/15/00	1530	20.7	6.54	7.98	3.02	0.008	0.20	0.014	1.71
SLI	Inlet to Silver Lake	3122	6/15/00	1200	20.2	6.76	8.29	2.85	0.007	0.14	0.036	1.61
SLO	Outlet of Silver Lake	3100	6/15/00	1230	20.5	6.72	8.78	2.91	0.013	0.21	0.058	2.16
SLP	Silver Lake Pipeline intake	2963	6/15/00	1330	21.1	6.83	9.27	2.91	0.000	0.20	0.045	2.34
OCTOBER 2000												
ARK	Arikaree glacier outflow	3785	9/21/00	0955	8.60	6.03	2.29	0.88	0.254	1.08	--	--
NAV	Navajo site	3720	10/5/00	1030	18.2	6.13	3.27	2.07	0.016	3.45	--	--
GL5	Green Lake 5	3620	10/5/00	1050	27.1	6.37	4.00	3.68	0.006	1.81	--	--
GL4	Green Lake 4	3550	10/5/00	0850	26.9	6.61	4.86	3.70	0.027	1.07	--	0.62
INL	Inlet to Lake Albion	3400	10/5/00	1255	17.8	6.71	6.35	2.36	0.035	0.11	0.009	0.89
ALB	Downstream of Lake Albion	3250	10/5/00	1325	20.8	6.76	9.16	3.02	0.006	0.05	0.052	1.08
SLI	Inlet to Silver Lake	3122	10/26/00	1140	24.8	6.68	11.2	3.39	0.000	0.12	--	0.96
SLO	Outlet of Silver Lake	3100	10/26/00	1215	18.7	6.61	8.83	2.72	0.005	0.00	--	1.28
SLP	Silver Lake Pipeline intake	2963	10/26/00	1300	21.6	6.87	11.2	3.02	0.000	0.00	--	1.42

*Alkalinity was measured as Acid Neutralizing Capacity, considered as equivalent to bicarbonate (HCO_3^-) for these waters.
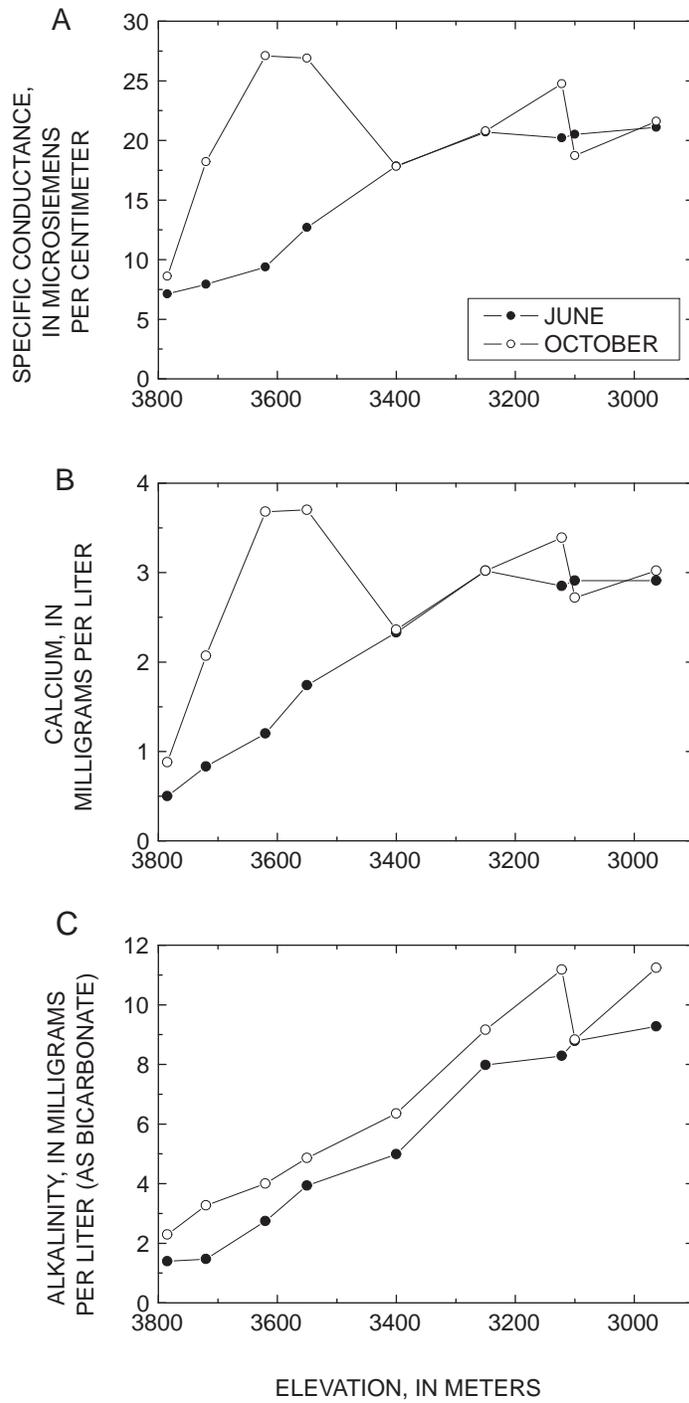
Figure 8.2. Graphs showing (A) specific conductance values, (B) calcium concentrations, and (C) alkalinity values as a function of elevation.

to dilution of geochemical weathering products by snowmelt runoff.

Ammonium (NH_4^+) concentrations were generally at or near detection limits of 0.0004 mg/L (table 8.1 and fig. 8.3b). The one exception was the Arikaree sampling site, with values in the 0.15 to 0.25 mg/L range. However, below this site, NH_4^+ values in stream water quickly decreased towards detection limits.

Nitrate (NO_3^-) concentrations were relatively high in stream waters compared to NH_4^+ concentrations (tables 8.1; fig. 8.3c). During snowmelt runoff in June, NO_3^- concentrations at the headwater areas ranged from 1.24 to 1.86 mg/L. Nitrate concentrations in June remained above 0.62 mg/L at all alpine sites. At treeline (below 3400 m), concentrations decreased to about 0.3 mg/L. In October, NO_3^- concentrations in the high-elevation areas above treeline were as high as 3.4 mg/L.

Dissolved organic nitrogen (DON) behaves very differently than NO_3^-. Concentrations of DON were always lower than 0.6 mg/L and at times below detection limits of 0.0098 mg/L (table 8.1 and fig. 8.4a). There was a tendency for DON concentrations to increase downstream.

Dissolved organic carbon (DOC) generally increased downstream (table 8.1 and fig. 8.4b) from about 0.5 mg/L in the alpine catchments to 2.5 mg/L in the forested catchments. Concentrations of DOC in June were about 1 to 2 mg/L greater than DOC concentrations at the same sites measured in October.

DISCUSSION

Surface waters in headwater catchments of North Boulder Creek are among the most pristine and sensitive streams in the world. Specific conductance values below 10 µS/cm are very low. To place the values in perspective, high-quality distilled water has a specific conductance value around 2 µS/cm. The specific conductance of stream water during snow melt runoff in this high-elevation catchment is near that of distilled water. Thus, surface waters at high-elevation in North Boulder Creek, with the low amount of solutes in the stream and the low amount of geochemical weathering in the basin relative to downstream locations such as within the city of Boulder, are very sensitive to pollutants of any kind.

Stream waters with low alkalinity values show extreme sensitivity to acidification. The U.S. Environmental Protection Agency has defined surface waters with alkalinity values less than 3.0 mg/L as sensitive to acidification (Herlihy and others, 1996). Acidification of surface waters has occurred in the northeastern United States as a result of emissions from coal-fired power plants and other sources. These gaseous emissions are converted to strong acid anions such as sulfate (SO_4^{2-}) and NO_3^- in rain and snow (Driscoll and Schafran, 1984). The very low alkalinity values in headwater catchments of North Boulder Creek suggest that even small increases in the atmospheric deposition of SO_4^{2-} and NO_3^- may cause acidification of these surface waters, particularly during snowmelt runoff.

Moreover, alkalinity values appear to be decreasing over time. A simple linear regression of alkalinity versus time shows that alkalinity in GL4 has been decreasing at the rate of 0.15 mg/L per year since the early 1980s (Caine, 1995). While the R^2 of 0.24 is low, the slope is significant at the a = 0.05 level (Williams and Tonnessen, 2000). In Caine's (1995) extensive analysis of temporal trends in water quality in the Green Lakes Valley, he reports on earlier records in the Green Lakes Valley that were summarized in Caine and Thurman (1990). At GL4, records of alkalinity measured in summer from 1969 to 1971 have an arithmetic mean of 4.9 mg/L, about the same as that predicted for the year 1980 by the regression trend at GL4. This analysis suggests that the decline in alkalinity at GL4 was initiated in the early 1980s.

Williams, Losleben, and others (1996) have shown that episodic acidification (alkalinity < 0 mg/L) of surface waters is now occurring in the headwater catchments above GL4, perhaps as a result of the increase of inorganic N deposition in
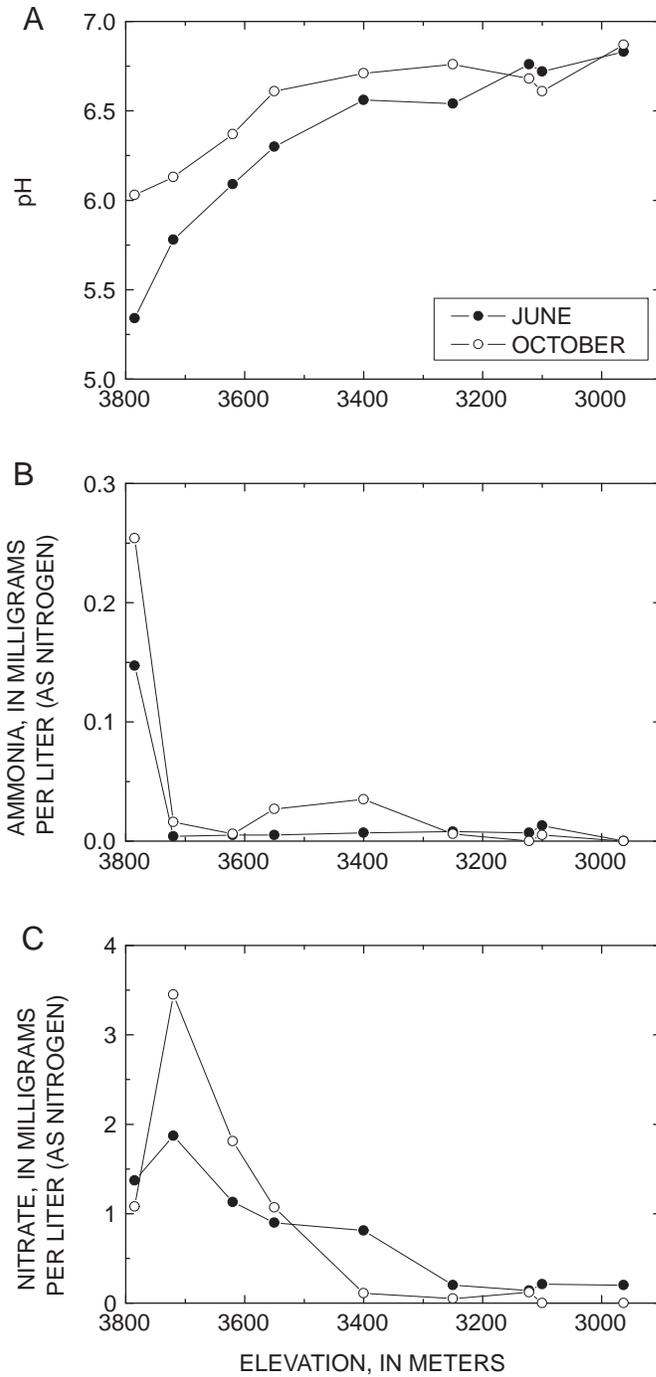
Figure 8.3. Graphs showing (A) pH, (B) ammonium concentrations, and (C) nitrate concentrations as a function of elevation.
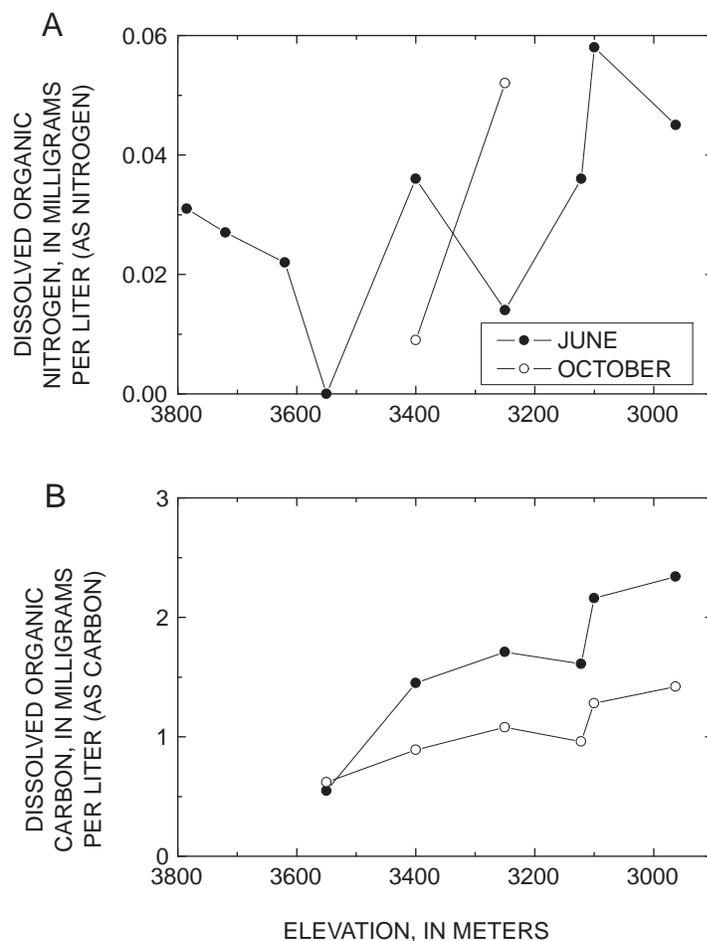
Figure 8.4. Graphs showing (A) dissolved organic nitrogen concentrations and (B) dissolved organic carbon concentrations as a function of elevation.

wetfall (Williams and Tonnessen, 2000). In 1994, alkalinity concentrations in surface waters draining the 0.09-km^2 Arikaree catchment were less than 0 mg/L for three weeks on the rising limb of the hydrograph during the initiation of snowmelt runoff, with the negative alkalinity values ranging from -0.2 to -0.4 mg/L.

The observed episodic acidification and decrease in alkalinity of surface waters was predicted in the early 1980s by Kling and Grant (1984). At that time there were no reports of acidification of surface waters (alkalinity < 0 mg/L) in the Rocky Mountains, but there was evidence that precipitation was becoming more acidic (Lewis and others, 1984). Kling and Grant (1984) predicted that acidification of surface waters in the Rocky Mountains would be detected first at the highest elevations in the Colorado Front Range, because of limited soil extent and flashy hydrographs at these high elevation sites, consistent with the results presented here.

The acidification of surface waters and resulting decrease in pH can cause changes in the aquatic resources of high-elevation catchments.

Zooplankton species, such as the dominant *Daphnia rosea*, begin decreasing below pH 5.5 to 5.8 and virtually disappear below pH 5.0 (Barmuta and others, 1990). In turn, decreases in the population of *Daphnia rosea* result in increases of more acid-tolerant species such as *Bosmina* spp., resulting in a restructuring of the natural zooplankton assemblages when pH decreases to about 5.5. Among the benthic invertebrates found in western streams, the mayfly larva (*Baetis* spp.) is very sensitive to acidic episodes, with populations decreasing rapidly once pH drops below 5.5 (Kratz and others, 1994). These species are important as food sources for native fish in high-elevation aquatic systems. Native fish species, such as the greenback cutthroat trout (*Oncorhynchus clarki stomias*) have sensitivity to acidic waters depending on the life stage exposed to acidic episodes. In general, fish population viability is expected to be reduced below pH 6 (Baker and others, 1990). In the eastern United States, streams with low ANC in Shenandoah National Park (Virginia) showed fish populations with decreased species richness, population density, condition factor, age distribution, and size compared to streams with higher ANC (Bulger and others, 1995; Dennis and others, 1995; MacAvoy and Bulger, 1995). Furthermore, a study of 13 streams in the Adirondack and Catskill Mountains in New York and the northern Appalachian Plateau in Pennsylvania showed long-term adverse effects on fish populations from episodic reductions in alkalinity similar to those we report for the Green Lakes Valley (Wigington and others, 1996). Fish populations in high-elevation catchments of the Colorado Front Range are at risk of reduced viability as a result of increasing amounts of inorganic N in wetfall.

In general, water quality of lakes in the Rocky Mountains are pristine compared to the global distribution of alpine/subalpine lakes, with the median value of NO_3^- concentrations less than 0.06 mg/L (Psenner, 1989). Similarly, NO_3^- values in high-elevation catchments in the Sierra Nevada are generally below 0.30 mg/L (Williams

and others, 1995). However, these high-elevation ecosystems are relatively sensitive to changes in the flux of energy, chemicals, and water compared to downstream ecosystems, because of extensive areas of exposed and unreactive bedrock, rapid hydrologic flushing rates during snowmelt, limited extent of vegetation and soils, and short growing seasons (Williams and others, 1993; National Acid Precipitation Assessment Program, 1998). Hence, small changes in atmospheric deposition have the potential to result in significant changes in ecosystem dynamics and water quality (Williams, Baron, and others, 1996). The high NO_3^- concentrations in North Boulder Creek relative to more pristine areas on the western slope of the Rocky Mountains and other high elevation mountain ranges suggest that atmospheric deposition of N is causing changes in ecosystem function within the headwater catchments of North Boulder Creek (Williams and Tonnesson, 2000).

Atmospheric deposition of inorganic N in wetfall to the central Rocky Mountains is relatively modest but greater than background levels. Agriculture, combustion of fossil fuels, and other human activities have altered the global cycle of N substantially, generally increasing both the availability and mobility of N over large regions of the Earth (Vitousek and others, 1997). Inorganic N deposition in annual wetfall from unpolluted regions of the world generally ranges from 0.1 to 0.7 kilogram per hectare per year (kg ha^{-1} yr^{-1}), based on extensive measurements of precipitation chemistry in remote areas of the southern hemisphere (Galloway and others, 1982, 1996; Likens and others, 1987; Hedin and others, 1995). The 2.5 to 3.5 kg ha^{-1} yr^{-1} of inorganic N deposition in wetfall to the Colorado Front Range is about five- to ten-fold greater than background amounts (Williams and Tonnessen, 2000). Compared to the northeastern United States, deposition of inorganic N in wetfall to the Rocky Mountains is similar to the 3.7 kg ha^{-1} yr^{-1} at Acadia National Park and about half of the 5.1 kg ha^{-1} yr^{-1} at the Hubbard Brook Experimental Forest as measured over the last ten years by the

National Atmospheric Deposition Program (Williams and others, 1998).

Orographic precipitation in the Rocky Mountains compounds the N-loading problem. In the northeastern United States, increases in NO_3^- leaching losses have been associated with high-elevation sites because of higher amounts of N deposition in wetfall (Driscoll and others, 1987). It is well documented that many high-elevation ecosystems receive higher doses of nutrients and pollutants than adjacent low-elevation ecosystems in the northeastern United States (Lovett and Kinsman, 1990; Lovett, 1994). The Continental Divide in the Colorado Rocky Mountains is generally higher than 4000 m in elevation, with 58 peaks in Colorado exceeding 4,267 m (14,000 feet) in elevation. As air masses rise to over 4000 m from surrounding lowlands, they cool adiabatically with resulting precipitation as air temperatures decrease below the dew point. Consequently, annual precipitation generally increases with increasing elevation in the Rocky Mountains (Barry, 1973). In turn, this increase in orographic precipitation with increasing elevation results in more N deposition in mountain areas compared to surrounding lowlands (Williams and Tonnesson, 2000). As in the northeastern United States, the highest rates of N deposition in the Rocky Mountains occur at the highest elevations. This orographic effect is much greater than in the northeastern United States, since the Rocky Mountains are generally two to three times the height of mountains in the northeast. Consequently, in high-elevation areas of the Rocky Mountains, even modest increases in the atmospheric content of anthropogenically-produced N will result in much greater deposition in wetfall of inorganic N compared to the northeastern United States.

Nitrate leaching to surface waters in the northeastern United States has been associated with catchments characterized by shallow soils and sites which have received little human disturbance (which presumably were close to input-output balance prior to receiving enhanced N deposition; Stoddard and Murdoch, 1991; Kahl

and others, 1993). In general, Pleistocene glaciation has resulted in catchments of the Colorado Front Range having soils that are limited in area and very shallow when present (Kling and Grant, 1984; Caine and Thurman, 1990; Baron, 1992). Moreover, these high-elevation areas have received little human disturbance compared to the eastern United States and Europe. The short growing season, location above treeline, and limited soil development result in little agricultural use, no logging, only limited grazing, and little development. Consequently, it appears that these high-elevation ecosystems were close to input-output balance prior to the enhanced N deposition that we report. Furthermore, the increases of anthropogenically-fixed N in the ambient atmosphere of the Colorado Front Range and resulting increases in the deposition of inorganic N in wetfall result in an uncontrolled experiment of N fertilization at the catchment level similar to controlled experiments in the northeastern United States (Kahl and others, 1993; Williams, Brooks, and others, 1996; Williams, Losleben, and others, 1996). As in the northeastern United States, limited extent of soils combined with little human disturbance results in the high-elevation catchments of the Rocky Mountains having little capacity to assimilate increases in atmospheric deposition of inorganic N.

Additionally, the storage and release of solutes from the seasonal snowpack in the form of an ionic pulse magnifies the aquatic problems caused by pollutants in wetfall. Here we define an ionic pulse as occurring when the initial fraction of snowmelt has ionic concentrations greater than the bulk average for the snowpack (Johannessen and Henriksen, 1978; Colbeck, 1981). Williams, Brooks, and others (1996) have shown that on Niwot Ridge, initial concentrations of NO_3^- in snowmelt at the plot scale (1 m^2) may be as high as 20 times those of bulk snowpack concentrations. At the ARIK site, the elevated NO_3^- and H^+ concentrations in surface waters at the onset of snowmelt are consistent with the storage and release of solutes from the seasonal

snowpack in the form of an ionic pulse. Storage and release of solutes from the snowpack in the form of an ionic pulse at the 0.09-km^2 ARIK site magnifies the concentration of pollutants in wetfall about 5-fold. The relatively high concentrations of NH_4^+ at the ARIK site suggest that the snowpack on the small glacier essentially acts as a giant snow lysimeter, providing information on the chemical content of snow and ice melt. Immediately below the Arikaree glacier, the NH_4^+ in streamwater is immobilized by biotic (microbial assimilation) and abiotic (adsorption by ion exchange on soil particles) processes. Thus, even during snowmelt runoff, much of the melted snow flows through the subsurface before contributing to stream flow.

Our results suggest that water quality in North Boulder Creek is being degraded at present levels of N deposition in wetfall (Williams and Tonnessen, 2000). These results may serve as an early warning system for high-elevation catchments in the Colorado Front Range. Protected areas such as national parks and wilderness areas with elevated amounts of N deposition are susceptible to N leakage because of stand maturity where forested, accumulation of N in soil, and particularly in high-elevation sites, low N retention capacity of soils and vegetation. All of these factors suggest that reductions of N emissions are needed to protect these environments (Fenn and others, 1998; Williams and Tonnessen, 2000).

SUMMARY

Our results demonstrate strong longitudinal trends in water quality in headwater streams of North Boulder Creek. The increase in specific conductance with distance downstream reflects longer residence time in ground-water reservoirs and enhanced geochemical weathering with distance downcanyon. Specific conductance values measured above Lake Albion were much higher in October than in June. The higher values in October reflect longer residence times in ground-water reservoirs and increased

geochemical weathering before waters contribute to stream flow. Alkalinity values during snowmelt runoff were as low as 1.5 mg/L at the highest elevation sites closest to the Continental Divide, such as ARIK. The low values of alkalinity at this time are driven in part by dilution of geochemical weathering products with snowmelt runoff. Values of alkalinity then increased downstream to about 9.15 mg/L at the lowest elevation site. In October, alkalinity values increased by 0.6 to 1.2 mg/L compared to values during snowmelt runoff. The higher values in the autumn sampling are the result of both the lack of dilute snowmelt runoff and increased residence time before contributing to stream flow. The low values of alkalinity at the headwaters of North Boulder Creek are a good indicator that this area is sensitive to acidification.

The value of pH during the June synoptic survey was about 5.4 at ARIK and then increased downstream to values near 7.0. As with specific conductance and alkalinity, pH values in the upper end of North Boulder Creek were much greater in October than in June. To illustrate, the lowest pH values of 6.0 at the high-elevation ARIK site was more than one-half of a pH unit greater than in June. The low pH values during June represent two processes: (a) dilution of geochemical weathering products by snowmelt runoff; and (b) possible titration by strong acid ions such as sulfate and nitrate. The pH values below 6.0 are in the range where biological damage may be occurring.

In contrast, nitrate (NO_3^-) concentrations were generally highest near the Continental Divide and decreased downstream. During snowmelt runoff in June, NO_3^- concentrations at the headwater areas ranged from 1.24 to 1.86 mg/L. Nitrate concentrations in June remained above 0.62 mg/L at all alpine sites. At treeline (below 3400 m), concentrations decreased to about 0.3 mg/L. In October, NO_3^- concentrations in the high-elevation areas above treeline were as high as 3.4 mg/L. These high NO_3^- concentrations in North Boulder Creek relative to more pristine areas on the western slope of the Rocky

Mountains and other high elevation mountain ranges suggest that atmospheric deposition of nitrogen is causing changes in ecosystem function within the headwater catchments of North Boulder Creek.

REFERENCES CITED

Baker, J.P., Bernard, D.P., Christensen, S.W., and Sale, M.J., 1990, Biological effects of changes in surface water acid-base chemistry: National Acid Precipitation Assessment Program, Report no. 13.

Barmuta, L.A., Cooper, S.D., Hamilton, S.K., Kratz, K.W., and Melack, J.M., 1990, Responses of zooplankton and zoobenthos to experimental acidification in a high-elevation lake (Sierra Nevada, California, U.S.A.): Freshwater biology, v. 23, p. 571-586.

Baron, J.S., 1992, Biogeochemical fluxes, *in* J.S. Baron, ed., Biogeochemistry of a subalpine ecosystem– Loch Vale Watershed: New York, Springer-Verlag, Ecological Studies ser. 90, p. 247.

Barry, R.G., 1973, A climatological transect on the east slope of the Front Range, Colorado: Arctic and Alpine Research, v. 5, p. 89-110.

Bulger, A.J., Dolloff, C.A., Cosby, B.J., Eshleman, K.N., Webb, J.R., and Galloway, J.N., 1995, The Shenandoah National Park– Fish in sensitive habitats (SNP:FISH) project– An integrated assessment of fish community responses to stream acidification: Water, Air, and Soil Pollution, v. 85, p. 309-314.

Burns, S.F., 1980, Alpine soil distribution and development, Indian Peaks, Colorado Front Range: Boulder, University of Colorado, Ph.D. dissertation, 360 p.

Caine, Nel, 1995, Temporal trends in the quality of streamwater in an alpine environment– Green Lakes Valley, Colorado Front Range, USA: Geografiska Annaler, v. 77a, p. 207-220.

_____1996, Streamflow patterns in the alpine environment of North Boulder Creek, Colorado Front Range: Zeitschrift fur Geomorphologie, v. 104, p. 27-42.

Caine, Nel and Thurman, E.M., 1990, Temporal and spatial variations in the solute content of an alpine stream, Colorado Front Range: Geomorphology, v. 4, p. 55-72.

City of Boulder, 2001, Drinking water quality report number 3: Boulder, Colo., Boulder Public Works Department, accessed May 10, 2002, at http://www.ci.boulder.co.us/publicworks/depts/utilities/water_quality/drinking/report01/index.htm

Colbeck, S.C., 1981, A simulation of the enrichment of atmospheric pollutants in snow cover runoff: Water Resources Research, v. 17, p. 1383-1388.

Dennis, T.E., MacAvoy, S.E., Steg, M.B., and Bulger, A.J., 1995, The association of water chemistry variables and fish condition in streams of Shenandoah National Park (USA): Water, Air, and Soil Pollution, v. 85, p. 365-370.

Driscoll, C.T. and Schafran, G.C., 1984, Short-term changes in the base neutralizing capacity of an acid Adirondack lake, New York: Nature, v. 310, p. 308-310.

Driscoll, C.T., Wyskowski, B.J., Cosentini, C.C., and Smith, M.E., 1987, Processes regulating temporal and longitudinal variations in the chemistry of a low-order woodland stream in the Adirondack region of New York: Biogeochemistry, v. 3, p. 225-241.

Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., and Stottlemyer, Robert, 1998, Nitrogen excess in North American ecosystems– Predisposing factors, ecosystem responses, and management strategies: Ecological Applications, v. 8, p. 706-733.

Galloway, J.N., Keene, W.C., and Likens, G.E., 1996, Processes controlling the composition of precipitation at a remote southern hemisphere location– Torres del Paine National Park, Chile: Journal of Geophysical Research, v. 101, p. 6883-6897.

Galloway, J.N., Likens, G.E., Keene, W.C., and Miller, J.M., 1982, The composition of precipitation in remote areas of the world: Journal of Geophysical Research, v. 87, p. 8771-8786.

Hedin, L.O., Armesto, J.J., and Johnson, A.H., 1995, Patterns of nutrient loss from unpolluted, old-growth temperate forests–- Evaluation of biogeochemical theory: Ecology, v. 76, p. 493-509.

Herlihy, A.T., Kaufmann, P.R., Stoddard, J.L., Eshleman, K.N., and Bulger, A.J., 1996, Effects of acidic deposition on aquatic resources in the Southern Appalachians with a special focus on Class I Wilderness Areas: Prepared for the Southern Appalachian Mountain Initiative, 91 p.

Johannessen, M. and Henriksen, A., 1978, Chemistry of snow meltwater– Changes in concentration during melting: Water Resources Research, v. 14, p. 615-619.

Kahl, J.S., Norton, S.A., Fernandez, I.J., Nadelhoffer, K.J., Driscoll, C.T., and Aber, J.D., 1993, Experimental inducement of nitrogen saturation at the watershed scale: Environmental Science and Technology, v. 27, p. 565-568.

Kling, G.W. and Grant, M.C., 1984, Acid precipitation in the Colorado Front Range– An overview with time predictions for significant effects: Arctic and Alpine Research, v. 16, p. 321-329.

Kratz, K.W., Cooper, S.D., and Melack, J.M., 1994, Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream: Freshwater Biology, v. 32, p. 161-183.

Lewis, W.M., Jr., Grant, M.C., and Saunders, J.F., III, 1984, Chemical patterns of bulk atmospheric deposition in the state of Colorado: Water Resources Research, v. 20, p. 1691-1704.

Likens, G.E., Keene, W.C., Miller, J.M., and Galloway, J.N., 1987, Chemistry of precipitation from a remote, terrestrial site in Australia: Journal of Geophysical Research, v. 92, p. 13299-13314.

Lovett, G.M., 1994, Atmospheric deposition of nutrients and pollutants in North America– An ecological perspective: Ecological Applications, v. 4, p. 629-650.

Lovett, G.M. and Kinsman, J.D., 1990, Atmospheric pollutant deposition to high-elevation ecosystems: Atmospheric Environment, v. 24A, p. 2767-2786.

MacAvoy, S.E. and Bulger, A.J., 1995, Survival of brook trout (*Salvelinus fontinalis*) embryos and fry in streams of different acid sensitivity in Shenandoah National Park, USA: Water, Air, and Soil Pollution, v. 85, p. 445-450.

Madole, R.F., 1982, Possible origins of till-like deposits near the summit of the Front Range in north-central Colorado: U.S. Geological Survey Professional Paper no. 1243, 31 p.

Murphy, S.F., Barber, L.B., Verplanck, P.L., and Kinner, D.A., 2003, Environmental setting and hydrology of the Boulder Creek Watershed– Chapter 1 *in* Murphy, S.F., Verplanck, P.L., and Barber, L.B., eds., Comprehensive water quality of the Boulder Creek Watershed, Colorado, during high-flow and low-flow conditions, 2000: U.S. Geological Survey Water-Resources Investigations Report 03-4045, p. 5-26.

National Acid Precipitation Assessment Program, 1998, Biennial report to Congress– An integrated assessment: Silver Spring, Md., 118 p.

Psenner, R., 1989, Chemistry of high mountain lakes in siliceous catchments of the Central Eastern Alps: Aquatic Sciences, v. 51, p. 108-128.

Stoddard, J.L. and Murdoch, P.S., 1991, Catskill Mountains, *in* Charles, D.F., ed., Acidic deposition and aquatic ecosystems: New York, Springer-Verlag, p. 237-271.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, D.G., 1997, Human alteration of the global nitrogen cycle– Sources and consequences: Ecological Applications, v. 7, p. 737-750.

Wigington, P.J., Jr., DeWalle, D.R., Murdoch, P.S., Kretser, W.A., Simonin, H.A., Van Sickle, J., and Baker, J.P., 1996, Episodic acidification of small streams in the northeastern United States– Ionic controls of episodes: Ecological Applications, v. 6, p. 389-407.

Williams, M.W., Bales, R.C., Brown, A.D., and Melack, J.M., 1995, Fluxes and transformations of nitrogen in a high-elevation catchment: Biogeochemistry, v. 28, p. 1-31.

Williams, M.W., Bardsley, Tim, and Rikkers, Mark, 1998, Overestimation of snow depth and inorganic nitrogen wetfall using NADP data, Niwot Ridge, Colorado: Atmospheric Environment, v. 32, p. 3827-3833.

Williams, M.W., Baron, J.S., Caine, Nel, Sommerfeld, Richard, and Sanford, Robert, Jr., 1996, Nitrogen saturation in the Colorado Front Range: Environmental Science and Technology, v. 30, p. 640-646.

Williams, M.W., Brooks, P.D., Mosier, Arvin, and Tonnessen, K.A., 1996, Mineral nitrogen transformations in and under seasonal snow in a high-elevation catchment in the Rocky Mountains, United States: Water Resources Research, v. 32, p. 3161-3171.

Williams, M.W., Brown, A.D., and Melack, J.M., 1993, Geochemical and hydrological controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California: Limnology and Oceanography, v. 38, p. 775-797.

Williams, M.W. and Caine, Nel, 2001, Hydrology and hydrochemistry, *in* Bowman, W. and Seastedt, T.R., eds., Alpine dynamics– The structure and function of an alpine ecosystem– Niwot Ridge, Colorado: New York, Oxford University Press, p. 75-98.

Williams, M.W., Losleben, M.V., Caine, Nel, and Greenland, D.E., 1996, Changes in climate and hydrochemical responses in a high-elevation catchment in the Rocky Mountains: Limnology and Oceanography, v. 41, p. 939-946.

Williams, M.W. and Tonnessen, K.A., 2000, Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA: Ecological Applications, v. 10, p. 1648-1665.