

Prepared in cooperation with the National Park Service

Atmospheric Deposition and Surface-Water Chemistry in Mount Rainier and North Cascades National Parks, U.S.A., Water Years 2000 and 2005–2006



Scientific Investigations Report 2008–5152

Cover photograph: Lake Louise from Tatoosh Range, looking northeast by
Rebecca A. Lofgren and Stefan Lofgren.

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By David W. Clow and Donald H. Campbell

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**U.S. Department of the Interior
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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km ²)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
cubic yard (yd ³)	0.7646	cubic meter (m ³)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
Flow rate		
acre-foot per day (acre-ft/d)	0.01427	cubic meter per second (m ³ /s)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Altitude, as used in this report, refers to distance above the vertical datum.

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C).

Water year, as used in this report, refers to the period October 1 through September 30 and is designated by the year in which it ends.

Abbreviations, acronyms, and symbols used in this report

DIN	dissolved inorganic nitrogen
MORA	Mount Rainier National Park
NAD83	North American Datum of 1983
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NOCA	North Cascades National Park
NPS	National Park Service
NRCS	Natural Resources Conservation Service
PCA	Principal Components Analysis
PNW	Pacific Northwest
SNOTEL	SNOpack TELelemetry
SWE	snow/water equivalent
TP	total phosphorus
TSI	Trophic Status Index
USGS	U.S. Geological Survey
VWM	volume-weighted mean
WACAP	Western Airborne Contaminants Assessment Project
cm	centimeters
ha	hectares
m	meters
nm	nanometers
kg/ha	kilograms per hectare
mg/L	milligrams per liter
µeq/L	microequivalents per liter
µg/L	micrograms per liter
µmol/L	micromoles per liter
µS/cm	microsiemens per centimeter
°C	degrees Celsius
<	less than
>	greater than
≤	less than or equal to
±	plus or minus

Atmospheric Deposition and Surface-Water Chemistry in Mount Rainier and North Cascades National Parks, U.S.A., Water Years 2000 and 2005–2006

By David W. Clow and Donald H. Campbell

Abstract

High-elevation aquatic ecosystems in Mount Rainier and North Cascades National Parks are highly sensitive to atmospheric deposition of nitrogen and sulfur. Thin, rocky soils promote fast hydrologic flushing rates during snowmelt and rain events, limiting the ability of basins to neutralize acidity and assimilate nitrogen deposited from the atmosphere. Potential effects of nitrogen and sulfur deposition include episodic or chronic acidification of terrestrial and aquatic ecosystems. In addition, nitrogen deposition can cause eutrophication of water bodies and changes in species composition in lakes and streams.

This report documents results of a study performed by the U.S. Geological Survey, in cooperation with the National Park Service, of the effects of atmospheric deposition of nitrogen and sulfur on surface-water chemistry in Mount Rainier and North Cascades National Parks. Inorganic nitrogen in wet deposition was highest in the vicinity of North Cascades National Park, perhaps due to emissions from human sources and activities in the Puget Sound area. Sulfur in wet deposition was highest near the Pacific coast, reflecting the influence of marine aerosols. Dry deposition generally accounted for less than 30 percent of wet plus dry inorganic nitrogen and sulfur deposition, but occult deposition (primarily fog) represents a potentially substantial unmeasured component of total deposition. Trend analyses indicate inorganic nitrogen in wet deposition was relatively stable during 1986–2005, but sulfur in wet deposition declined substantially during that time, particularly after 2001, when emissions controls were added to a large powerplant in western Washington. Surface-water sulfate concentrations at the study site nearest the powerplant showed a statistically significant decrease between 2000 and 2005–06, but there was no statistically significant change in alkalinity, indicating a delayed response in surface-water alkalinity.

Seasonal patterns in surface-water chemistry and stream-flow are strongly influenced by melting of seasonal snow-packs, which release large amounts of dilute, slightly acidic water to terrestrial and aquatic ecosystems during spring

snowmelt. Concentrations of sulfate, alkalinity, and base cations in surface water declined rapidly during snowmelt, then gradually recovered during summer and fall. Preferential elution of acidic solutes from the snowpack at the beginning of snowmelt may cause episodic acidification in small alpine streams; evidence is provided by a stream sample collected at one of the sites during spring 2006 that was acidic (pH = 4.8, alkalinity = -18 microequivalents per liter) and had high concentrations of nitrate and sulfate and low concentrations of weathering products. Rain-on-snow events caused sharp declines in specific conductance, which was measured continuously using an in-stream sensor. A strong correlation was observed between measured specific conductance and measured alkalinity ($r^2 = 0.76$), permitting estimation of alkalinity from specific-conductance data using a regression equation. Estimated alkalinity declined by an order of magnitude during the rain-on-snow events, in one case to 8 microequivalents per liter. Actual declines in alkalinity might be greater because the regression equation accounts only for dilution effects; at low concentrations, the relation between specific conductance and alkalinity is likely to be nonlinear and have a negative intercept (negative alkalinity). Thus, episodic acidification is possible during rain-on-snow events. The scale of episodic acidification is unknown, but if it occurs, it could have detrimental effects on aquatic life and amphibians.

Historical lake-survey data indicate that most lakes are oligotrophic and have low nitrogen and phosphorus concentrations. Nitrogen limitation is more common in lakes in Mount Rainier National Park than in North Cascades National Park due to higher nitrate concentrations at North Cascades. The slightly higher surface-water nitrate concentrations at North Cascades National Park are consistent with higher inorganic nitrogen deposition that occurs there relative to Mount Rainier National Park. Nitrogen fixation associated with red alders may be an additional source of nitrogen to low-elevation streams in North Cascades National Park. Future monitoring for effects of atmospheric deposition of nitrogen in the parks needs to focus on high-elevation ecosystems to avoid the confounding effects of nitrogen fixation by alders.

Introduction

High-elevation aquatic ecosystems in national parks in the Pacific Northwest are sensitive to atmospheric deposition of pollutants, such as sulfur and nitrogen compounds, for several reasons. Alpine and subalpine soils have little ability to neutralize acidic deposition or assimilate atmospherically deposited nitrogen because the soils typically are thin and poorly developed, bedrock is resistant to weathering, and vegetation is sparse (Campbell and others, 1995). In addition, alpine/subalpine areas receive abundant precipitation, which moves quickly through the coarse soils. These characteristics allow pollutants to reach aquatic ecosystems with little alteration, particularly during periods of snowmelt, when hydrologic flushing rates are high (Clow and Sueker, 2000).

Sulfur and nitrogen compounds are emitted into the atmosphere from a variety of anthropogenic activities, with a range of environmental consequences that are summarized by the U.S. Environmental Protection Agency (2001). Sulfur dioxide is released primarily by coal-burning powerplants and is a major component of acidic deposition. Nitrogen oxide and ammonia also can be important contributors to acidic deposition. Nitrogen oxide emissions are primarily from vehicle exhaust and powerplants fired by coal and natural gas. Ammonia emissions are derived mainly from agricultural activities, such as livestock and crop production. Sulfur dioxide and nitrous oxide undergo chemical reactions in the atmosphere to form acidifying compounds, such as sulfuric acid and nitric acid. When deposited on terrestrial and aquatic ecosystems, these compounds reduce soil and surface water pH, with potential adverse effects on sensitive plants and aquatic species. Most ammonia (NH_3) emissions are converted to ammonium (NH_4^+) in the atmosphere, which in turn undergoes conversions in terrestrial ecosystems that can generate acidity (Stoddard, 1994). Nitrogen compounds also act as nutrients that can contribute to eutrophication of aquatic ecosystems, leading to changes in water chemistry and species composition in lakes and streams (Aber and others, 1989; Stoddard, 1994). Nitrous oxide emissions contribute to the formation of ground-level ozone, which is the primary constituent of smog (U.S. Environmental Protection Agency, 2001). High concentrations of ozone can impair lung function in humans and can damage leaves and needles of sensitive plant species. Additionally, sulfate and nitrate aerosols form particulates that are major components of regional haze, which impairs visibility and is an important concern in national parks and wilderness areas (National Park Service, 2002).

The State of Washington has three national parks and five wilderness areas classified as Class 1 under the Clean Air Act of 1977. The Clean Air Act and amendments stipulate that Class 1 areas receive the highest level of air-quality protection (National Park Service, 2002). State air-quality agencies and the U.S. Environmental Protection Agency are responsible for evaluating proposed new emissions sources to determine whether they might affect air-quality-related values in Class 1

areas, and if so, require that the best available control technology be used to limit emissions.

Federal land managers, such as the National Park Service and USDA Forest Service, have no direct control on permit requests but are important in the decisionmaking process, providing monitoring and assessment data to the regulatory agencies. They need information from scientific assessments of the possible effects of new emissions sources on soils, vegetation, and visibility in order to make sound recommendations on permit applications.

Air-quality-related values are being affected at Mount Rainier National Park (MORA) and North Cascades National Park (NOCA), which receive air pollution from local, regional, and possibly global sources (National Park Service, 2002). Local and regional sources include vehicles, powerplants, and industrial facilities in the Puget Sound area, which includes the cities of Seattle, Tacoma, and Vancouver in Washington and Portland in Oregon. Visibility impairment and high ozone concentrations have been documented at MORA and at NOCA; ozone concentrations showed a statistically significant increase between 1996 and 2005 (www2.nature.nps.gov/air/Pubs/pdf/gpra/GPRA_AQ_ConditionsTrendReport2006.pdf, accessed December 2007). Both of the parks have lakes and streams considered highly sensitive to atmospheric deposition of pollutants, and some lakes have acid-neutralizing capacities of less than 50 microequivalents per liter ($\mu\text{eq/L}$) (Larson and others, 1994; Larson and others, 1999).

In 2005, the U.S. Geological Survey (USGS), in cooperation with the National Park Service, began a study with the objective of assessing potential effects of atmospheric deposition of nitrogen and sulfur on surface-water chemistry in Mount Rainier and North Cascades National Parks.

Purpose and Scope

The purpose of this report is to (1) describe spatial and temporal patterns in atmospheric deposition of nitrogen and sulfur in Mount Rainier and North Cascades National Parks, (2) describe seasonal responses of surface-water chemistry to atmospheric-deposition inputs at two sites in each park, with special focus on the snowmelt period, and (3) review historical lake-survey data in the context of possible influences of nitrogen and sulfur deposition on surface-water chemistry in the parks.

Study Approach

A combination of wet-, bulk-, and dry-deposition monitoring data was used to characterize atmospheric deposition of nitrogen and sulfur. Wet-deposition data were collected at five low-elevation sites in Washington during 2000–05 through the National Atmospheric Deposition/National Trends Network (NADP/NTN) (fig. 1). To obtain data at high elevation, the National Park Service operates a bulk-deposition monitoring site at Paradise (elevation 1,560 m, fig. 1) in Mount Rainier

National Park. The sampler at Paradise provides the best available estimate of atmospheric deposition of inorganic nitrogen and sulfur to high-elevation areas in MORA, and it fills an important information gap. Deposition data for high-elevation sites are crucial for establishing dose/response relations for high-elevation aquatic ecosystems, which are commonly highly sensitive to atmospherically deposited pollutants. Additional high-elevation bulk deposition data are available

for the winter period through snowpack sampling. Although it only covers the winter months, snowpack sampling provides additional spatial coverage in areas where operation of NADP/NTN sites is impractical because of limited access and deep winter snowpacks. Dry deposition data are collected near three NADP/NTN sites in western Washington by the U.S. Environmental Protection Agency's Clean Air Status and Trends (CASTNET) program (fig. 1).

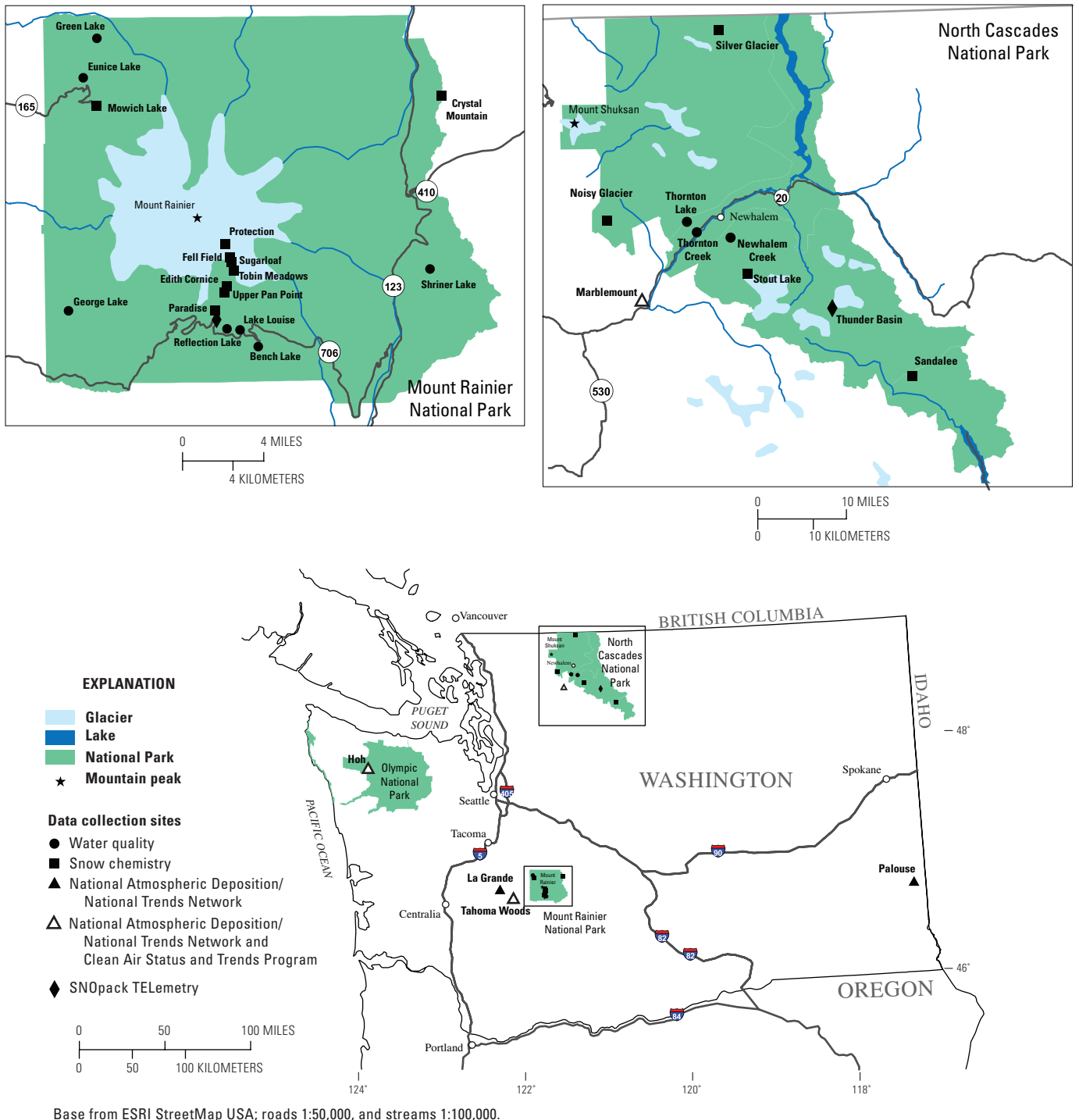


Figure 1. Locations of Mount Rainier National Park and North Cascades National Park and monitoring locations in Washington State.

Meteorologic and hydrologic conditions during the study were compared to long-term averages to provide context for the observed seasonal patterns in surface-water chemistry.

Seasonal responses of surface-water chemistry to atmospheric inputs were characterized by measuring water chemistry and streamflow at two sites in each park during water years 2005 and 2006 (October 2004–September 2006). The sites included two lake outlets in MORA and two stream sites in NOCA; temporary gages were installed at each site to obtain discharge data. Site selection was based on the following criteria: (1) availability of historical data, (2) anticipated sensitivity to atmospheric deposition of pollutants, as indicated by low surface-water specific conductivity, and (3) access. Water-quality data for the four study sites are stored in the USGS National Water Information System (NWIS) database (<http://waterdata.usgs.gov/nwis/qw>, accessed March 2008).

The historical data used in this study were obtained from a lake-water chemistry database containing data from the 1985 Western Lake Survey (<http://www.epa.gov/emap2/html/data/surfwatr/data/wls.html>, accessed January 2008), unpublished surface-water chemistry databases maintained by the NPS, and statistical summaries of lake chemistry published in journal articles and USGS reports.

Regional Characteristics

Mount Rainier National Park and North Cascade National Park are in the central and northern Cascade Range, a 1,100-km, north-south-trending range extending from northern California to southern British Columbia. Both parks are in the western part of the State of Washington, approximately 100 to 200 km inland (east) from the Pacific Ocean (fig. 1). MORA is approximately 90 km southeast of Seattle/Tacoma, and NOCA is approximately 100 km northeast of Seattle/Tacoma. MORA was established in 1899 and is 954 km² in area. NOCA was created in 1968 and is 2,772 km² in area. Most of the land in both parks is managed as wilderness, which precludes development and the use of motorized vehicles.

Geomorphic setting. Mount Rainier is the dominant geomorphic feature at MORA and is its highest peak (4,392 m); it is an active volcano rising approximately 3,000–3,500 m above surrounding terrain. The last significant eruption was 500–600 years ago (Fiske and others, 1963). It has 91 km² of snowfields and glaciers, which cover its upper flanks. Alpine meadows occur at middle elevations, and dense coniferous forest dominates at lower elevations.

Terrain at NOCA is steep and rugged, with large areas of alpine peaks and glaciers dissected by deep, heavily forested river valleys. Glaciers cover 117 km², which is more than in any other park in the United States, excluding Alaska. Elevation ranges from 100 m at Marblemount to 2,782 m at Mount Shuksan.

Climate. Prevailing winds in the Cascades are from the west, and storms are primarily frontal systems originating from the Pacific Ocean (Nelson, 1991). There are notable differences in precipitation and temperature on the western

and eastern slopes of the Cascades crest. The western slope has a temperate maritime climate, with abundant, orographically driven precipitation. The eastern slope has a more arid, continental climate due to a rain-shadow effect. Average annual precipitation at low elevations on the western slope is approximately 1 m, increases to nearly 5 m at the crest, and decreases to approximately 0.5 m at low elevations on the eastern slope (Dethier, 1979). At low elevations, most of the annual precipitation falls as rain, but at higher elevations, the dominant form of precipitation is snow. Seasonal snowpacks can reach depths in excess of 5 m.

The eastern slope has colder winter temperatures and warmer summer temperatures than the western slope (Arno and Hammerly, 1984). Average annual air temperatures in the Cascades range from 4° to 10°C (Hunt, 1974; Arno and Hammerly, 1984). Winter temperatures vary from near freezing to –18°C on the western slope and –35°C on the eastern slope (Arno and Hammerly, 1984). The freezing level is highly variable, and rain-on-snow events are common in the 1,000- to 3,000-m elevation zone, particularly on the western slope.

Hydrology. Streamflow exhibits marked seasonality in response to the accumulation and subsequent melting of deep seasonal snowpacks. During winter, streamflow typically is low because most precipitation falls and is stored as snow. Streamflow increases sharply in the spring, when the snowpack begins to melt. Peak streamflow typically occurs during the snowmelt period (May–June), and most of the annual runoff occurs during that time. Streamflows gradually decrease through the summer until fall, when rain becomes more common. Fall rainstorms and winter rain-on-snow events cause sharp, short-lived increases in streamflows and can cause severe flooding at middle and low elevations.

Geology. Mount Rainier is a stratovolcano, consisting of alternating layers of lava, mudflows, and pyroclastic material. It formed during the Pleistocene on a basement of older volcanic, sedimentary, and metamorphic rocks of Eocene age (Fiske and others, 1963). Chemically, most of the volcanic rocks are andesitic, although dacite, basalt, and rhyolite occur as well. The volcanic rocks were intruded by granitic rocks (primarily granodiorite) during the Miocene era (Fiske and others, 1963). The granitic rocks weather much more slowly than the volcanic rocks and thus tend to have shallower soils and less capacity to buffer acidic deposition than the volcanic rocks.

Bedrock geology in NOCA is complex; granitic and high-grade metamorphic rocks form a central core that is bounded on the east and west sides by separate suites of sedimentary, volcanic, and metamorphic rocks (Staatz and others, 1972). The granitic rocks in the central core are predominantly granodiorite and quartz diorite and are relatively resistant to weathering.

Trace amounts of calcite are present in some of the metamorphic rocks in the Cascades, and where it is present, calcite provides additional buffering capacity to water due to its high chemical weathering rate (Drever and Hurcomb, 1986). Glacial till is another important source of buffering capacity because soils that form on it tend to be relatively deep. Till is common in valley bottoms and to a lesser extent on hillslopes.

Soils. Soils in alpine and subalpine areas of the Cascades are predominantly Inceptisols, which are poorly developed soils with low cation-exchange capacity and low base saturation (Nelson, 1991). Alpine/subalpine areas that were glaciated during the Holocene and late Pleistocene typically have soils that show little profile development and thin organic horizons. They usually are medium to coarse textured, with moderate to high permeability. Talus deposits, which are common at the base of cliffs in alpine areas, have little organic matter, are extremely coarse textured, and have very high permeability.

Forest soils are mostly Ultisols, which are more highly weathered than Inceptisols (Nelson, 1991). Forest soils tend to have higher buffering capacity than alpine/subalpine soils because they are deeper, have well-developed soil profiles with thick organic horizons, and have higher cation-exchange capacities than alpine/subalpine soils.

Vegetation. Treeline in the northern Cascade Mountains ranges from approximately 1,400- to 1,900-m elevation (Nelson, 1991). Below treeline, dense forests of Douglas fir (*Pseudotsuga menziesii*) grow, with lesser western hemlock (*Tsuga heterophylla*) and western red cedar (*Thuja plicata*) (Nelson, 1991). In disturbed and riparian areas, maple (*Acer macrophyllum*), poplar (*Populus balsamifera*), and red alder (*Alnus rubra*) grow. Red alder can be a significant source of nitrogen to streams because its roots are a host to an actinomycete that fixes atmospheric nitrogen (Edmonds, 1980; Luken and Fonda, 1983).

Near treeline, there is a transition to subalpine and alpine vegetation with increasing elevation. Species on western slopes of the Cascade Range include Pacific silver fir (*Abies amabilis*), subalpine fir (*Abies lasiocarpa*), mountain hemlock (*Tsuga mertensiana*), and Alaska cedar (*Chamaecyparis nootkatensis*) (Nelson, 1991). On the drier eastern slopes, white-bark pine (*Pinus albicaulis*) and Englemann spruce (*Picea engelmannii*) dominate (Nelson, 1991). Recently deglaciated terrain, talus fields, and bedrock exposures have only sparse vegetation.

Site Characterization

The study sites in MORA where seasonal variations in surface-water chemistry were measured included Eunice Lake and Lake Louise (fig. 1). Eunice Lake is in the northwestern corner of the park, and Lake Louise is in the south-central part of the park. Both lakes are small, shallow, and at moderately high elevation (table 1). Their drainage basins are small and steeply sloping. The Eunice stream gage was approximately 50 m downstream from the lake outlet. The Lake Louise stream gage was approximately 20 m downstream from the lake outlet. Steep slopes and thin, coarse soils forming on volcanic rock promote fast hydrologic flushing rates; because the basins are small and receive abundant precipitation, water residence times are less than one year. Most precipitation falls as snow, which typically accumulates to depths of 3 to 7 m during winter. Total annual precipitation, estimated using the USGS StreamStats program (Ries and others, 2004), was 257 cm at Eunice Lake and 259 cm at Lake Louise. The Natural Resources Conservation Service (NRCS) operates a SNOTEL (SNOPack TELEmetry) snow-monitoring site at Paradise, which is 2 km northwest of Lake Louise. Total annual precipitation at Paradise during 1988–2007 averaged 293 cm (ftp://ftp.wcc.nrcs.usda.gov/data/snow/snotel/table/history/washington/21c35s_p.txt/, accessed January 2008). Peak snow water equivalent (SWE) at Paradise averaged 192 cm during 1988–2007; the peak usually occurs during May or June. Both lakes are near treeline, and most of the area in the basins is alpine/subalpine in character. Bedrock in the Eunice Lake basin is primarily basalt and andesite, with lesser diorite and granodiorite. Bedrock in the Lake Louise basin is andesite and granodiorite (Fiske and others, 1964).

The study sites in NOCA where seasonal patterns in water chemistry were monitored included Thornton Creek and Newhalem Creek (fig. 1), which are in the central part of the park. Their drainage basins are substantially larger than the drainage basins of the study sites in MORA (table 1). The gages were at relatively low elevation, but the basins

Table 1. Site characteristics for surface-water monitoring sites in Mount Rainier and North Cascades National Parks.

Site Name	Latitude (NAD83)	Longitude (NAD83)	Elevation at gage (m)	Maximum elevation in basin (m)	Basin area (ha)	Estimated annual precipitation (cm)	Runoff, 2005 (cm)	Runoff, 2006 (cm)
Eunice Lake outlet	46°57'17"	121°52'44"	1,634	1,820	29	257	133	173
Lake Louise outlet	46°46'21"	121°42'56"	1,430	1,844	211	259	194	279
Newhalem Creek	48°38'21"	121°13'27"	146	2,150	4,144	310	214	246
Thornton Creek	48°38'58"	121°18'28"	420	2,200	1,160	262	312	347

have nearly 2,000 m of relief (table 1). Estimated annual precipitation in the Thornton Creek basin is 262 cm, and in the Newhalem Creek basin, it is 310 cm. At the Thunder Basin NRCS SNOTEL site 22 km southeast from Newhalem (Thunder Basin, elevation 1,280 m), total annual precipitation averaged 180 cm during 1988–2007; peak SWE averaged 84 cm and typically occurs during early to mid-April. Most precipitation falls as rain at lower elevations in the NOCA study basins, but snow dominates at the higher elevations. Hillslopes in the Thornton Creek and Newhalem Creek basins are steep and densely forested at elevations below approximately 1,500 m; higher elevations are alpine in character, with small glaciers in cirques. The Thornton Creek basin is underlain by granodiorite, schist, and orthogneiss, and the Newhalem Creek basin is underlain by banded gneiss, schist, and orthogneiss (Staatz and others, 1972; Tabor and Haugerud, 1999).

Methods

Wet- and Dry-Deposition Sampling

Wet-deposition data were obtained for all available years from the NADP/NTN Web site (<http://nadp.sws.uiuc.edu/>, accessed January 2008). The NADP/NTN is a nationwide network that included more than 250 precipitation monitoring sites in 2006. NADP/NTN calculates solute deposition by multiplying concentration by precipitation amount; weekly deposition values are summed to estimate seasonal and annual deposition.

Dry-deposition data were obtained for the three most recent years of available data (2002–2004) from the U.S. Environmental Protection Agency Clean Air Status and Trends Web site (<http://www.epa.gov/castnet/>, accessed January 2008). CASTNET is a nationwide network with more than 80 stations in operation in 2006. The NADP/NTN and CASTNET programs use standardized methods at all of the sites, allowing analysis of geographic patterns.

Bulk Deposition Sampling

Atmospheric deposition has been measured by the National Park Service at Paradise, in the south-central part of MORA (fig. 1), since 1989. The sampler at Paradise is an Aerochem wet-deposition sampler, which until 2002 was operated using NADP/NTN protocols during summer and as a bulk deposition sampler during winter. Difficult access precluded following strict NADP/NTN protocols during winter because the collection bucket would often overflow with snow between site visits. An inverted funnel was fitted to the top of the bucket during winter, reducing the size of the opening and the catch efficiency. Since 2002, it has been operated as a bulk precipitation sampler throughout the year. Precipitation volume is estimated from a National Weather Service

meteorological site at Paradise. Although evaporation and dry deposition could affect solute concentrations of precipitation collected using bulk samplers, the effect probably is minimal during winter (Clow and others, 2002).

Snowpack Sampling

Depth-integrated snowpack samples were collected by the U.S. Geological Survey and National Park Service at NOCA and MORA during spring 2005 and spring 2006 as part of the Western Airborne Contaminants Assessment Project (WACAP) and Pacific Northwest (PNW) snow chemistry projects. At NOCA, the same sites were sampled in 2005 and 2006. In MORA, dangerous snow and weather conditions in 2006 prevented resampling of the sites that were used in 2005, so nearby sites were substituted.

Samples for analyses of major-element chemistry were collected as follows: (1) a snowpit was dug from the snow surface to the ground, (2) approximately 5 cm of snow was removed from the snow surface and from the face of one wall of the pit by using a clean plastic shovel to expose only clean, fresh snow, (3) a thin column of snow was incrementally removed from the cleaned face and placed in a precleaned 10-L Teflon bag, and (4) the bag was closed, sealed, and placed in a cooler containing dry ice for transport to the laboratory. Samples were kept frozen until processed in the laboratory. Processing procedures and additional details regarding sampling methods are described in Ingersoll (1995).

Snowpack depth was recorded, and density, temperature, and snow morphology were measured in 10- to 40-cm increments from the snow surface to the base of the pack. Thermometers were calibrated to within $\pm 0.5^\circ\text{C}$ in an ice-water bath before use. The density, temperature, and snow-morphology data were used to determine whether the snowpack had begun to melt, which would render it unsuitable for snow chemistry sampling.

Water Sampling and Analyses

Water samples were collected as part of this study from the two lake outlets in MORA and two streams in NOCA along well-mixed reaches by using grab sampling methods (Wilde and others, 1998). Samples were collected in 1-L plastic bottles, which were washed and soaked using 18-megohm deionized water before use. Sampling frequency varied, with highest frequency (weekly) during periods of snowmelt, and lowest frequency (monthly) during fall. Samples were not collected from November through February because deep snowpacks limited access to the lakes, and flow generally was low. An automated water sampler (autosampler) was used to collect water samples from the Eunice Lake outlet during springtime to obtain samples during the rising limb of the snowmelt hydrograph. Several samples were collected from the epilimnion of Eunice Lake and Lake Louise for comparison with chemistry at the lake outlets.

Water samples were filtered onsite within 2 hours of collection, except those collected using the autosampler, which were filtered in a field laboratory within 24 hours of being removed from the field. Samples were retrieved from the autosampler every 2 weeks; deep snowpacks surrounding the autosampler helped keep samples cool during that time. Equipment cleaning, sampling, and filtration followed protocols in the USGS National Field Manual (Wilde and others, 1998). The fraction of sulfate derived from marine aerosols in a sample was calculated by multiplying the chloride concentration in the sample by the sulfate:chloride ratio in seawater, which is 0.1092 (Gregor and others, 2004).

Laboratory Methods and Quality Assurance

Alkalinity, pH, and specific conductance were measured in the laboratory on unfiltered aliquots of the sample within 1 week of collection. Alkalinity was measured by Gran titration (Gran, 1952), and pH was measured using an electrode designed for low-ionic-strength water. Calcium, magnesium, and silica were determined by inductively coupled plasma spectroscopy on filtered, acidified samples within 2 months of collection. Sodium, potassium, ammonium, sulfate, nitrate, and chloride were measured by ion chromatography on filtered, unacidified aliquots within 1 month of collection. Dissolved organic carbon (DOC) was measured by UV-promoted persulfate oxidation and infrared spectrometry, and ultra-violet absorbance (UVA) was measured at 254 nm. DOC and UVA were measured within 1 month of collection. Detection limits were less than 1 $\mu\text{mol/L}$ for all dissolved constituents, except DOC, which had a detection limit of 0.3 mg/L.

Quality-assurance procedures included collection and analyses of field blanks and field splits, which accounted for 10 percent of the total sample load. Solute concentrations in all of the blanks were less than the detection limit for all constituents. Median differences of field splits were $\leq 1 \mu\text{mol/L}$, except for alkalinity and calcium, for which median differences were $\leq 2 \mu\text{mol/L}$.

Sample analyses were performed at the U.S. Geological Survey research laboratory in Boulder, Colorado. Laboratory quality-assurance checks included routine analyses of certified high-purity standards traceable to the National Institute of Standards and USGS standard reference samples (Ludtke and Woodworth, 1997) within each analytical run. The laboratory also participated in blind-audit performance tests conducted by the USGS and by the National Laboratory for Environmental Testing, National Water Research Institute, Environment Canada (Blum and Alkema, 2000). Results of the blind-audit tests indicated analyses were accurate to within 6 percent for all constituents. Analytical results were checked for each sample based on charge balance; all samples had charge balances within 13 percent or 18 $\mu\text{eq/L}$.

Hydrologic Data Collection

Discharge (streamflow) at the lake outlets and in the streams listed in table 1 was calculated from stage (water depth), which was monitored using submersible pressure transducers connected to automatic dataloggers. Hourly averages were calculated from stage measurements that were made every minute. Minor datum corrections to the pressure transducer record were made on the basis of manual stage readings obtained from reference staff gages.

Manual discharge measurements were made over a range of flows using a current meter (Rantz and others, 1982a). A rating equation was created for each site, allowing computation of discharge from the adjusted stage data (Rantz and others, 1982b).

Equipment malfunctions caused some gaps in the stage record. Regression equations were developed to relate discharge at the study sites to discharge at the closest USGS streamgaging stations; the regression equations were used to estimate discharge at the study sites for periods when equipment at those stations was not operating. Data gaps accounted for 0 to 35 percent of the record at the four gages. Correlations between discharge at the study sites and the gages used for reconstruction ranged from 70 to 98 percent.

Statistical Analyses

Trend analyses were performed on precipitation and deposition of solutes in precipitation using the Spearman's rho test, which is a nonparametric test that is relatively resistant to the effect of data outliers (Helsel and Hirsch, 1992). In this report, a p-value of less than 0.05 was considered statistically significant. LOWESS (LOcally-WEighted Scatterplot Smoothing) lines were fitted to nitrogen and sulfur deposition data by weighted least squares to illustrate variations in temporal patterns (Cleveland and Devlin, 1988).

Multiple linear regression was used to determine the relative importance of precipitation and solute concentrations on atmospheric deposition of solutes; the method involves using a least-squares approach to model the dependent variable using one or more independent variables (Helsel and Hirsch, 1992). The nonparametric Wilcoxon signed-rank test was used to test for differences in sulfate and alkalinity concentrations at Eunice Lake during 2000, 2005, and 2006 (Helsel and Hirsch, 1992).

Principal Components Analysis (PCA) was used evaluate geochemical processes influencing surface-water chemistry. PCA is a statistical technique for analyzing the variance of complex data sets in a manner that identifies how solutes vary together (covariance) (Lins, 1985). Solute groups that exhibit covariance are grouped into components, which can be interpreted in terms of specific processes. A one-way analysis of variance (ANOVA) was used to test for differences in nutrient concentrations among lakes in quadrants of the parks at $p < 0.05$ (Webster and Oliver, 2001).

Meteorologic and Hydrologic Conditions During Study

Precipitation

Precipitation was below the recent 20-year average (1988–2007) during 2005 and 2006 in both parks. Climate records at the Paradise SNOTEL site in MORA indicate that total precipitation during water year 2005 was 215 cm, and during water year 2006 it was 280 cm; average annual precipitation during 1988–2007 was 293 cm (ftp://ftp.wcc.nrcs.usda.gov/data/snow/snotel/table/history/washington/21c35s_p.txt, accessed January 2008). At the Thunder Basin SNOTEL site in NOCA, total precipitation during water year 2005 was 143 cm, and during water year 2006 it was 153 cm; average annual precipitation during 1988–2007 was 180 cm (ftp://ftp.wcc.nrcs.usda.gov/data/snow/snotel/table/history/washington/20a07s_p.txt, accessed January 2008).

There were substantial differences in the percentage of precipitation falling as rain compared to that falling as snow in 2005 and 2006. At Paradise and Thunder Basin, approximately one-half of the precipitation fell as snow in 2005, whereas in 2006, two-thirds to three-fourths fell as snow. Most of the rain fell during fall and spring, but there also were substantial rain-on-snow events during winter. Summers were relatively dry.

Streamflow

Streamflow at the study sites where the temporary gages were installed in MORA and NOCA showed strong seasonal patterns and shorter storm-event-driven variations, reflecting inputs from fall rainstorms, winter rain-on-snow events, and spring snowmelt (fig. 2). During both water years of the study, streamflow was low at the beginning of the water year (October) due to dry antecedent conditions. Fall rainstorms caused short, sharp spikes in streamflow, reflecting rapid runoff from thin, coarse-grained soils. Seasonal snowpacks began

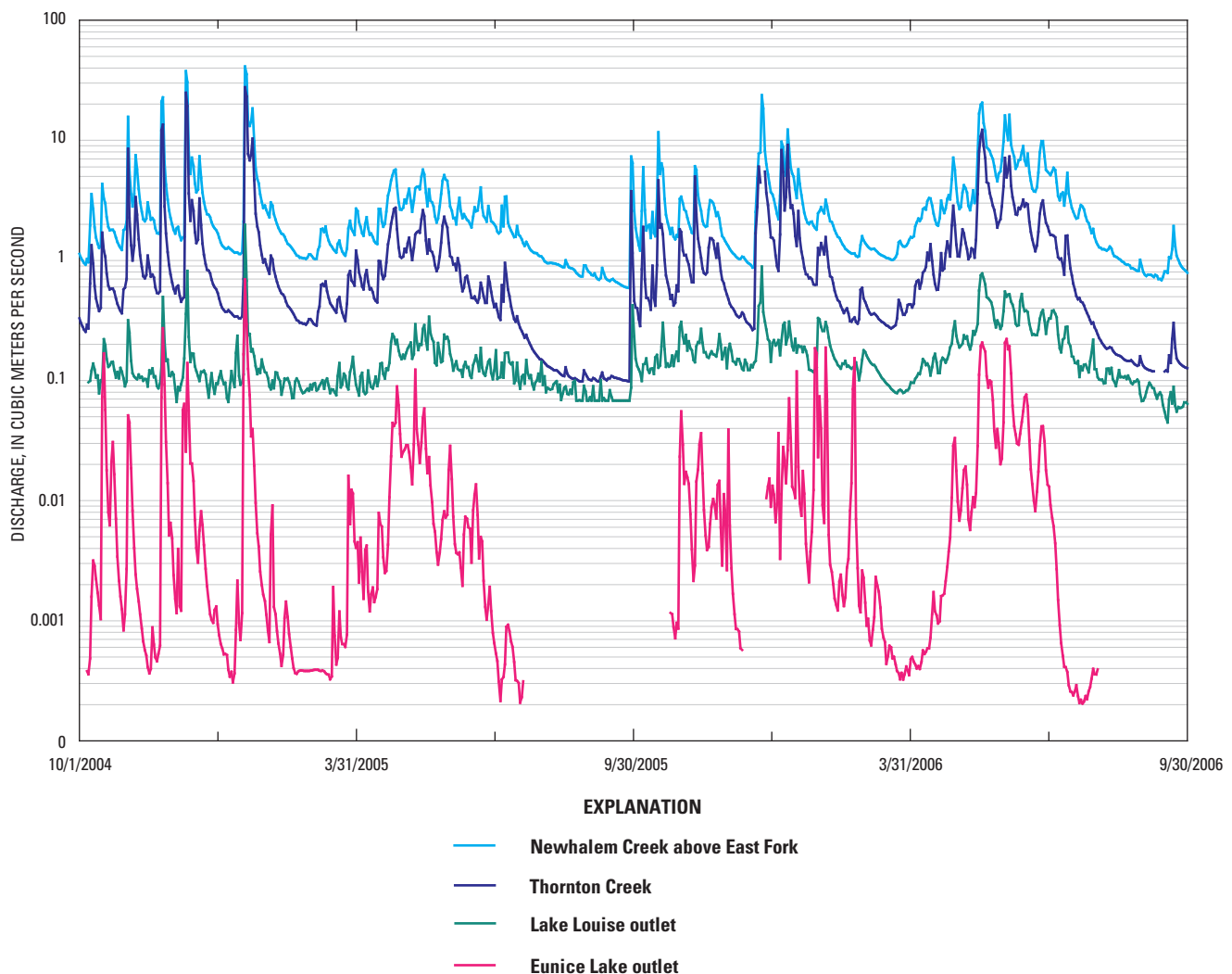


Figure 2. Mean daily discharge during water years 2005 and 2006 at study sites in Mount Rainier National Park and North Cascades National Park.

accumulating during November as mean daily air temperatures cooled. Rain falling on snowpacks 1 to 2 m in depth caused large midwinter discharge peaks. Some of the increased streamflow probably was due to direct rainfall runoff. In some cases, however, melting of the snowpack occurred as well, as indicated by a loss in SWE from the snowpack during mid-winter precipitation events. For example, at Paradise during mid-January 2005, a multiday storm deposited 24.9 cm of precipitation, and there was a loss of 12 cm of SWE from the snowpack. Average daily air temperatures at Paradise during the storm ranged from 5.0 to 6.9°C, so much of the precipitation must have fallen as rain that melted some of the snow as it passed through the snowpack.

Streamflow declined during late winter/early spring, then increased gradually in March as snowmelt began. Deeper snowpacks in 2006 delayed the onset and peak of snowmelt runoff and caused substantially higher and longer runoff in 2006 compared to 2005.

The timing, duration, and magnitude of runoff peaks can provide information about the geographic scale of meteorologic events and about the hydrologic characteristics of the study basins. Runoff peaks from the fall rainstorms and winter rain-on-snow events were sharp and nearly contemporaneous among the study sites, indicating that the study basins were responding to broad, regional-scale synoptic weather patterns (fig. 2). Discharge peaks at the NOCA sites were higher and of longer duration than those at the MORA sites, reflecting larger basin size and longer water residence times in the NOCA basins. The duration of discharge peaks at Eunice Lake was noticeably shorter than at the other sites, and streamflow at the Eunice Lake outlet often decreased to zero during late summer. This indicates that the Eunice Lake basin has relatively little subsurface storage capacity.

Atmospheric Deposition of Inorganic Nitrogen and Sulfur

Spatial and Temporal Patterns in Wet Deposition and Emissions

Atmospheric deposition of nitrogen and sulfur refers to nitrogen and sulfur that fall on the landscape, which may occur as wet deposition (rain and snow), dry deposition (aerosols and dust), or occult deposition (primarily fog). Wet deposition of a given solute is the total mass of that solute falling on a landscape in precipitation and is calculated by multiplying solute concentration in precipitation by precipitation amount. It is important to consider concentrations as well as the solute deposition amounts because both may influence the chemistry of aquatic and terrestrial ecosystems.

To evaluate spatial patterns in wet deposition in Washington, data on average inorganic nitrogen (ammonium plus nitrate) and sulfate concentrations in wet deposition were compiled for the six most recent years of available data (2000–05) from the Washington NADP/NTN sites (table 2).

Spatial patterns in concentrations of inorganic nitrogen in wet deposition appear to reflect variations in local and regional emissions and in precipitation amounts. Concentrations of ammonium and nitrate in precipitation were lowest at the Hoh site, near the Ranger Station in Olympic National Park (fig. 1, table 2). This was expected because the Hoh site is upwind from most regional sources of nitrogen emissions, and it receives abundant precipitation that dilutes solute concentrations. The other NADP/NTN sites in western Washington (Marblemount, La Grande, and Tahoma Woods) had substantially higher ammonium and nitrate concentrations, which may

Table 2. Average annual volume-weighted mean concentrations in wet deposition during 2000–05 at National Atmospheric Deposition Program/National Trends Network sites in Washington State.

[m, meters; $\mu\text{eq/L}$, microequivalents per liter; cm, centimeters]

Site ID	Site name	Year operation began	Elevation (m)	Ammonium ($\mu\text{eq/L}$)	Nitrate ($\mu\text{eq/L}$)	Inorganic Nitrogen ($\mu\text{eq/L}$)	Sulfate ($\mu\text{eq/L}$)	Hydrogen ($\mu\text{eq/L}$)	Calcium ($\mu\text{eq/L}$)	Precipitation (cm)
WA14	Hoh	1981	176	0.7	1.6	2.2	4.9	4.6	1.7	305
WA19	Marblemount	1985	123	1.5	5.0	6.6	5.0	8.1	1.3	192
WA21	La Grande	1985	617	2.8	5.5	8.3	7.6	8.9	1.7	93
WA24	Palouse	1986	766	9.6	7.8	17.5	7.1	5.2	2.9	46
WA99	Tahoma Woods	2000	421	1.5	3.6	5.1	4.6	6.8	1.3	121
	Paradise ¹	1989	1,560	2.1	3.5	5.6	7.5	7.3	3.1	262

¹A bulk-deposition site that is operated by the National Park Service at Paradise in Mount Rainier National Park is also included. Data for Paradise covers 2000 through spring 2005, except for 2001, which was excluded because of a data gap.

primarily reflect effects of regional nitrogen emissions from the Puget Sound area. Ammonium and nitrate concentrations were highest at the site in eastern Washington (Palouse), which is in an area with substantial agricultural land use and relatively low precipitation. Ammonium, which is derived mostly from agricultural emissions of ammonia, was notably higher at Palouse than at the other NADP/NTN sites in Washington. The importance of precipitation amount on nitrogen concentrations can be seen in figure 3A, which shows a strong inverse relation between precipitation amount and nitrogen concentrations ($r^2=0.87$); this relation may be due to “wash-out” of solutes from the atmosphere by precipitation. One implication is that deposition of inorganic nitrogen (fig. 4), which is the product

of concentration times precipitation amount, varied much less than concentrations of inorganic nitrogen (fig. 3). Wet deposition of inorganic nitrogen during 2002–04 ranged from 0.81 to 2.01 kilograms per hectare (kg/ha) at NADP/NTN sites in Washington State. During 2002–04, wet deposition of inorganic nitrogen was highest at Marblemount, near North Cascades National Park, where it was 40 percent greater than average for Washington State NADP/NTN sites; this spatial pattern may reflect Marblemount’s proximity to nitrogen emissions in the Puget Sound area.

Spatial variations in sulfate concentrations in precipitation were less variable than those of the nitrogen species, perhaps because marine aerosols are an important background

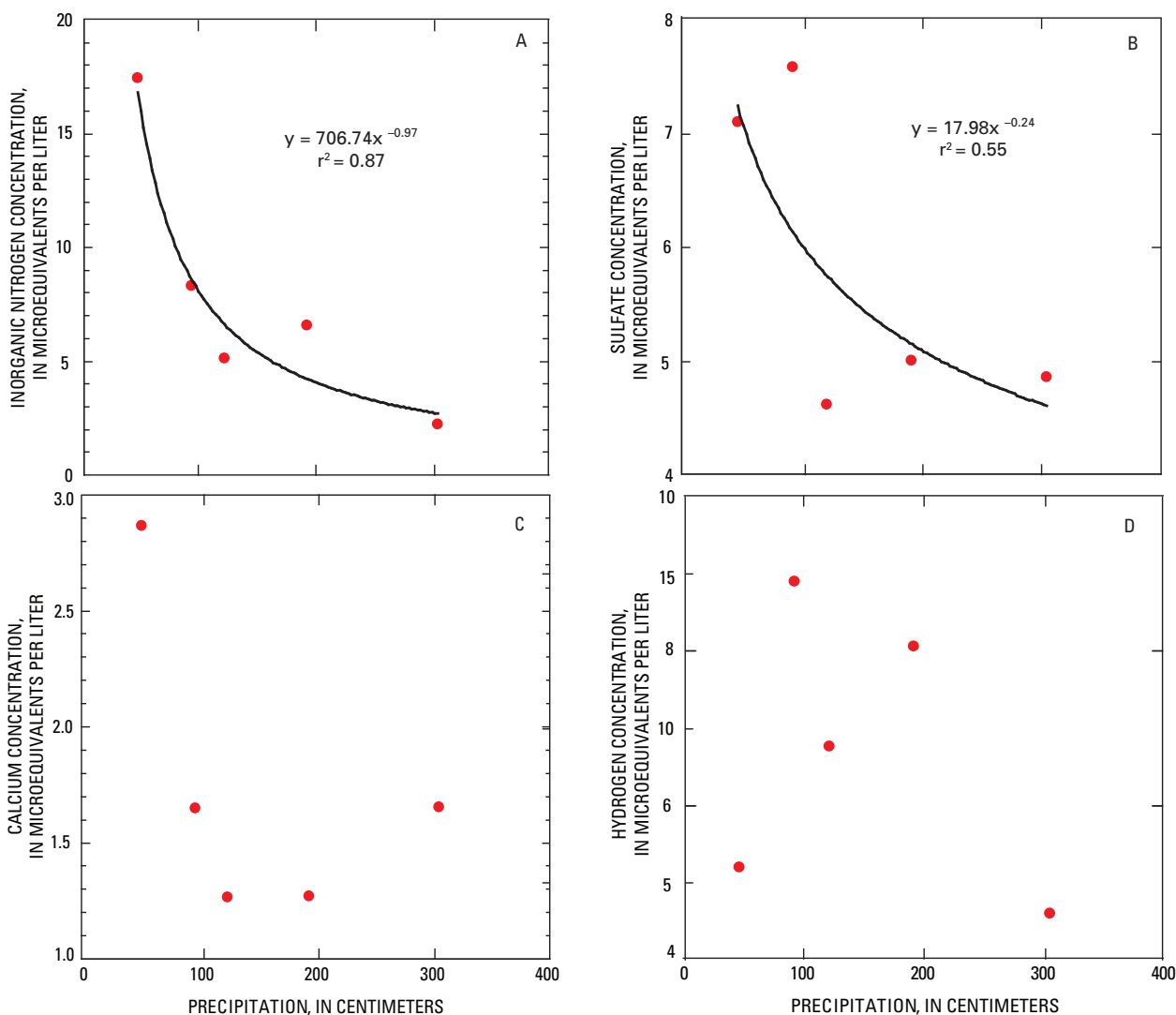


Figure 3. Relation between annual average precipitation amount and average concentrations of (A) inorganic nitrogen, (B) sulfate, (C) calcium, and (D) acidity at five National Atmospheric Deposition/National Trends Network sites in Washington State during 2005–06.

source of sulfur in precipitation, particularly near the coast. Sulfate concentrations varied inversely with precipitation amount, as was the case for nitrogen, but the correlation with precipitation was weaker ($r^2=0.55$, fig. 3B). Wet deposition of sulfur during 2002–04 ranged from 0.51 to 2.88 kg/ha and was relatively low at the driest sites and relatively high near the Pacific coast, reflecting the influence of marine aerosols (fig. 4).

Calcium concentrations in precipitation were highest at Palouse (table 2), which is a relatively dry site that is surrounded by agricultural fields and has several unpaved roads nearby (<http://nadp.sws.uiuc.edu/>, accessed January 2008). Dust from agricultural activities and unpaved roads can be an important source of calcium in precipitation and can reduce the acidity of precipitation through neutralization reactions (Hutchinson and others, 1986; Gillette and others, 1992; Sequeira, 1993). Although the driest site had the highest calcium concentrations, there was not a statistically significant relation between calcium concentration and precipitation amount (fig. 3C).

Precipitation acidity (hydrogen ion) was highest at La Grande and Marblemount, followed by Tahoma Woods, reflecting relatively high inputs of nitrogen and sulfur compounds (table 2). This spatial pattern indicates that emissions in the Puget Sound area may influence precipitation acidity at the La Grande, Marblemount, and Tahoma Woods sites. Acidity was lowest at the Hoh site, which is upwind from local and regional

sources of acidity. Precipitation acidity also was relatively low at Palouse, probably due to neutralization of acidity by calcium carbonate compounds associated with agricultural and road dust (Gillette and others, 1992). There was no discernible relation between acidity and precipitation amount (fig. 3D).

To evaluate changes in inorganic nitrogen and sulfur deposition over time, trend analyses were performed on precipitation amount and deposition of nitrogen species (NH_4 , NO_3 , total inorganic nitrogen), sulfur, acidity, and calcium for the four sites with long-term records going back to the early to mid-1980s (Hoh, Marblemount, La Grande, and Palouse). The trend analyses were performed on the entire record for each site using the Spearman's rho test (Helsel and Hirsch, 1992). All of the sites with long-term records had significant downward trends in sulfur deposition for the period of record through 2005 ($p < 0.02$; fig. 5). A fifth site, Tahoma Woods, had a downward trend from 2000, when it began operating, through 2005 (fig. 5). No sites had statistically significant trends in deposition of any of the other solutes tested.

Time-series plots reveal substantial complexity in sulfur deposition trends (fig. 5). It appears that substantial declines in sulfur deposition at Marblemount, La Grande, and Tahoma Woods occurred after 2000 (fig. 5). A multiple-regression analysis of sulfur deposition indicated that most of the change in sulfur deposition during 2002–05 at those sites was due to decreases in sulfate concentrations rather than precipitation amount.

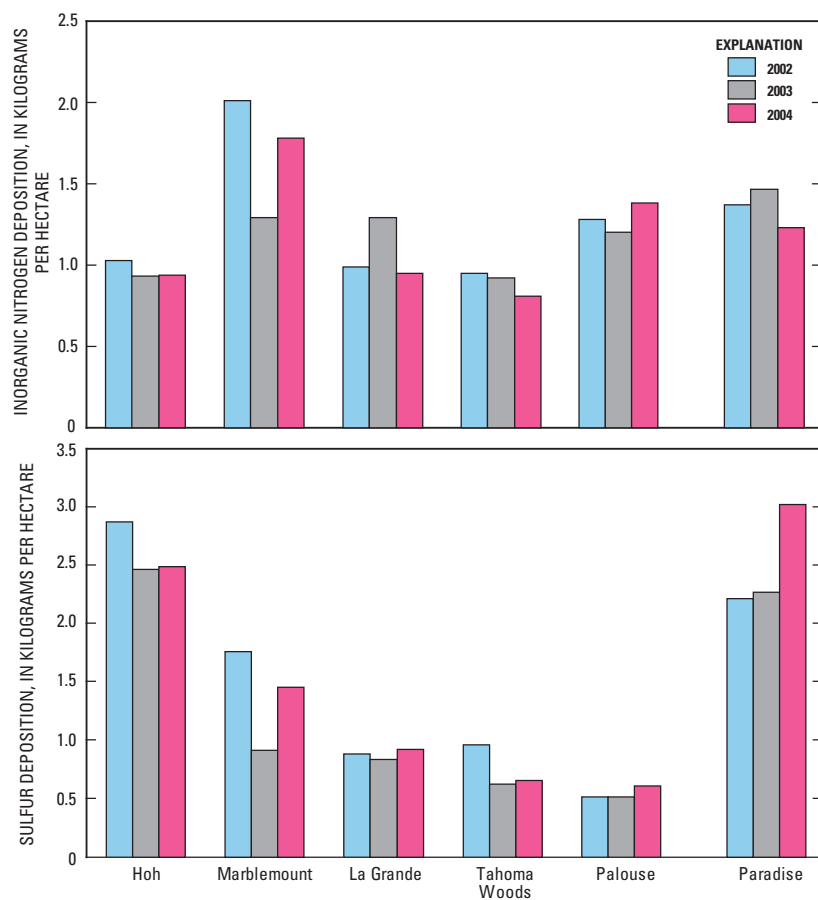


Figure 4. Deposition of inorganic nitrogen and sulfur at National Atmospheric Deposition/National Trends Network sites and at Paradise during 2002–04.

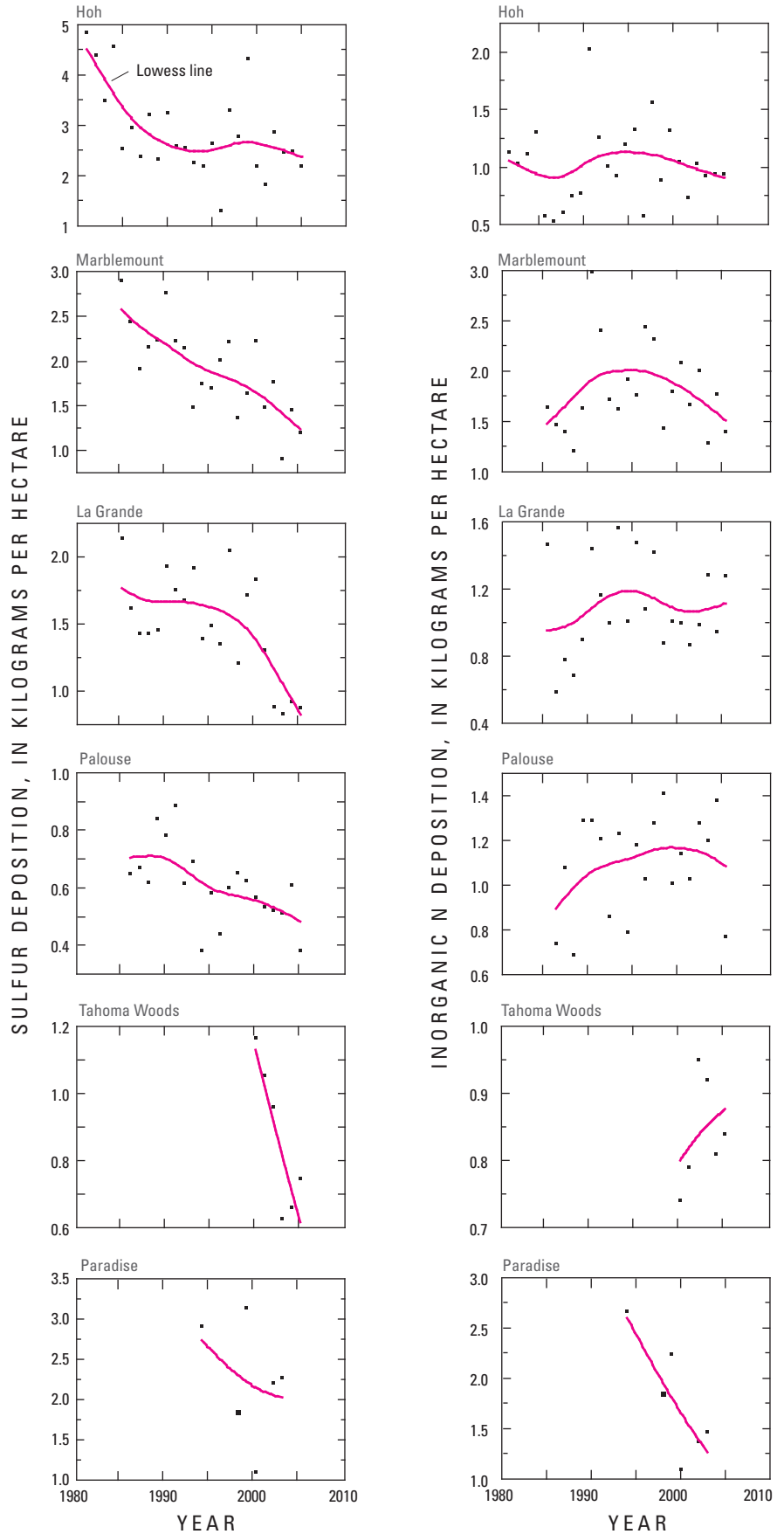


Figure 5. Temporal patterns in deposition of sulfur (S) and inorganic nitrogen (N) at Paradise and at National Atmospheric Deposition/National trends Network sites in Washington State. Only complete years of data are shown.

Data in the U.S. Environmental Protection Agency emissions inventory database (<http://www.epa.gov/ttn/chief/net/critsummary.html>, accessed July 2008) indicate that average annual sulfur dioxide emissions in Washington State during 1995–2005 decreased sharply beginning in 2001. Most of the change was due to a decline in sulfur emissions from the Centralia powerplant, 50 km west of MORA (fig. 6). Centralia was the largest source of sulfur emissions in the Western United States from the late 1990s through 2001, but scrubbers were installed in 2001–02 (WESTAR, 2001). The Centralia powerplant emitted 87,756 tons of sulfur dioxide in 1999; installation of the scrubbers reduced the plant’s emissions to 3,355 tons by 2005. The similarity in timing of declines in sulfur emissions at Centralia and sulfur deposition at Marblemount, La Grande, and Tahoma Woods indicates that emissions controls probably have reduced sulfur deposition in the area downwind from the powerplant. In contrast, nitrous oxide emissions in Washington have shown little change during the last decade; average annual nitrous oxide emissions during 1995–2005 were 18,628 tons, and no consistent temporal patterns existed among sites.

Bulk Deposition at Paradise

At Paradise, deposition of inorganic nitrogen was similar to that at other sites in Washington, but sulfur deposition was relatively high compared to most NADP/NTN sites in Washington (fig. 4). Although some of the difference might be due to use of a bulk collector rather than wet-only collectors, which are used at NADP/NTN sites, previous research in the Rocky Mountains suggests the effect may be small (Clow and others, 2002). High sulfur deposition at Paradise is at least partly attributable to orographically enhanced precipitation;

sulfate concentrations at Paradise were not substantially different from the NADP/NTN sites in Washington (table 2).

Trend analyses were performed on quarterly deposition values at Paradise for 2000 through mid-2005 (National Park Service, unpublished data, 2006) using the Spearman’s rho test. No significant trends were identified, but gaps in the record limit the power of the trend tests. It is noteworthy that sulfur deposition in 2002–04 was not substantially different from previous years, despite reduced emissions after installation of scrubbers on the Centralia powerplant in 2002 (fig. 5). This is in contrast to the strong declines in sulfur deposition at other sites downwind from Centralia beginning in 2002. The reason for the lack of change in deposition of sulfur at Paradise is unknown, but it suggests that Centralia might not be the primary source of sulfur in deposition at Paradise. It is possible that Paradise is above the critical atmospheric mixing zone, which would increase the dominance of regional emissions relative to local emissions.

Snowpack Chemistry

Deposition of nitrogen and sulfur in seasonal snowpacks was substantially different in 2005 and 2006 at NOCA; this was due to differences in SWE and in solute concentrations. SWE was 48 percent higher, and concentrations were 1 to 11 percent higher in 2006 than in 2005; as a result, deposition was 58 to 67 percent higher in 2006 than in 2005.

Nitrogen deposition was greater than sulfur deposition in both parks, particularly in NOCA (fig. 7). Average nitrogen deposition at the sites in NOCA was twice as high (0.99 kg/ha) as at the sites in MORA (0.48 kg/ha), which is consistent with spatial patterns noted in the NADP/NTN nitrogen deposition data. Average sulfur deposition amounts were similar at the two parks (0.42 and 0.43 kg/ha).

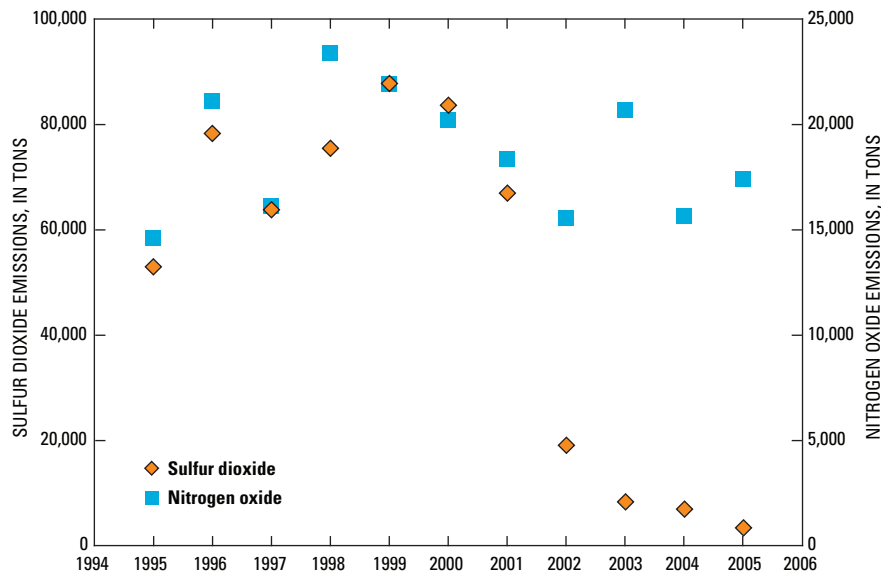


Figure 6. Emissions of sulfur dioxide (SO_2) and nitrogen oxide (NO_x) in Washington State during 1995–2005 (<http://www.epa.gov/castnet/>, accessed January 2008).

Nitrogen deposition was particularly high at Noisy Glacier, which is the westernmost snow-sampling site in NOCA (fig. 7; fig. 1). The relatively high nitrogen deposition at the Noisy Glacier site may reflect its proximity to emissions sources in the Puget Sound area. Noisy Glacier also receives abundant orographically enhanced snowfall because it is on the windward side of the mountain range.

Nitrogen and sulfur deposition in snow at MORA exhibited considerable spatial variability (fig. 7; fig. 1).

Dry Deposition

Dry deposition is measured at CASTNET sites in Mount Rainier (near Tahoma Woods), North Cascades (near Marblemount), and Olympic (near Hoh ranger station) National Parks. The data indicate that dry deposition accounts for less than 15 to 30 percent of total nitrogen and 10 to 22 percent of total sulfur deposition (fig. 8). The applicability of CASTNET dry-deposition data to ecosystems, however, is uncertain because dry deposition is strongly dependent on deposition substrate (Fenn and others, 2003). In addition, occult deposi-

tion (primarily fog) may be a substantial unmeasured component of total deposition (Fenn and others, 2003). Although the CASTNET data probably underestimate total deposition of inorganic nitrogen and sulfur to ecosystems in the Pacific Northwest, the data are useful for comparisons among CASTNET sites because of the use of standardized methods for the dry-deposition measurements.

Total deposition of nitrogen was greatest at the CASTNET site in NOCA (NCS415), primarily due to high amounts of wet-deposited nitrate (fig. 9). Total nitrogen deposition at this site was 2.0 kg/ha in 2004, compared to 1.3 kg/ha at the site in Olympic National Park (OLY421), and 1.1 kg/ha in MORA (MOR409). Total sulfur deposition was greatest at the CASTNET site in Olympic National Park, primarily due to high amounts of wet-deposited sulfate, as expected given its proximity to the Pacific Ocean. Total sulfur deposition in 2004 at the site in Olympic National Park was 2.5 kg/ha, at the site in NOCA it was 1.5 kg/ha, and in MORA it was 0.93 kg/ha. There were no statistically significant trends in deposition of dry nitrogen, dry sulfur, total nitrogen, or total sulfur, but the record is relatively short, making trend detection difficult.

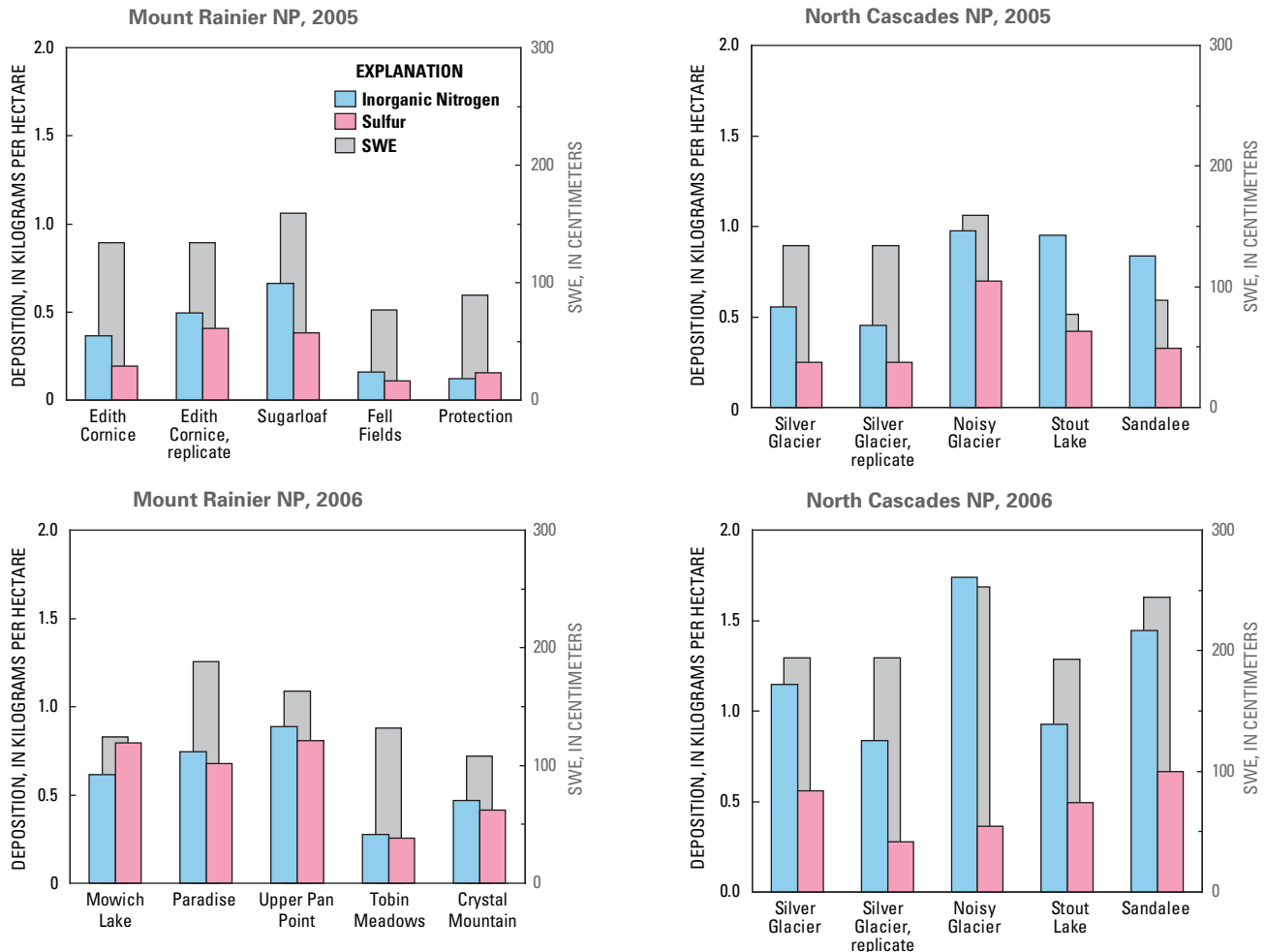


Figure 7. Deposition of inorganic nitrogen and sulfur, and snow water equivalent (SWE) in snow sites in Mount Rainier National Park and North Cascades National Park during 2005–06.

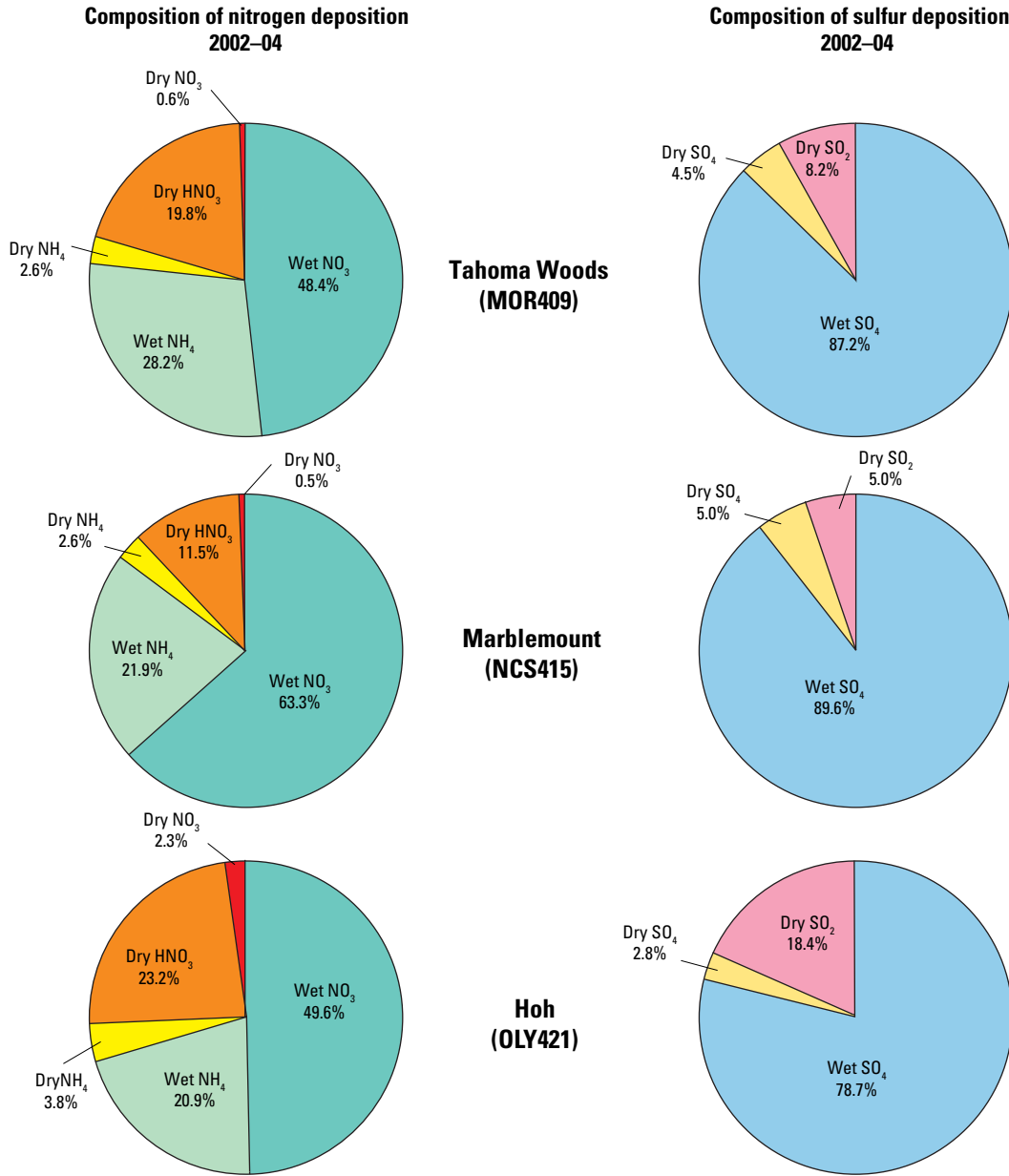


Figure 8. Composition of nitrogen and sulfur deposition at Clean Air Status and Trends sites in Washington State during 2002-04 (3-year average). (Percentages do not equal 100 because of rounding.)

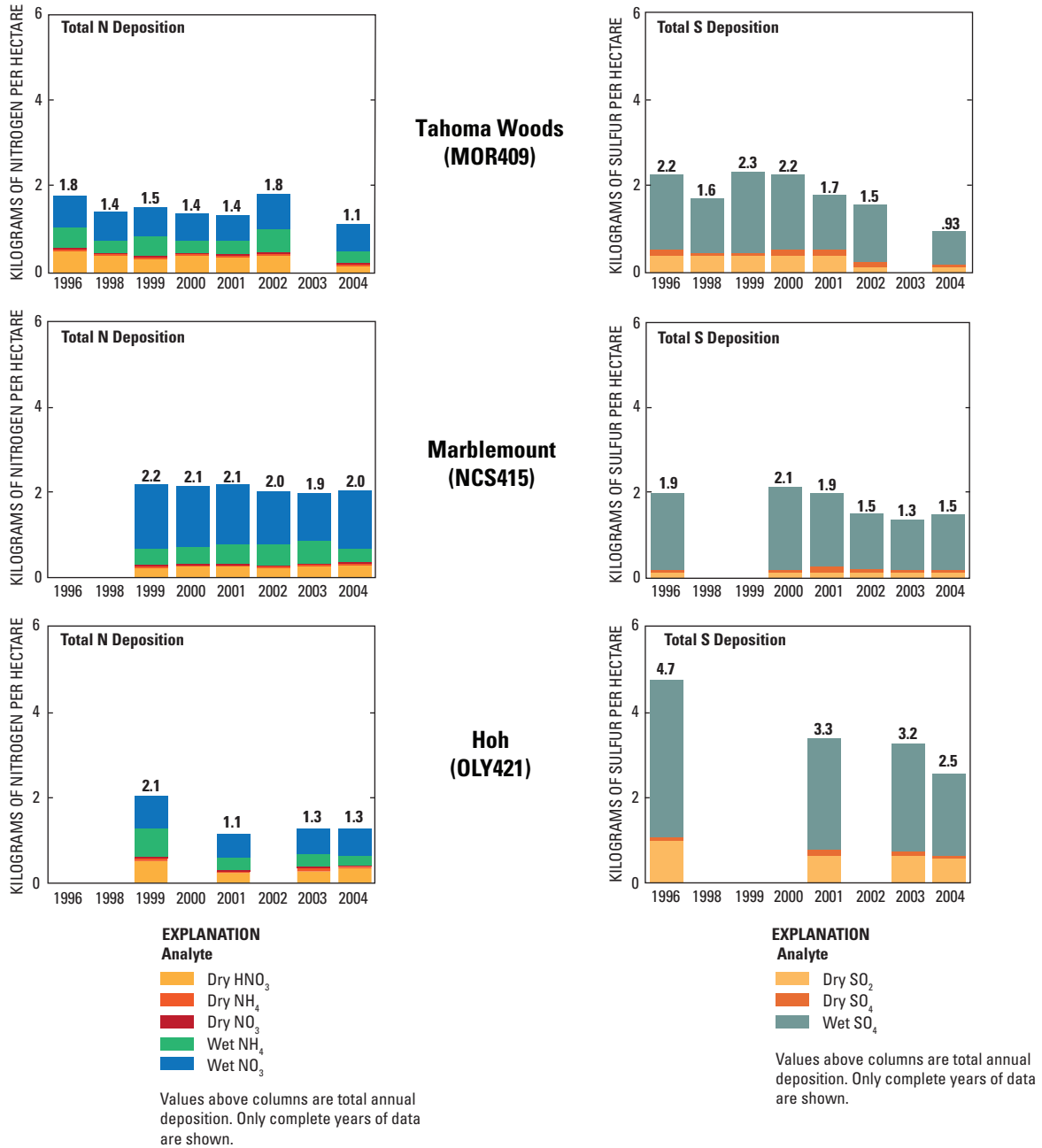


Figure 9. Total nitrogen and sulfur deposition at Clean Air Status and Trends sites in Washington State.

Surface-Water Chemistry

Volume-Weighted Mean Solute Concentrations

Specific conductance is a simple indicator of total solute load in natural waters and is highly correlated with alkalinity, so it reflects basin sensitivity to nitrogen and sulfur deposition. Volume-weighted mean (VWM) specific-conductance values for the study period at the outlets to Eunice Lake and Lake Louise were quite low (7.3 and 7.9 $\mu\text{S}/\text{cm}$, respectively), reflecting the sensitivity of these basins to atmospherically deposited nitrogen and sulfur (table 3). These values are less than one-half of the average specific-conductance values measured in MORA during the 1985 Western Lake Survey (Eilers and others, 1987) and during a more extensive lake survey conducted in 1988 (Larson and others, 1994) (table 4). Specific conductance at the two sites in NOCA was somewhat higher than at the MORA sites; VWM specific-conductance values at Newhalem Creek and Thornton Creek were 16.6 and 14.2 $\mu\text{S}/\text{cm}$, respectively. These values are comparable to those measured in NOCA during the Western Lake Survey and during lake surveys conducted during 1989–93 by Larson and others (1999) (table 4).

Volume-weighted mean alkalinities at Eunice Lake and Lake Louise were 26.1 and 41.7 $\mu\text{eq}/\text{L}$, respectively, (table 3), less than one-half of the average lake alkalinity measured during the MORA lake surveys (Eilers and others, 1987; Larson and others, 1994). Seasonal variability probably accounts for less than 20 percent of the difference in alkalinities between this study and the lake surveys, based on comparison of VWM and summer alkalinity concentrations measured in the present study. The low alkalinity values of Eunice Lake and Lake Louise indicate that they are sensitive to episodic acidification and make them good candidates for monitoring of potential acid deposition effects in the park. Volume-weighted mean alkalinities for the two streams in NOCA were 105.9 $\mu\text{eq}/\text{L}$ at Thornton Creek and 111.1 $\mu\text{eq}/\text{L}$ at Newhalem Creek, approximately twice as high as the average alkalinity measured during the NOCA lake surveys (Eilers and others, 1987; Larson and others, 1999). The relatively high alkalinity of the NOCA streams is attributable to differing basin characteristics. The two streams monitored during the present study are in relatively large basins with abundant soil and vegetation. The NOCA lake surveys focused on small basins at higher elevation with thin, patchy soils and sparse vegetation that provide only minimal buffering capacity. Although access to high-elevation surface-water systems is difficult, especially during winter and spring, they are better candidates for monitoring of potential episodic acidification than the low-elevation streams monitored in this study because they are much more sensitive to acidic deposition.

Volume-weighted mean nitrate concentrations were very low at the sites in MORA (0.5 and 1.0 $\mu\text{eq}/\text{L}$) but were somewhat higher at the sites in NOCA (3.4 and 5.7 $\mu\text{eq}/\text{L}$; table 3). The higher concentrations at the sites in NOCA could be due in part to the higher nitrogen deposition that the area

receives, as indicated by spatial patterns in NADP/NTN and snowpack chemistry data (figs. 4 and 7). Another possible source of nitrogen in the NOCA streams could be nitrogen-fixing bacteria associated with red alders (Edmonds, 1980; Luken and Fonda, 1983), which are present along the riparian corridors in both study basins in NOCA (no alders have been observed in the Eunice Lake or Lake Louise basins). To test this hypothesis, samples were collected in early September 2006 from the gage on Thornton Creek (420-m elevation) and from the Thornton Lake outlet (1,394-m elevation), which is in the headwaters of the Thornton Creek drainage, above the elevation where alders grow. The nitrate concentrations during this sampling event were 4.1 $\mu\text{eq}/\text{L}$ at the Thornton Creek gage and 0.6 $\mu\text{eq}/\text{L}$ at the Thornton Lake outlet. Although this finding should be further tested through additional sampling along transects covering a range of elevations, the results are consistent with the hypothesis that the primary source of nitrate at the gage on Thornton Creek is nitrogen fixation rather than atmospheric deposition. This finding does not preclude deleterious effects from atmospheric deposition of nitrogen at high elevations. In fact, Larson and others (1999) documented a positive correlation between nitrate concentrations and elevation in lakes they sampled in NOCA during 1989–93. Their lake surveys focused on high-elevation lakes, above elevations where red alder is common, thus minimizing the effect of alders. Despite the difficulty of access, it is important that long-term monitoring that is intended to identify potential effects of nitrogen deposition be conducted above the elevation where alders grow (about 1,000 m).

Volume-weighted mean sulfate concentrations at Eunice Lake and Lake Louise were 7.4 and 8.2 $\mu\text{eq}/\text{L}$, respectively (table 3). Volume-weighted mean sulfate concentrations at Thornton Creek and Newhalem Creek were 9.1 and 23.2 $\mu\text{eq}/\text{L}$, respectively. Sea salt accounted for ≤ 1.8 $\mu\text{eq}/\text{L}$ of sulfate in the surface water, with the remainder coming from atmospheric deposition, except at Newhalem Creek. Mass-balance calculations indicate that in the Newhalem basin, streamflow export of sulfate is approximately four times as large as wet deposition of sulfate; this indicates that there probably is a mineral weathering source of sulfur in that basin (for example, pyrite or chalcopyrite). It might be possible to test this hypothesis using stable isotopes of sulfur (Turk and others, 1993).

Seasonal Patterns in Surface-Water Chemistry

There were strong seasonal patterns in solute concentrations in the streams at all of the study sites, primarily reflecting the mixing of varying proportions of slightly acidic snowmelt with low to moderately alkaline ground water (figs. 10–13). Snowmelt inputs were greatest during springtime and lowest during fall and winter. Although the seasonal patterns were similar between years, earlier snowmelt in 2005 caused seasonal patterns in surface-water chemistry to occur earlier as well. Because snowmelt ended earlier in 2005, there was a longer period of high solute concentrations during summer 2005 relative to summer 2006 (figs. 10–13).

Table 3. Solute concentrations in surface water at study sites, 2005–06 water years.[$\mu\text{eq/L}$, microequivalents per liter; $\mu\text{S/cm}$, microsiemens per centimeter; $\mu\text{mol/L}$, micromoles per liter; mg/L , milligrams per liter]

	Alkalinity ($\mu\text{eq/L}$)	Specific conduc- tance ($\mu\text{S/cm}$)	Hydrogen ($\mu\text{eq/L}$)	Calcium ($\mu\text{eq/L}$)	Magne- sium ($\mu\text{eq/L}$)	Sodium ($\mu\text{eq/L}$)	Potassium ($\mu\text{eq/L}$)	Ammonium ($\mu\text{eq/L}$)	Silica ($\mu\text{mol/L}$)	Chloride ($\mu\text{eq/L}$)	Sulfate ($\mu\text{eq/L}$)	Nitrate ($\mu\text{eq/L}$)	Dissolved organic carbon (mg/L)	Sea-salt corrected sulfate ¹ ($\mu\text{eq/L}$)
Eunice Lake outlet (n=32)														
standard deviation	15.0	1.4	2.6	8.0	1.2	4.8	1.1	5.4	7.5	3.1	2.0	2.7	0.4	1.7
average	32.6	7.5	0.9	28.0	5.3	22.3	2.3	2.2	29.5	14.6	7.4	0.9	0.9	5.8
VWM average	26.1	7.3	0.5	28.3	5.9	22.6	1.6	0.6	31.2	16.9	7.4	1.0	0.4	5.5
Lake Louise outlet (n=30)														
standard deviation	11.2	1.6	0.1	7.4	1.7	5.3	0.6	0.8	12.5	2.4	2.2	0.6	0.3	1.9
average	44.8	8.2	0.3	36.2	8.6	25.7	2.2	0.4	66.1	9.5	8.8	0.4	1.0	7.8
VWM average	41.7	7.9	0.3	35.2	8.4	24.5	2.1	0.3	62.0	9.9	8.2	0.5	0.6	7.1
Newhalem Creek (n=25)														
standard deviation	28.5	3.4	0.2	18.3	6.5	6.6	2.8	0.9	16.8	2.0	6.6	2.9	0.3	6.4
average	128.9	18.9	0.1	110.6	25.0	26.1	15.3	0.6	70.2	6.3	28.3	5.9	0.8	27.6
VWM average	111.1	16.6	0.1	97.0	21.0	22.1	13.3	0.6	59.7	5.6	23.2	5.7	0.8	22.6
Thornton Creek (n=25)														
standard deviation	55.4	6.4	0.2	36.7	11.0	11.2	5.8	1.0	19.9	4.3	5.3	2.1	0.2	4.8
average	160.8	20.4	0.1	114.1	33.1	30.5	16.6	0.6	70.2	10.9	12.4	4.2	0.8	11.2
VWM average	105.9	14.2	0.1	81.0	24.3	21.1	11.2	0.3	52.2	7.2	9.1	3.4	0.7	8.3

¹Sea-salt corrected sulfate is sulfate in stream water minus sulfate from atmospherically deposited sea salt.

Table 4. Average solute concentrations during lake surveys in Mount Rainier National Park (MORA) and North Cascades National Park (NOCA).[m, meters; ha, hectares; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; $\mu\text{eq}/\text{L}$, microequivalents per liter; $\mu\text{g}/\text{L}$, micrograms per liter; \leq , equal to or less than; --, no data]

Survey	Data source	Number of lakes	Elevation (m)	Depth (m)	Area (ha)	Specific conductance ($\mu\text{S}/\text{cm}$)	pH	Ammonium ($\mu\text{eq}/\text{L}$)	Nitrate ($\mu\text{eq}/\text{L}$)	Sulfate ($\mu\text{eq}/\text{L}$)	Alkalinity ($\mu\text{eq}/\text{L}$)	Total Phosphorus ($\mu\text{g}/\text{L}$)
MORA, 1985	1	5	1,449	8.7	2.9	25.7	6.3	0.3	0.1	27.5	202.2	4.7
MORA, 1988	2	27	1,547	13.8	5.5	15.2	6.7	0.2	0.2	--	122.0	11.0
NOCA, 1985	1	6	1,735	34.4	26.8	10.3	6.5	≤ 0.1	0.4	29.1	68.3	1.2
NOCA, 1989–93	3	58	1,503	7.1	14.5	24.2	7.0	0.4	0.5	--	52.0	7.0
Western Lake Survey, high-elevation lakes in northern Cascade Mountains	1	87	1,500	17.3	12.6	24.0	6.6	0.2	0.6	29.5	197.1	3.9

Data sources:

1. Western Lake Survey, Eilers and others, 1987.
2. MORA lake survey, Larson and others, 1994.
3. NOCA lake surveys, Larson and others, 1999.

The following general patterns were observed for solutes derived primarily from mineral weathering (specific conductance, base cations, silica, alkalinity), with some variation by solute, as discussed in more detail in the next paragraph. Concentrations of weathering products generally were moderate at the beginning of the water year and increased through the winter, reflecting increasing hydrologic residence times and interaction between water and geologic substrates (soil and rock) (figs. 10–13). Concentrations peaked just before the onset of snowmelt (April) and started to decrease when snowmelt began (May) due to the influx of very dilute snowmelt water. Annual minimum concentrations occurred near the time of peak snowmelt, with the precise timing varying by solute, site, and year. Concentrations gradually increased through the summer as snowmelt tapered off.

The behavior of individual solutes during snowmelt is of particular interest because of the potential for episodic acidification. Base cations (calcium, magnesium, sodium, potassium), silica, and dissolved organic carbon reached their minima slightly after peak snowmelt, indicating that their concentrations were primarily controlled by mixing of dilute snowmelt with relatively concentrated subsurface water (soil water and ground water). The fact that solute concentrations reached their minima after the peak in snowmelt runoff probably is related to flushing of solutes from the soil, where solutes accumulate during winter (Clow and Drever, 1996).

Seasonal patterns in alkalinity generally were similar to those of the other weathering products, although there were some important exceptions. At Lake Louise in 2005, the annual minimum in alkalinity concentrations was coincident with the annual maximum in sulfate concentrations, and the minimum occurred on April 30, before the snowmelt peak (fig. 10). These results indicate that, although much of the sea-

sonal variation in alkalinity was due to dilution, some of the decrease in alkalinity probably was due to a pulse of sulfuric acid released from the melting snowpack.

At Eunice Lake, a sample collected in mid-April 2006 (fig. 11) had an alkalinity of $-18 \mu\text{eq}/\text{L}$, a pH of 4.8, and very low concentrations of weathering products ($\leq 6.0 \mu\text{mol}/\text{L}$). The sample also had anomalously high concentrations of sulfate, nitrate, and ammonium (16.5, 15.0, and $6.0 \mu\text{eq}/\text{L}$, respectively) compared to other Eunice Lake outlet water samples. Although the sample was collected from the outlet stream, streamflow at the time was very low ($< 0.1 \text{ m}^3/\text{s}$) and water in the stream probably was not outflow from Eunice Lake, based on the anomalous chemistry. Flushing of organic acids from the soil can be ruled out because of the low concentrations of weathering products and dissolved organic carbon in the sample. The chemistry of this sample is consistent with preferential elution of acidic components from the snowpack (Mulvaney and others, 1988; Berg, 1992). Although there was little flow in the stream, the water may be representative of small pools in the stream channel or wetlands that form at the onset of snowmelt. The chemistry of the sample is indicative of episodic acidification, and this type of water may pose a hazard for sensitive aquatic species and amphibians that live in stream or wetland environments (Barmuta and others, 1990; Stoddard, 1995).

Seasonal patterns in sulfate concentrations were generally similar to those of solutes derived from weathering, except that seasonal maxima sometimes occurred somewhat later, on the rising limb of the snowmelt hydrograph, rather than prior to the beginning of snowmelt. The seasonal maxima occurs later for sulfate than for weathering products because sulfate is derived from melting snow as well as from flushing of sulfate temporarily stored in the soil in organic and inorganic forms.

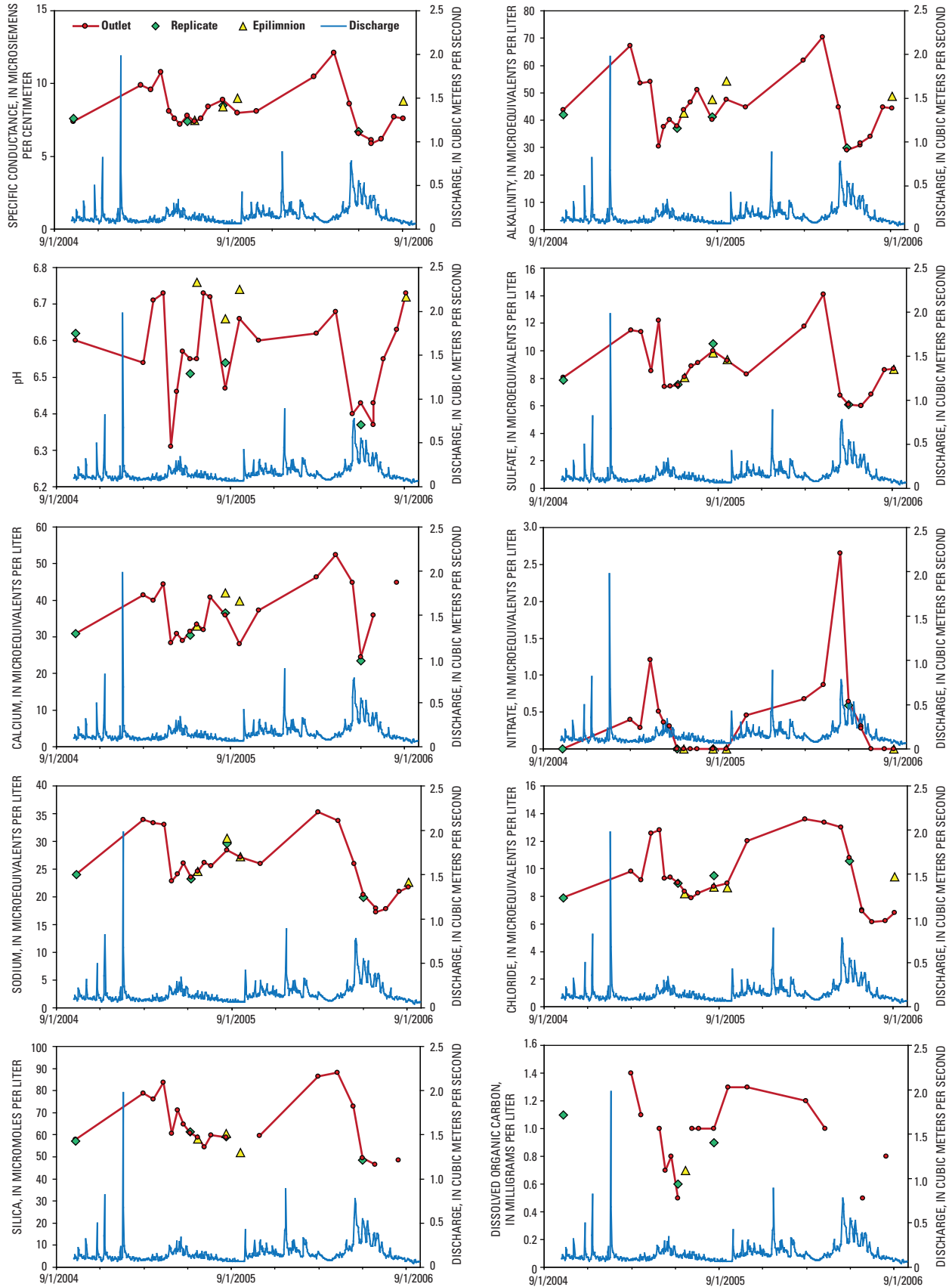


Figure 10. Seasonal patterns in solute concentrations and discharge at Lake Louise outlet.

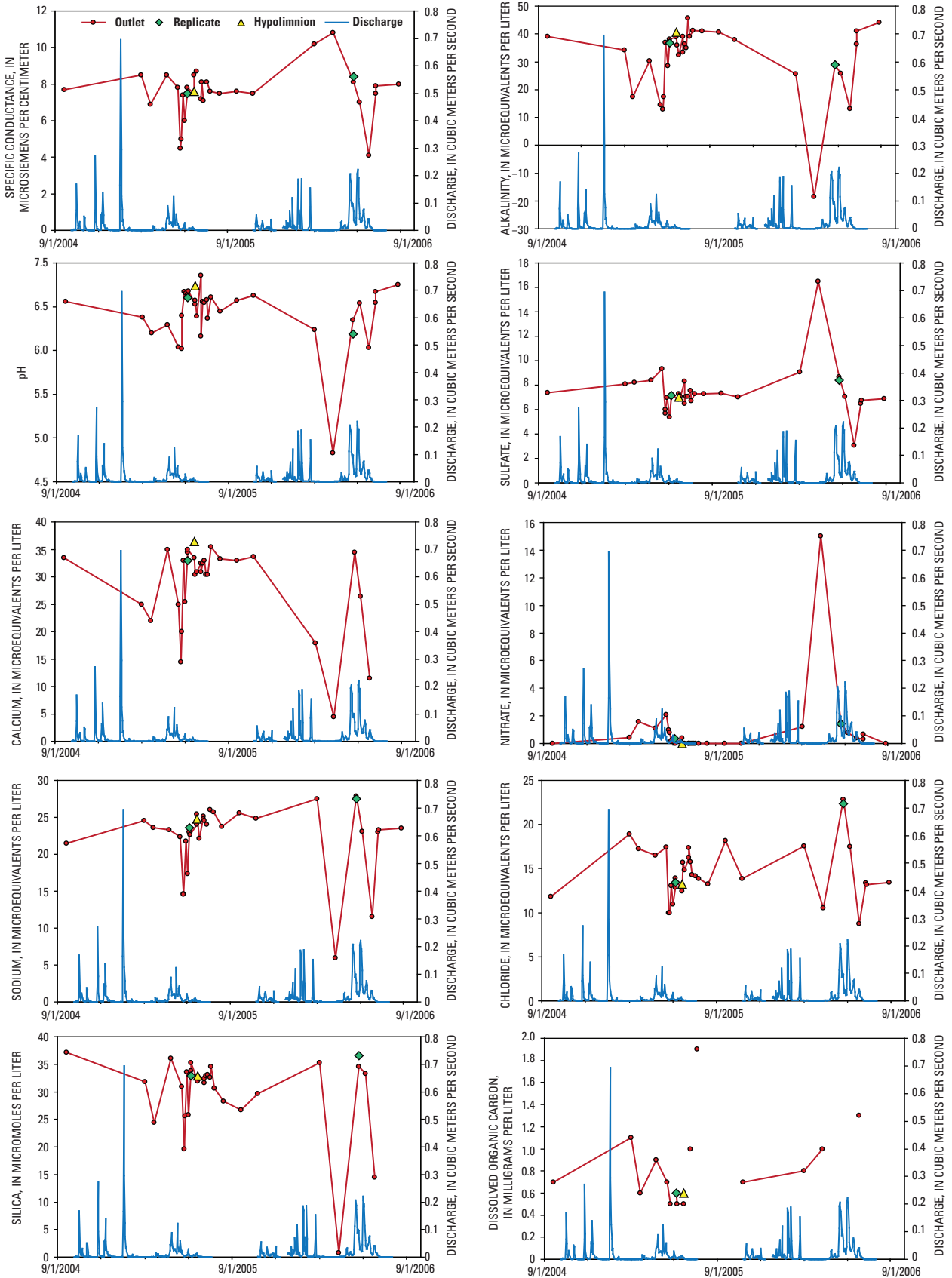


Figure 11. Seasonal patterns in solute concentrations and discharge at Eunice Lake outlet.

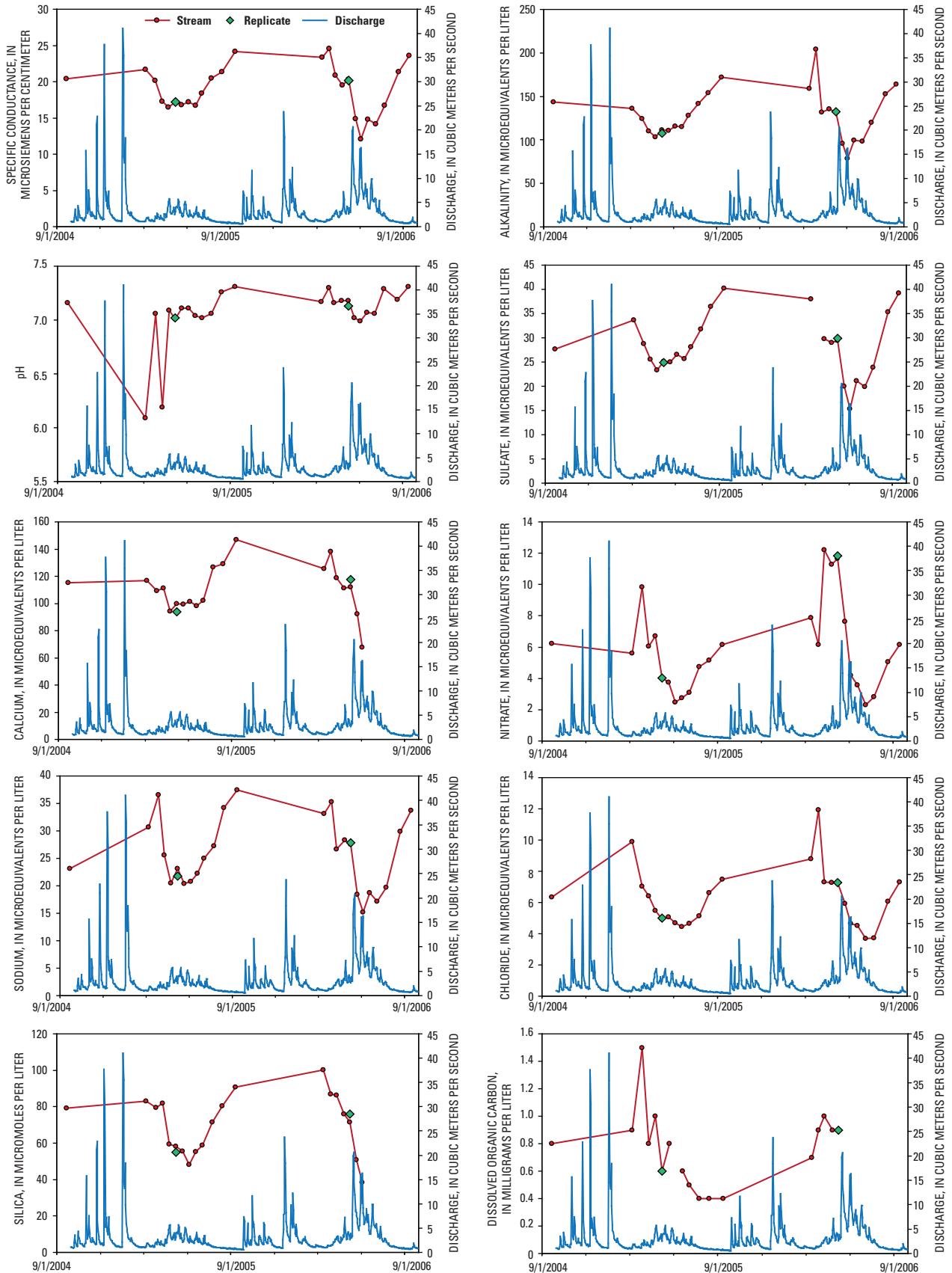


Figure 12. Seasonal patterns in solute concentrations and discharge at Newhalem Creek, above East Fork.

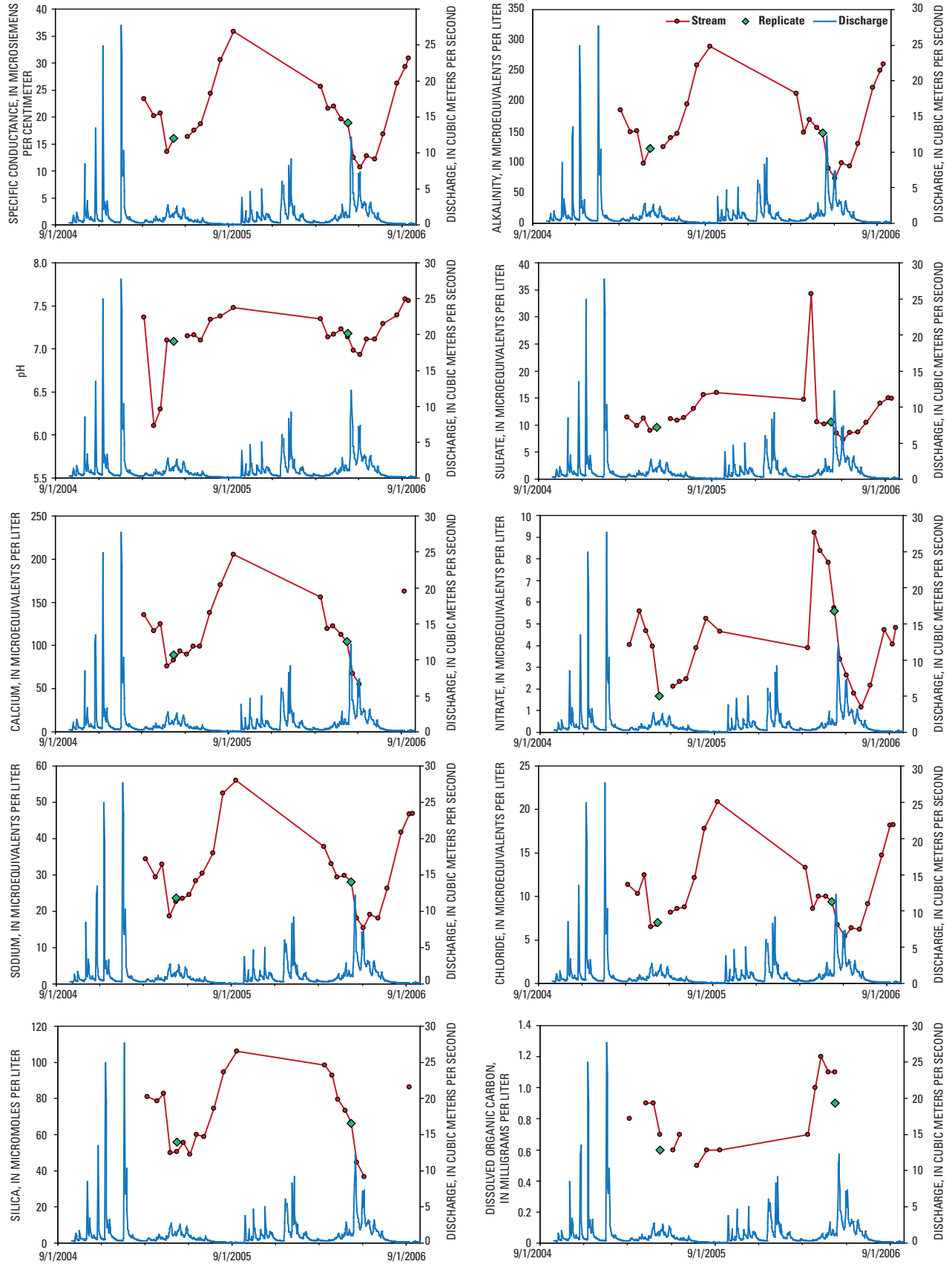


Figure 13. Seasonal patterns in solute concentrations and discharge at Thornton Creek.

Seasonal patterns in nitrate concentrations were somewhat different from those for other solutes, reflecting differences in sources and cycling processes. In general, nitrate concentrations increased from the beginning of the water year through the winter as uptake by terrestrial and aquatic biota declined. Nitrate reached a maximum during the rising limb of the snowmelt runoff peak, reflecting release of an ionic pulse of nitrate from the snowpack and(or) flushing of nitrate from catchment soils. The nitrate concentration peak was relatively short, and concentrations declined as snowmelt decreased.

On the falling limb of the snowmelt runoff peak, behavior of nitrate at the sites in MORA diverged from that of the sites in NOCA. At MORA, nitrate concentrations continued to decline through the summer to values below the analytical detection limit due to biotic uptake. At NOCA, however, nitrate concentrations increased from the end of snowmelt through the growing season. Furthermore, nitrate concentrations in the NOCA streams usually were substantially higher than in atmospheric deposition. This, and the seasonal pattern in nitrate concentrations (high during growing season), could be interpreted as being indicative of nitrogen saturation. The contribution of nitrate from biologic fixation in red alder stands is, however, a more likely explanation, as previously discussed.

Hydrogeochemical Processes Controlling Surface-Water Chemistry

Plots of the relation between solute concentration and discharge can provide insight into hydrologic and geochemical processes controlling surface-water chemistry. Simple mixing of two water sources of differing concentrations will produce a parabolic curve in a plot of concentration in relation to discharge (fig. 14). At the study sites, stream-water concentrations of most solutes are highest just before snowmelt, when relatively concentrated ground water is the dominant source of water in the stream. During snowmelt, very dilute snowmelt water is added to the stream, creating a mixture with an intermediate concentration. As snowmelt inputs increase on the rising limb of the snowmelt hydrograph, stream-water concentrations decline along a parabolic path until they reach a minimum on the plot of concentration in relation to discharge. Subsequently, on the falling limb of the snowmelt hydrograph, snowmelt inputs decline and stream-water concentrations rise. If the concentrations of the two source waters are constant, the concentration/discharge curve will follow the same parabolic path on the falling limb of the snowmelt hydrograph as it did on the rising limb (fig. 14A). However, if the concentration of one or both of the source waters varies over time, the rising and falling limb curves will not coincide, leading to hysteresis in the concentration/discharge plot (fig. 14B). Two important processes commonly lead to variations in source-water concentrations in alpine settings: flushing of subsurface pore waters with dilute, slightly acidic snowmelt (Clow and Drever, 1996), and preferential elution of solutes from the snowpack (Berg, 1992).

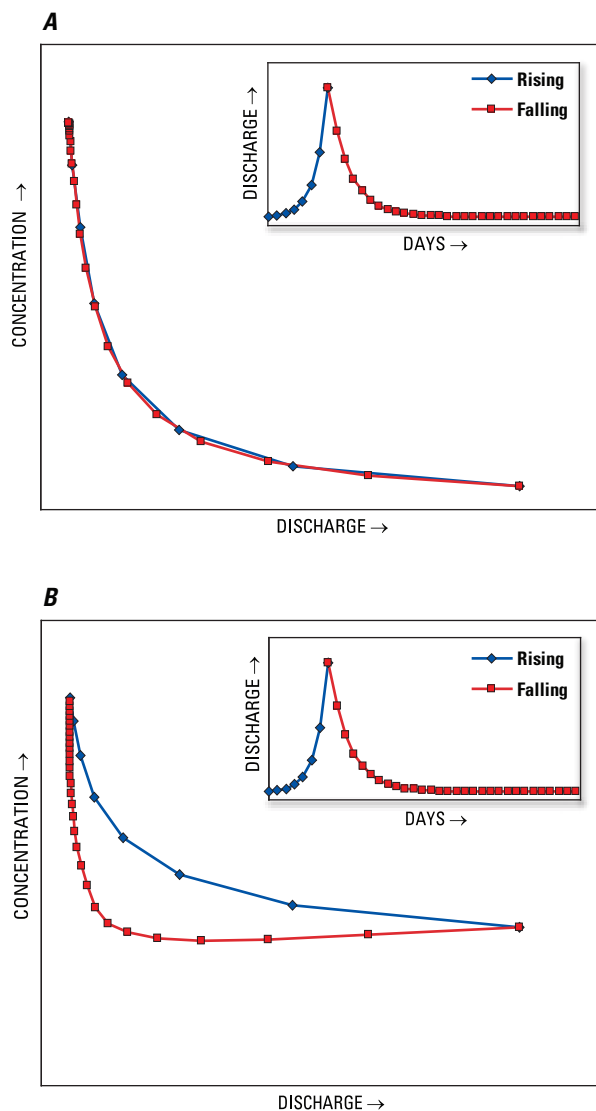


Figure 14. Plots showing relation between surface-water solute concentrations and discharge under assumptions of (A) constant subsurface-water concentrations, and (B) variable subsurface-water concentrations.

Surface-water chemistry at all of the sampling sites in this study exhibited hysteresis, which was more pronounced during the relatively wet year of 2006 than in 2005. The data from Lake Louise provide the clearest example. At the Lake Louise outlet, solute concentrations showed little hysteresis in 2005, but they showed strong hysteresis in 2006, with concentrations higher on the rising limb than on the falling limb of the snowmelt hydrograph (fig. 15). The lack of hysteresis in 2005 indicates that neither flushing of subsurface waters nor preferential elution of solutes from the snowpack had a strong influence on source-water concentrations that year. The strong hysteresis in 2006 is best explained by flushing of solutes from the subsurface reservoir. Alkalinity is commonly absent in snowmelt, so preferential elution from the snowpack cannot explain its hysteretic behavior. Higher alkalinity on the rising

limb of the snowmelt runoff peak is associated with flushing of base cations from the subsurface reservoir. Flushing of the subsurface reservoir may actually include several processes, including (1) physical dilution of water in the subsurface, and (2) geochemical processes such as cation exchange and dissolution of reactive secondary minerals. Cation exchange affects only the behavior of cations, whereas dissolution of secondary minerals, such as amorphous aluminosilicates, is more likely to affect the behavior of silica.

For cations, dilution of subsurface water probably has more of an influence on their hysteretic behavior than cation exchange because the amount of acidity in the snowpack available for cation exchange is small compared to the flux of cations entering the stream. This interpretation is supported by the behavior of chloride, which shows very strong hysteresis, despite not being subject to cation-exchange processes (fig. 15). Dilution of subsurface water by infiltrating snowmelt water is likely the dominant process causing hysteresis of chloride. The difference in hysteretic behavior of chloride and silica provides an indication of the relative importance of dilution of subsurface water and dissolution of reactive secondary minerals in influencing the behavior of silica. Chloride concentrations continue to decline on the falling limb of the snowmelt hydrograph, but silica is relatively invariant, indicating that another process, such as dissolution of amorphous aluminosilicates, is important (fig. 15).

Response of Surface-Water Chemistry to Storms

The effect of storms on stream and lake-outlet chemistry in MORA and NOCA is poorly known due to a lack of data. Assessing stream-chemistry response to storms requires collection of water chemistry at high frequency during storms, which has not been done in the study areas. The focus of the present study was on characterization of seasonal patterns in stream chemistry rather than changes in the chemistry during storms. However, the collection of continuous streamflow and specific-conductance data, which was done as part of this study, may allow some inferences regarding how stream chemistry might respond to storms.

At Lake Louise, several storms during the winter of 2004–05 caused precipitous declines in specific conductance and large increases in discharge while air temperatures were well above freezing, indicating that the storms contributed substantial amounts of dilute rainwater and melted snow to the lake (fig 16). During the storm on January 18–19, 2005, for example, specific conductance declined from 9 to 2 $\mu\text{S}/\text{cm}$, discharge increased by an order of magnitude, and air temperatures ranged from 7.4°C to 8.0°C.

It would be useful to know how surface-water alkalinity responded to storms because of potential damage to sensitive aquatic biota that can occur from episodic acidification. Because storm samples were not collected from the lake outlet, it was not possible to evaluate alkalinity responses directly. However, a strong relation between specific conductance and alkalinity exists ($r^2 = 0.76$; fig. 17), indicating it might be

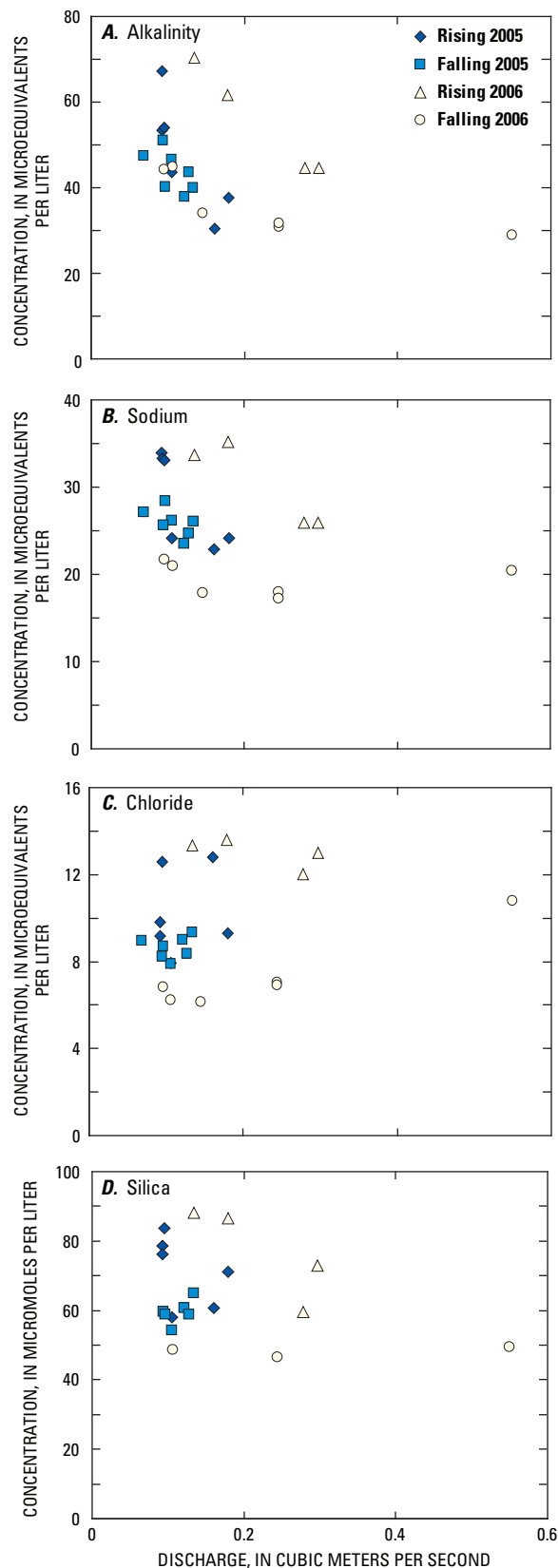


Figure 15. Plots showing relations between concentration and discharge at Lake Louise outlet for (A) alkalinity, (B) sodium, (C) chloride, and (D) silica, during 2005–06.

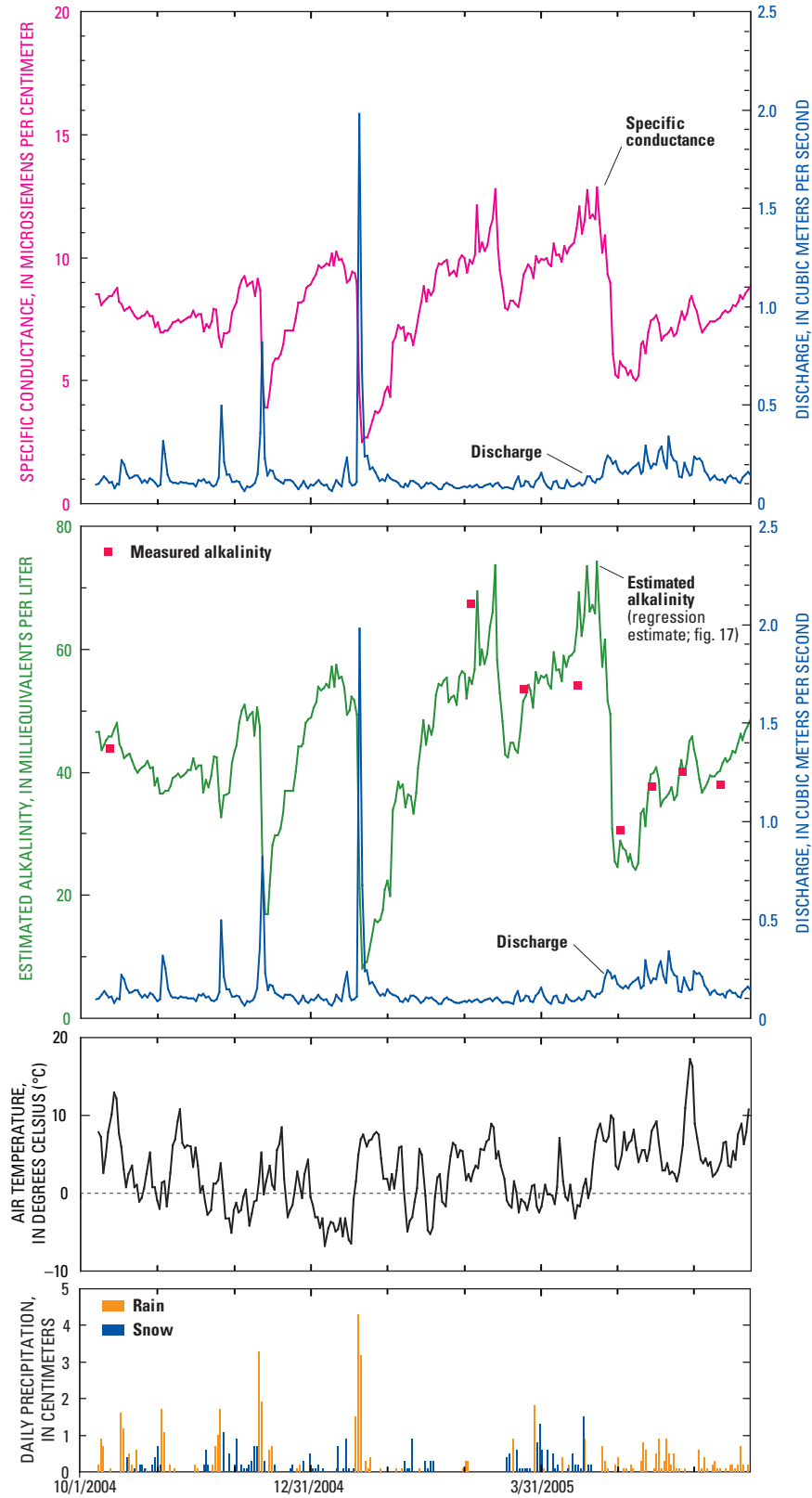


Figure 16. Time-series plot showing discharge, specific conductance, alkalinity, air temperature, and daily precipitation at Lake Louise outlet in response to storms.

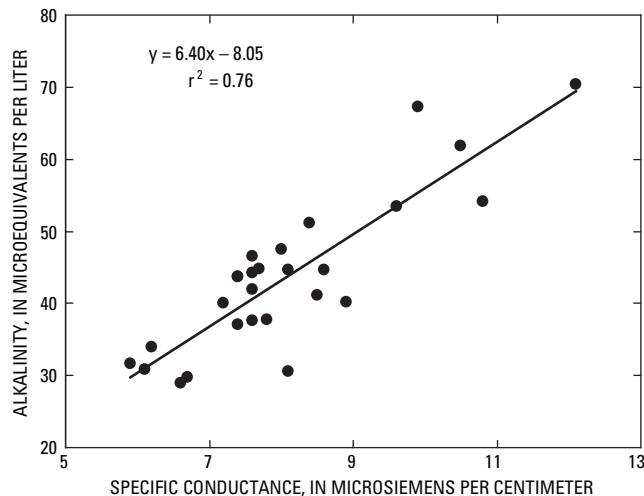


Figure 17. Relation between specific conductance and alkalinity in samples collected at the Lake Louise outlet during 2005–06.

possible to estimate alkalinity from the continuous record of specific conductance at the gages. This was done for the Lake Louise outlet for several rain-on-snow events that occurred during the winter of 2004–05 (fig. 16). Estimated alkalinity declined from 50 to 17 $\mu\text{eq/L}$ during the storm in early December 2004, and it dropped from 57 to 8 $\mu\text{eq/L}$ during the mid-January 2005 storm (fig. 16). Although the relation between specific conductance and alkalinity appears linear, estimates that are outside the range of the “calibration data” should be interpreted with caution. Within the range of observed data, dilution may be the primary process controlling specific conductance and alkalinity. At lower concentrations, however, it may be anticipated that the relation between specific conductance and alkalinity may become nonlinear. The addition of increasing amounts of slightly acidic snowmelt will cause alkalinity to become negative as specific conductance approaches zero. Results of this analysis indicate that, although episodic acidification may or may not have occurred during the storms, alkalinity probably declined by approximately an order of magnitude. If precipitation events with higher acidity occur, episodic acidification during storms is possible and perhaps likely.

Comparison of Solute Concentrations at Eunice Lake in 2000 and 2005–2006

During 2000, intensive sampling was performed at the Eunice Lake outlet as part of a pilot USGS and NPS study of episodic acidification in MORA. These data provide an opportunity to evaluate whether the sulfur emissions reductions that took place in the area upwind from the park during the early 2000s are having the desired effect, that is, reductions in surface-water sulfate and increases in surface-water alkalinity.

A daily time-series plot of sulfate concentrations shows that, with the exception of the April 2006 sample, concentrations on any given day usually were substantially lower in 2005–06 than in 2000 (fig. 18). The plot also shows that the timing of minima and maxima in sulfate were different each year, which is due to differences in the timing of snowmelt. A Wilcoxon signed-rank test on sulfate concentrations in samples collected on the same day of the water year in 2000 and 2005–06 indicated that the differences in concentrations were statistically significant ($p < 0.003$). These results are consistent with substantial declines in sulfur emissions at Centralia, and in sulfur deposition at the NADP sites in and near the west side of MORA, during the early 2000s. A similar plot and statistical test for alkalinity indicated no significant differences in alkalinity concentrations between 2000 and 2005–06 (fig. 18). These results suggest that, although sulfate concentrations appear to be responding to declines in sulfur emissions and sulfur deposition, any corresponding changes in alkalinity have been small and confounded by the complex biogeochemical processes controlling base cations. Alkalinity responses may be delayed relative to those of sulfate because it may take time for cations in the soil exchange pool to be replenished. Lower sulfate deposition is expected to eventually reduce leaching of base cations from soils and help protect ecosystems from future acidification.

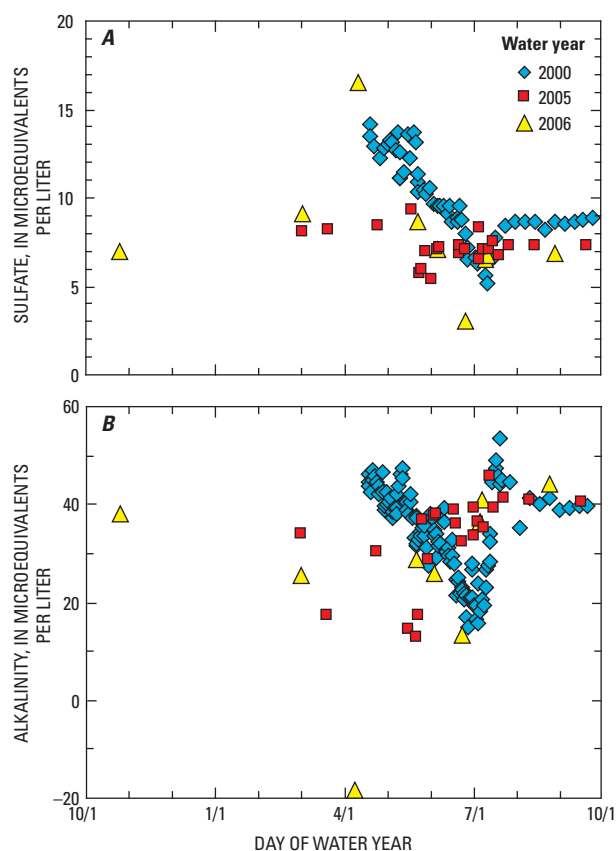


Figure 18. Time-series plots of (A) sulfate, and (B) alkalinity concentrations at Eunice Lake outlet during water years 2000, 2005, and 2006.

Synthesis of Historical Lake-Chemistry Data

Data Sets

Substantial sets of lake-chemistry data are available for MORA and NOCA. The MORA data sets include (1) detailed chemistry on five lakes sampled as part of the 1985 Western Lake Survey (Eilers and others, 1987; Nelson, 1991); (2) statistical summaries of pH, specific conductance, alkalinity, and nutrients in 27 lakes from a survey conducted in 1988 (Larson and others, 1994); (3) a USGS report on water quality in relation to acidification (Turney and others, 1986); and (4) data in an unpublished database maintained by MORA staff, which contains chemical data from 65 lakes and ponds sampled by NPS between 1988 and 2004 as part of ongoing monitoring. The primary NOCA data sets include (1) detailed chemistry on six lakes sampled as part of the 1985 Western Lake Survey (Eilers and others, 1987; Nelson, 1991); (2) a statistical summary of alkalinity concentrations in 14 lakes sampled in 1983–84 (Brakke and Loranger, 1986); (3) statistical summaries of lake pH, specific conductance, alkalinity, and nutrients from lake surveys conducted during 1989 through 1993 in which a total of 58 lakes were sampled (Larson and others, 1999); and (4) data in an unpublished database maintained by NOCA staff, which primarily contains data on pH, alkalinity, nutrients, and field properties collected through a variety of studies in the park during 1970–99.

Although the number of lake-water samples collected in the parks is large, most were analyzed only for pH, specific conductance, and alkalinity; nonetheless, they provide a useful database for evaluating acidification status. Slightly less than one-half of the samples were analyzed for nutrients, including nitrate, ammonium, orthophosphate, and total phosphorus; data from these samples allow determination of lake trophic status and nutrient limitation. A small subset of samples collected in MORA (less than 15 percent) and NOCA (less than 1 percent) were analyzed for all major constituents, including pH, specific conductance, alkalinity, cations, anions, and nutrients. These samples are valuable because data can be checked for quality using charge-balance calculations and because they provide sufficient information for identifying major processes responsible for contributing solutes to surface waters.

It should be noted that the average solute concentrations calculated for lakes using data in the unpublished NPS water-chemistry databases should be interpreted with caution because the number and timing of samples collected from the lakes vary substantially.

Lake Characteristics

Lakes in MORA and NOCA typically are cold, clear, and dilute (Larson and others, 1994). The dominant solutes include calcium, sodium, bicarbonate (alkalinity), and silica. Their

depth and area are highly variable, but on average, they are small and shallow (table 4). They generally are at high elevation and are snow- and ice-covered most of the year; ice-out usually occurs during late May through early July. Epilimnion lake temperatures typically warm into the 10–20°C range during summer, with shallow lakes warming more than deep lakes. Summertime water temperatures tend to be warmer in lakes on the eastern side than on the western side of the parks, reflecting warmer summertime air temperatures on the eastern side (Larson and others, 1994) and earlier and smaller volumes of snowmelt. In most shallow lakes, transparency as measured by secchi disk was equal to total lake depth (Larson and others, 1994). In deeper lakes, transparency was positively correlated with lake depth, indicating that shallower lakes tended to have a higher density of light-scattering particles and be more productive (Larson and others, 1999). Shallow lakes generally do not stratify, but deeper lakes stratify during winter and during summer (Larson and others, 1994; Larson and others, 1999). Stratification breaks down in the deep lakes during spring snowmelt and fall overturn, when strong winds and isothermal temperatures in the lakes promote mixing. Dissolved oxygen concentrations usually are near saturation at the surface. In stratified lakes, dissolved oxygen generally decreases with depth.

Acidification Status and Sensitivity

In calcium-sodium-bicarbonate lakes in basins where silicate mineral weathering is the dominant source of solutes, the specific conductance of water samples reflects their total ionic load and thus is a measure both of how dilute the water is and of basin sensitivity to acidification and nitrogen deposition. The covariance of sensitivity to acidification and nitrogen deposition occurs because the types of basin characteristics that are conducive to low specific conductance and alkalinity (thin, rocky soils and steep topographic slopes) also limit nitrogen assimilation rates. Thin, rocky soils and steep slopes are conducive to fast hydrologic flushing rates. This limits interaction between percolating water and soil and vegetation through which chemical weathering and nitrogen uptake occur.

Survey data collected by Brakke and Loranger (1986), Larson and others (1994), and Larson and others (1999) indicate that lakes in MORA and NOCA are dilute, with an average specific conductance of ≤ 26 $\mu\text{S}/\text{cm}$ (table 4), similar to the average specific conductance of high-elevation lakes sampled in the northern Cascades region during the Western Lake Survey (Eilers and others, 1987) (table 4). Thus, lakes in MORA and NOCA should be relatively sensitive to acidification and nitrogen deposition.

Lake-survey data indicate that the pH of lakes in MORA and NOCA is circumneutral, averaging 6.3 to 7.0 (table 4). Survey data indicate that lakes in MORA tend to have slightly lower pH values than lakes in NOCA (table 4). The minimum pH measured in the lake surveys was 5.9, indicating that none of the survey lakes were acidic at the time of sampling.

Lake alkalinity concentrations in NOCA tend to be low and on average are approximately one-half of those in MORA, indicating that NOCA lakes are more sensitive to acidification than those in MORA (table 4). None of the synoptic data are indicative of acidification (alkalinity < 0 µeq/L), although 37 percent of the NOCA lakes sampled during the 1986 synoptic had alkalinities ≤100 µeq/L, and 68 percent had alkalinities ≤200 µeq/L (Brakke and Loranger, 1986). In the Western Lake Survey, only the Sierra Nevada region had a greater percentage of lakes with alkalinity ≤ 200 µeq/L than the Cascades region (Nelson, 1991). Alkalinity in NOCA is correlated with bedrock type, with lakes in granitic and metamorphic terrain having the lowest alkalinities; these lakes were concentrated in the northern part of NOCA (Brakke and Loranger, 1986). Alkalinity is negatively correlated with elevation (Brakke and Loranger, 1986), consistent with findings in the Western Lake Survey (Nelson, 1991). The negative correlation probably reflects decreasing amounts of soil and vegetation at higher elevations (Larson and others, 1999).

Alkalinity concentrations in NOCA and MORA lakes usually are only slightly less than the sum of sea-salt-corrected base cation concentrations (fig. 19) (Weast, 1987), indicating that contributions from strong-acid and organic-acid anions to the total solute load are small (Nelson, 1991). A strong correlation was noted between alkalinity and the sum of sea-salt-corrected base cations for Cascades lakes in the Western Lake Survey ($r^2 = 0.99$); it was inferred that alkalinity and base cations were derived from a common source, such as mineral weathering (Drever and Hurcomb, 1986). A similar conclusion can be drawn for lakes in MORA and NOCA.

It should be noted that inferences about acidification from the synoptic data pertain only to the season in which they are collected, which was late summer/early fall. Only limited inferences can be made regarding the potential for episodic acidification based on the synoptic data. Lakes with low alkalinity during late summer/early fall are likely to be sensitive to episodic acidification, but quantitative predictions cannot be made with available synoptic data.

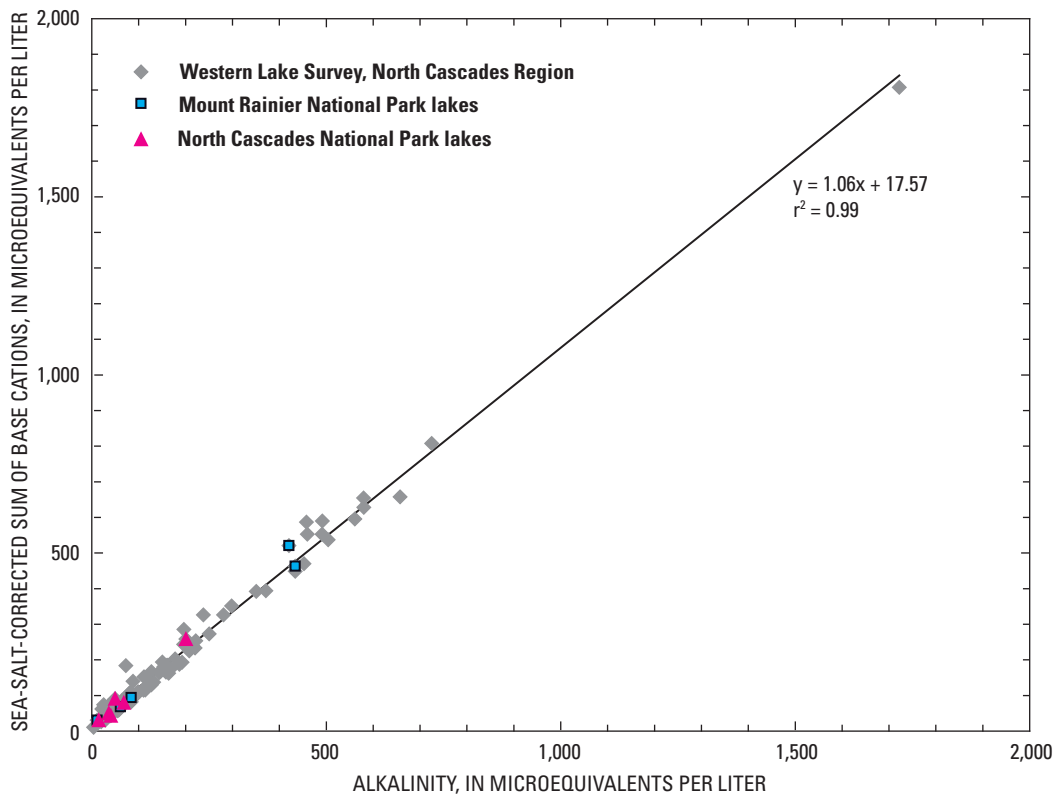
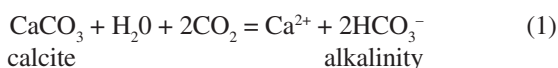


Figure 19. Relation between alkalinity and sea-salt-corrected sum of base cations in samples collected during the 1985 Western Lake Survey (WLS) in the North Cascades region, and in the subset of lakes sampled in Mount Rainier National Park (MORA) and North Cascades National Park (NOCA). Sea-salt correction performed using ion ratios in seawater (Weast, 1987).

Geochemical Processes Influencing Lake Chemistry

Epilimnion water samples that had complete analyses of all major dissolved constituents and that met quality-assurance criteria were analyzed using Principal Components Analysis (PCA). The objective was to gain insight into processes responsible for the overall chemical character of surface water in the parks.

The PCA identified several components; the most important component, accounting for 28 percent of the variance in the data set, weighted heavily on specific conductance and concentrations of calcium, magnesium, and alkalinity. This component probably represents mineral weathering. It is noteworthy that, although silica makes up an important fraction of the total solute load in most water samples and silicate minerals are by far the most abundant minerals in local bedrock, silica did not load heavily on the first PCA component. This may indicate that multiple processes, some of which do not substantially affect the solutes identified in component 1, control silica concentrations. Seasonally varying processes, such as uptake/release of silica by diatoms or precipitation/dissolution of amorphous aluminosilicates in soils, may explain this behavior. Alternatively, carbonate minerals such as calcite, which comprise only a small fraction of the bedrock, may have a disproportionate influence on surface-water chemistry (Drever and Hurcomb, 1986). These weathering reactions release substantial alkalinity, as shown in the following reaction:



The second component, accounting for 20 percent of data-set variance, weighted on concentrations of ammonium and potassium. These solutes can be released from lake sediments by mineralization of organic matter. A third component, accounting for 16 percent of the variance in the data, weighted on silica and total phosphorus, which are important components of lake diatoms and algal biomass. This component may represent seasonal uptake of silica and phosphorus by diatoms and other aquatic plants.

Nutrient Concentrations

The concentrations of nitrate and ammonium in MORA lakes were very low, averaging 0.2 $\mu\text{eq/L}$ in the 1988 lake survey (table 4) (Larson and others, 1994). Lake nitrate and ammonium concentrations in NOCA typically are somewhat higher; they averaged 0.5 and 0.4, respectively, in the 1989–93 lake surveys (table 4) (Larson and others, 1999). A positive relation was identified between lake nitrate concentrations and elevations in NOCA, which is probably attributable to atmospheric deposition of nitrogen (Larson and others, 1999). It is somewhat surprising that average ammonium concentrations were nearly as high as average nitrate concentrations (table 4), which is unusual in pristine surface waters, except under

reducing conditions. Data in the unpublished NPS databases indicate that ammonium concentrations were typically highest in hypolimnion samples, perhaps reflecting release of inorganic nitrogen from lake sediments. Lake sediments typically are anoxic, which promotes mineralization of organic nitrogen to inorganic nitrogen; the inorganic nitrogen is released into the hypolimnion of the lake as ammonium by dispersion. It is noteworthy that in the Western Lake Survey, ammonium concentrations were substantially less than nitrate concentrations (table 4).

Nutrient concentrations in the lakes showed substantial interannual variability. The relatively long record of the MORA data set allows qualitative evaluation of temporal patterns in the data, although data gaps limit the power of trend analyses (fig. 20). Most lake nitrate concentrations were very low (fig. 20). Total phosphorus concentrations did not exhibit any obvious temporal patterns (fig. 20).

Trophic Status

Trophic status of lakes is an indication of their overall productivity, and it can be evaluated using a variety of indices. Oligotrophic lakes typically have high transparency, high dissolved-oxygen concentrations, low nutrient concentrations, low particulate organic matter concentrations, and low algal biomass (Carlson, 1977). Eutrophic lakes have the opposite characteristics, and mesotrophic lakes have intermediate characteristics. Trophic status was evaluated for the MORA and NOCA lakes on the basis of total phosphorus (TP) concentrations in epilimnion samples using the method developed by Carlson (1977). Trophic-state index (TSI) was calculated as:

$$\text{TSI}(\text{TP}) = 14.42(\ln \text{TP}) + 4.15 \quad (2)$$

where TP is in micrograms per liter. TSI(TP) was calculated based on average TP concentrations for lakes in the unpublished NPS water-chemistry databases and for lakes sampled during the 1985 Western Lake Survey. Although the averages calculated from the NPS databases do not represent a statistically valid summary because samples were collected at varying frequencies from individual lakes, they can provide a preliminary indication of the trophic status of park lakes. In MORA, 47 percent of the lakes had TSI(TP) values less than 30, indicating that they were oligotrophic; 47 percent of the lakes had TSI(TP) values ≥ 30 and < 50 , placing them in the mesotrophic category; and 6 percent of lakes had TSI(TP) values ≥ 50 , indicating that they were eutrophic (fig. 21). In NOCA, TSI(TP) values indicated that 67 percent of the lakes were oligotrophic, 32 percent were mesotrophic, and 1 percent were eutrophic (fig. 21). All of the lakes that fell in the eutrophic category were less than 1 meter deep, possibly because the shallow depths in these lakes promote warm water temperatures, which can stimulate aquatic plant growth. Shallow depths also may allow more interaction between the water column and anoxic sediments, resulting in increased total phosphorus concentrations. Although lakes sampled in the 1985 Western Lake Survey tended to be more oligotrophic than the lakes in the

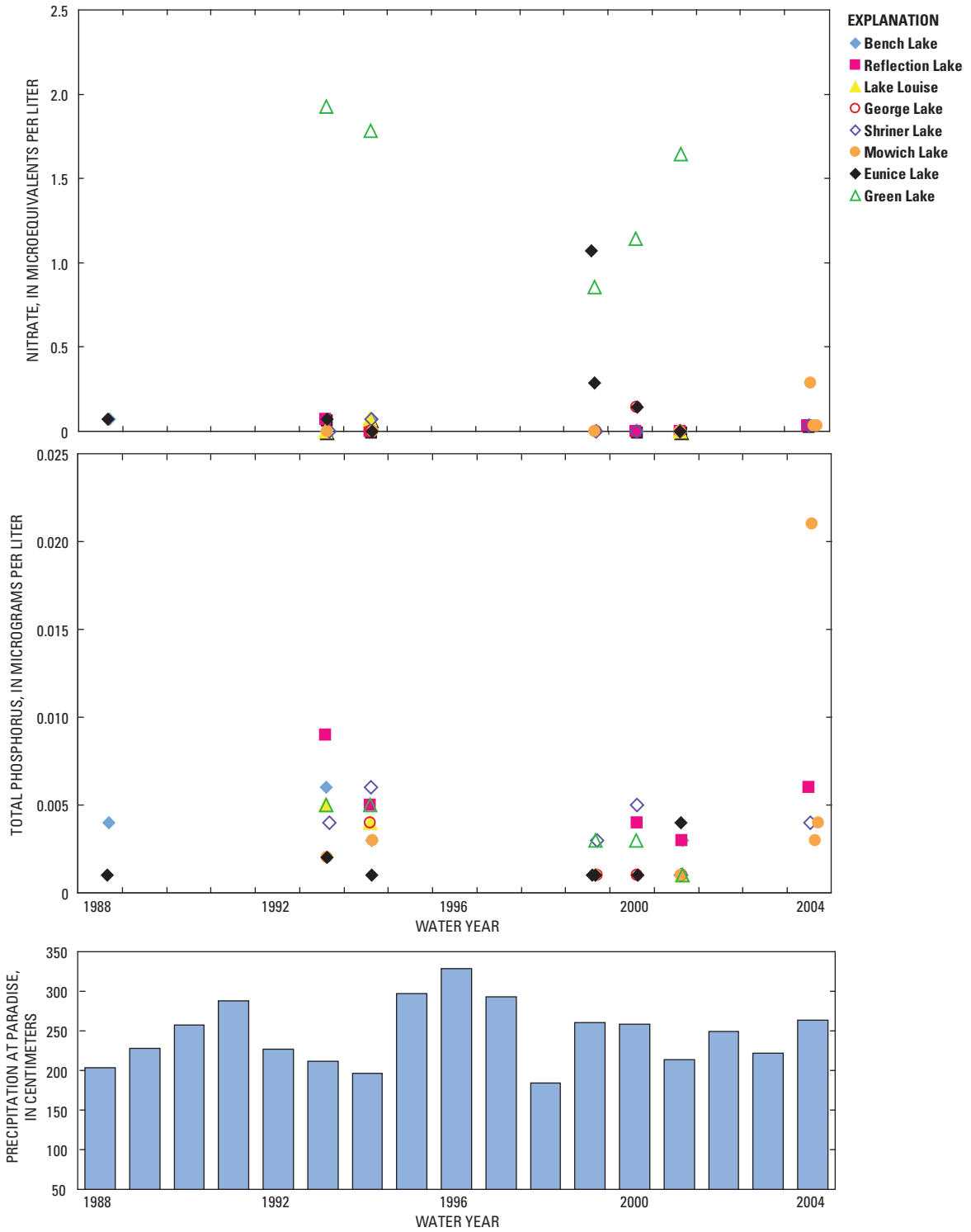


Figure 20. Variations in nitrate and total phosphorus concentrations and annual precipitation at Mount Rainier National Park lakes over time, 1988–2004.

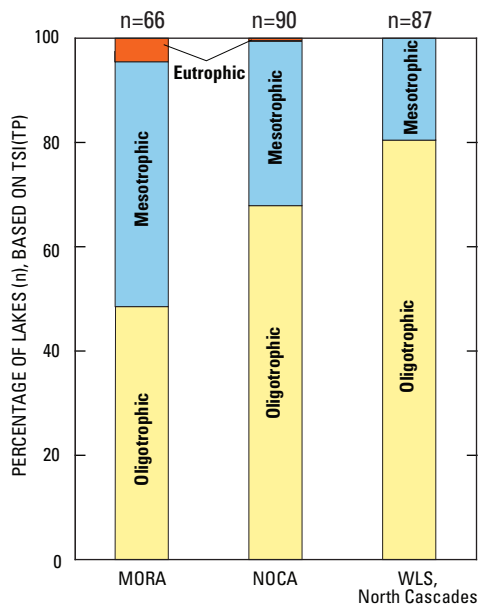


Figure 21. Distribution of trophic status of lakes in Mount Rainier National Park (MORA), North Cascades National Park (NOCA) during 1985–2004, and in the North Cascades Region during the 1985 Western Lake Survey (WLS). Trophic state index (TSI[TP]) calculated as in Carlson (1977).

NPS databases, direct comparisons are problematic because of differences in laboratories and in the timing and number of samples collected at individual lakes.

There were no statistically significant trends in TSI(TP) at any individual lakes in MORA or NOCA. A box plot showing the range of TSI(TP) in MORA lakes over time suggests a temporal pattern in which TSI(TP) decreased to lower than normal during 1999–2001, and subsequently returned to previously observed values (fig. 22). The reason for the apparent drop in TSI(TP) is unclear but could be related to

variations in climate; except for 1998, the mid- to late 1990s was a relatively wet period in the Pacific Northwest (fig. 20), suggesting the drop in TSI(TP) might have been caused by dilution of phosphorus in the lakes. Alternatively, the apparent drop in TSI(TP) could be an artifact of sampling different lakes in different years.

It should be noted that TSI(TP) is considered valid as an index of trophic status only if phosphorus is the limiting nutrient. A separate trophic state index, TSI(Chl-*a*), can be calculated using chlorophyll-*a* when such data are available (Carlson, 1977). The equation for TSI(Chl-*a*) is:

$$TSI(Chl-a) = 9.81(\ln Chl-a) + 30.6 \quad (3)$$

where Chl-*a* is in micrograms per liter (Carlson, 1977). Chlorophyll-*a* and total phosphorus data are available for Reflection Lake, in south-central MORA, from a study conducted during 1984–85 (Funk and others, 1985). Median TSI(Chl-*a*) and TSI(TP) values at Reflection Lake during the study were 28.4 and 30.0, respectively (Funk and others, 1985). The TSI(TP) values derived from the 1984–85 study are consistent with those calculated for Reflection Lake based on total phosphorus in the MORA lake database (median TSI(TP) = 27.2) and are indicative of a system that was borderline oligotrophic/mesotrophic. This might be due to local pollution sources rather than atmospheric deposition, because Reflection Lake is close to a road and is popular with park visitors.

A third trophic index, based on secchi disk readings, has sometimes been used to characterize lake productivity (Carlson, 1977). This index, TSI(SD), does not work well in MORA or NOCA for characterizing the distribution of lake productivity because a large percentage of lakes have transparencies equal to total lake depth (Larson and others, 1994). However, TSI(SD) should work well for tracking productivity in individual lakes over time, provided that the lakes are sufficiently deep and that seasonal variability in lake clarity can be accounted for.

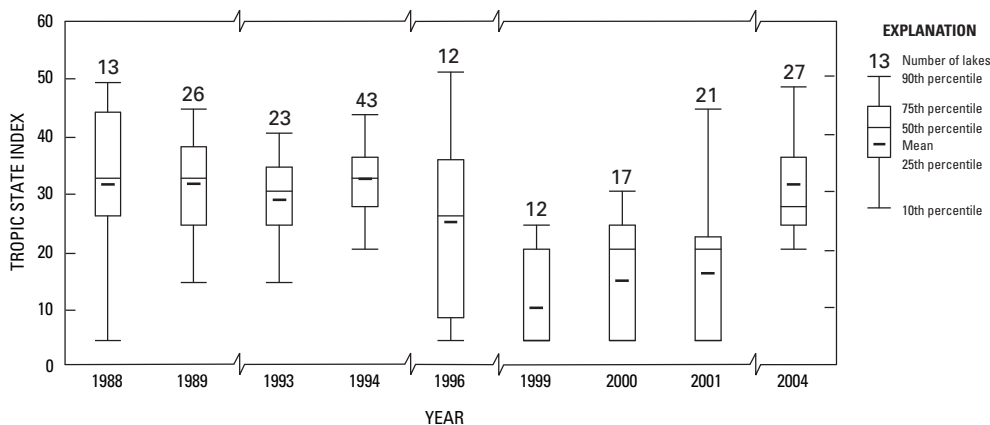


Figure 22. Variations in distribution of trophic state index based on total phosphorus (TSI[TP]) over time at lakes in Mount Rainier National Park during 1988–2004, calculated as in Carlson (1977).

Nutrient Limitation

Growth of lake phytoplankton usually is limited by nitrogen, phosphorus, or a combination of the two (Morris and Lewis, 1988). Nutrient limitation can be assessed using the ratio of dissolved inorganic nitrogen to total phosphorus (DIN:TP), which has been shown to effectively predict nutrient limitation, as indicated by good agreement with in-situ nutrient enrichment experiments (Lafrancois and others, 2003; Sickman and others, 2003). DIN:TP data indicate that phytoplankton growth in MORA lakes was limited by nitrogen in 32 percent of lakes (DIN:TP < 0.5), by nitrogen + phosphorus (co-limitation) in 39 percent of lakes (DIN:TP \geq 0.5 and < 4.0), and by phosphorus in 29 percent of lakes (DIN:TP \geq 4.0; fig. 23). Nitrogen limitation was much less common in NOCA lakes than in MORA lakes, reflecting a combination of higher DIN and lower TP at NOCA than at MORA. Phytoplankton growth in NOCA lakes was limited by nitrogen in 3 percent of lakes, by nitrogen + phosphorus in 71 percent of lakes, and by phosphorus in 26 percent of lakes.

Previous studies indicate that the distribution of nutrient limitation among nitrogen-, (nitrogen + phosphorus)-, and phosphorus-limitation in MORA and NOCA lakes is common among high-altitude lakes in the Western United States. Of the high-elevation lakes sampled in the northern Cascades during the 1985 Western Lake Survey, 35 percent were nitrogen limited, 36 percent were co-limited by nitrogen + phosphorus, and 29 percent were phosphorus limited. A lake survey in the Snowy Range of Wyoming documented that most of the sampled lakes ($n = 18$) were co-limited by nitrogen + phosphorus (Lafrancois and others, 2003). The Snowy Range study also documented that phytoplankton species composition responded strongly to nutrient concentrations; chrysophytes favored low nitrogen concentrations, whereas chlorophytes favored higher

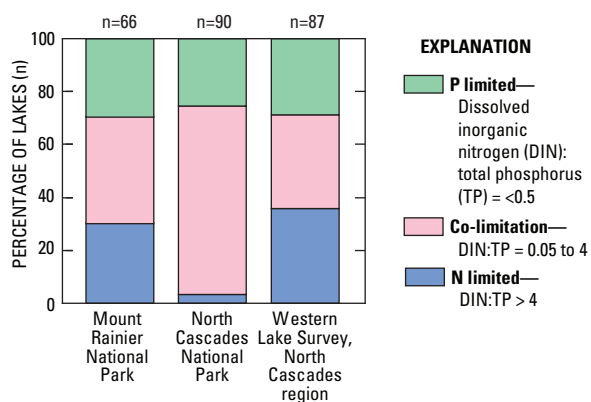


Figure 23. Percentage of lakes in Mount Rainier National Park (MORA), North Cascades National Park (NOCA), and in North Cascades region during the Western Lake Survey (WLS) limited by phosphorus (P), nitrogen plus phosphorus (co-limitation), and nitrogen (N) during 1985–2004 based on classification method of Morris and Lewis (1988).

nitrogen concentrations. Phytoplankton were measured by Larson and others (1994) as part of the 1988 lake survey but were not compared to nutrient concentrations.

Comparison of DIN:TP with TSI(TP) shows that most of the phosphorus-limited lakes fell in the oligotrophic category based on TSI(TP) (fig. 24). Lakes exhibiting concurrent limitation by nitrogen + phosphorus fell in the oligotrophic and mesotrophic categories. Eutrophic lakes were limited by nitrogen, reflecting their high TP concentrations. It is worth noting that these results apply only to the summer period because that is when the lake samples were collected. During springtime, it may be expected that the lakes would tend to be more P-limited due to the relatively high concentrations of nitrogen released from snowmelt.

There was an inverse logarithmic relation between DIN:TP and TSI(TP), as expected, because TSI(TP) is a positive function of TP and DIN:TP is an inverse function of TP (fig. 24). A suite of hypothetical samples with constant DIN (0.6 $\mu\text{eq/L}$) and variable total phosphorus (0 to 135 $\mu\text{g/L}$) would plot along the line shown in figure 24. Addition of nitrogen to the system through atmospheric deposition would tend to increase the DIN:TP ratio in lakes and make them plot above the line. Thus, deviations above the line could help identify lakes affected by excess nitrogen deposition.

Spatial patterns in nutrient concentrations and trophic indices were evaluated by comparing group means for lakes in different geographic regions of the parks using a one-way analysis of variance (ANOVA) on epilimnion samples, with a 95-percent level of significance. MORA was divided into four quadrants, including northwest (NW, $n=12$), northeast (NE, $n=27$), southeast (SE, $n=7$), and southwest (SW, $n=15$). Mean nitrate concentrations were significantly higher in the northwest quadrant (0.7 $\mu\text{eq/L}$) than in the northeast quadrant (0.1 $\mu\text{eq/L}$) of MORA, which could reflect higher rates of nitrogen deposition in the northwestern part of the park due to its proximity to the Puget Sound area. Total phosphorus was higher in the northeast quadrant (9 $\mu\text{g/L}$) than in the northwest (4 $\mu\text{g/L}$) and southwest quadrants (4 $\mu\text{g/L}$). DIN:TP was lower in the northeast (1.6) than in the northwest (7.7) and southwest quadrants (6.2). Most lakes in the eastern part of MORA were nitrogen limited, or co-limited by nitrogen + phosphorus; in the western part of the park, most lakes were co-limited by nitrogen + phosphorus or were phosphorus limited. This pattern is consistent with the western part of the park receiving higher nitrogen deposition than the eastern part of the park. Aquatic ecosystems in the eastern part of the park also may be able to assimilate nitrogen more effectively than those in the west due to higher summer temperatures and a longer growing season.

Spatial patterns in nutrient concentrations and trophic indices were evaluated in NOCA based on the geographic grouping of Larson and others (1999), who divided the park into two regions, referred to here as NW ($n=60$) and SE ($n=31$). The only statistically significant difference in group means was for TSI(TP), which was higher in the SE (31.5) than in the NW (25.3). This might reflect lower precipitation inputs in the southeastern region.

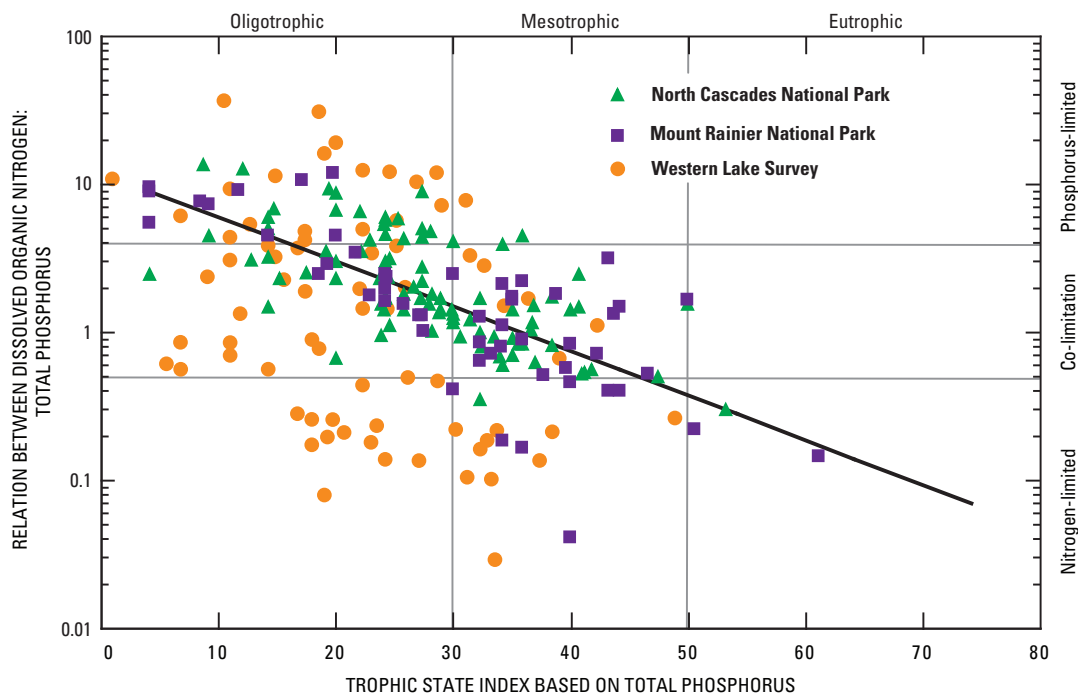


Figure 24. Relation between dissolved organic nitrogen:total phosphorus (DIN:TP) and trophic state index based on total phosphorus (TSI[TP]) in samples from Mount Rainier National Park (MORA), North Cascades National Park (NOCA), and in North Cascades region during the Western Lake Survey (WLS), 1985–2004. TSI[TP] calculated as in Carlson (1977).

Summary and Conclusions

Thin, rocky soils, abundant precipitation, and fast hydrologic flushing rates make aquatic ecosystems in Mount Rainier and North Cascades National Parks sensitive to effects of atmospherically deposited nitrogen and sulfur. This report documents the results of a study of the effects of atmospheric deposition of nitrogen and sulfur on surface-water chemistry in Mount Rainier (MORA) and North Cascades (NOCA) National Parks, which was done by the U.S. Geological Survey in cooperation with the National Park Service. The report describes (1) spatial and temporal patterns in atmospheric deposition of nitrogen and sulfur compounds, (2) seasonal responses in surface-water chemistry to atmospheric-deposition inputs at two sites in each park, particularly during snowmelt, and (3) a review of historical lake-survey data to determine the influence of nitrogen and sulfur deposition on surface-water chemistry in the parks.

Wet deposition of inorganic nitrogen during 2002–04 ranged from 0.81 to 2.01 kilograms per hectare at National Atmospheric Deposition /National Trend Network sites in Washington State. Wet deposition of inorganic nitrogen was highest in the vicinity of North Cascades National Park, which

might reflect the influence of emissions in the Puget Sound area. Wet deposition of sulfur during 2002–04 ranged from 0.51 to 2.88 kilograms per hectare, and deposition was highest near the Pacific coast, reflecting the influence of marine aerosols. Excluding fog, wet deposition accounted for ≥ 70 percent of total inorganic nitrogen deposition and ≥ 78 percent of total sulfur deposition. Long-term trend analyses indicate wet deposition of inorganic nitrogen was relatively stable during 1986–2005, but wet deposition of sulfur declined substantially during that time, particularly after 2001, when emissions controls were added to a large powerplant upwind from Mount Rainier National Park. Surface-water sulfate concentrations at the study site nearest the powerplant, Eunice Lake, showed a statistically significant decrease between 2000 and 2005–06. However, there was not a statistically significant change in alkalinity at the Eunice Lake outlet. This may reflect a delayed response to changes in sulfur deposition and complex biogeochemical processes controlling base cations and alkalinity.

Seasonal patterns in solute chemistry and streamflow are strongly influenced by melting of seasonal snowpacks, which release large amounts of dilute, slightly acidic water to the terrestrial and aquatic ecosystems during spring snowmelt. Solute concentrations decline rapidly during snowmelt, then gradually recover during summer and fall. Preferential elution

of acidic solutes from snowpack at the beginning of snowmelt may cause sharp drops in pH and alkalinity in small alpine streams. A streamwater sample collected during spring 2006 was acidic (pH = 4.8, alkalinity = $-18 \mu\text{eq/L}$) and had high concentrations of nitrate and sulfate and low concentrations of weathering products. This chemistry is indicative of episodic acidification due to preferential elution of acidic components from melting snow. The scale of episodic acidification is unknown, but it might be restricted to small pools of nearly-stagnant water that form in stream channels and local depressions at the beginning of snowmelt. Nonetheless, it could have detrimental effects on aquatic life and amphibians.

Midwinter rain-on-snow events also have potential to cause episodic acidification. Lake-outlet alkalinity was estimated for several midwinter rain-on-snow events based on changes in specific conductance, which was monitored by using an in-stream sensor. Results indicated that alkalinity declined by an order of magnitude during the rain-on-snow events. In one case, modeled alkalinity declined to $8 \mu\text{eq/L}$. High-elevation surface waters in North Cascades National Park are likely to be similarly sensitive.

Historical lake-survey data indicate that surface-water nitrate concentrations were very low in Mount Rainier National Park (average $\leq 0.2 \mu\text{eq/L}$) and in North Cascades National Park (average $\leq 0.5 \mu\text{eq/L}$). The slightly higher surface-water nitrate concentrations at North Cascades National Park are consistent with higher inorganic nitrogen deposition that occurs there relative to Mount Rainier National Park. At low elevations in North Cascades National Park (below approximately 1,000 m), nitrogen fixation associated with red alder appears to contribute substantial nitrogen to stream water. Future monitoring for effects of atmospheric deposition of nitrogen should focus on high-elevation ecosystems to avoid the confounding effects of nitrogen fixation by alders.

Historical lake-survey data indicate that most lakes in the two parks are oligotrophic and have low concentrations of nitrogen and phosphorus. Nitrogen limitation was more common at MORA than at NOCA due to lower dissolved inorganic nitrogen concentrations and higher total phosphorus concentrations at MORA. Spatial patterns in nutrient status and limitation indices suggest that nitrogen deposition may be affecting the northwest part of MORA more than other parts of the park. There were no significant differences in nitrogen concentrations between lakes in the northwestern part of NOCA compared to those in the southeastern part of the park. However, lake surveys have documented a positive relation between nitrate concentrations and elevation in alpine lakes in the NOCA, suggesting that atmospheric deposition of nitrogen may be affecting high-elevation lakes in the park. Total phosphorus concentrations tend to be higher on the eastern side of both parks, which may reflect drier conditions and warmer summertime conditions there compared to the western side of the parks.

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For more information concerning this publication, contact:
Director, USGS Colorado Water Science Center
Box 25046, Mail Stop 415
Denver, CO 80225
(303)236-4882

Or visit the Colorado Water Science Center Web site at:
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