Atmospheric Deposition of Nutrients, Pesticides, and Mercury in Rocky Mountain National Park, Colorado, 2002

By M. Alisa Mast, Donald H. Campbell, George P. Ingersoll, William T. Foreman, and David P. Krabbenhoft

Water-Resources Investigations Report 03–4241

U.S. Department of the Interior
U.S. Geological Survey

Contents

Figures

Tables

Conversion Factors and Abbreviations

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
hectare (ha)	2.471	acre
kilogram (kg)	2.205	pound (lb)
liter (L)	0.264	gallon (gal)

Temperature can be converted from degree Celsius (°C) to degree Fahrenheit (°F) using the following equation:

$$°F = 1.8(°C) + 32$$

Vertical coordinate information is referenced to the National Geodectic Vertical Datum of 1929 (NGVD 29); horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Additional Abbreviations

kg N/ha	kilograms of nitrogen per hectare
mg/L	milligrams per liter
mg N/L	milligrams of nitrogen per liter
mL	milliliter
ng/L	nanograms per liter
µg/L	micrograms per liter
µm	micrometer
µS/cm	microsiemens per centimeter at 25 degrees Celsius
$\delta^{18}O$	difference between the ratios of isotopes of oxygen $^{18}O/^{16}O$, in a sample and a standard
$\delta^{15}N$	difference between the ratios of isotopes of nitrogen $^{15}N/^{14}N$, in a sample and a standard
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
MDN	Mercury Deposition Network
NADP	National Atmospheric Deposition Network
NWQL	National Water Quality Laboratory
RMNP	Rocky Mountain National Park
SNOTEL	Snowpack Telemetry
USGS	U.S. Geological Survey
VWM	volume-weighted mean

Atmospheric Deposition of Nutrients, Pesticides, and Mercury in Rocky Mountain National Park, Colorado, 2002

By M. Alisa Mast, Donald H. Campbell, George P. Ingersoll, William T. Foreman, and David P. Krabbenhoft

Abstract

Nutrients, current-use pesticides, and mercury were measured in atmospheric deposition during summer in Rocky Mountain National Park in Colorado to improve understanding of the type and magnitude of atmospheric contaminants being deposited in the park. Two deposition sites were established on the east side of the park: one at an elevation of 2,902 meters near Bear Lake for nutrients and pesticides, and one at an elevation of 3,159 meters in the Loch Vale watershed for mercury. Concentrations of nutrients in summer precipitation at Bear Lake ranged from less than 0.007 to 1.29 mg N/L (milligrams of nitrogen per liter) for ammonium and 0.17 to 4.59 mg N/L for nitrate and were similar to those measured at the Loch Vale National Atmospheric Deposition Network station, where nitrogen concentrations in precipitation are among the highest in the Rocky Mountains. Atrazine, dacthal, and carbaryl were the most frequently detected pesticides at Bear Lake, with carbaryl present at the highest concentrations (0.0079 to 0.0952 µg/L (micrograms per liter), followed by atrazine (less than 0.0070 to 0.0604 µg/L), and dacthal (0.0030 to 0.0093 µg/L). Mercury was detected in weekly bulk deposition samples from Loch Vale in concentrations ranging from 2.6 to 36.2 ng/L (nanograms per liter).

Concentrations in summer precipitation were combined with snowpack data from a separate study to estimate annual deposition rates of these contaminants in 2002. Annual bulk nitrogen deposition in 2002 was 2.28 kg N/ha (kilograms of nitrogen per hectare) at Bear Lake and 3.35 kg N/ha at Loch Vale. Comparison of wet and bulk deposition indicated that dry deposition may account for as much as 28 percent of annual nitrogen deposition, most of which was deposited during the summer months. Annual deposition rates for three pesticides were estimated as 45.8 mg/ha (milligrams per hectare) of atrazine, 14.2 mg/ha of dacthal, and 54.8 mg/ha of carbaryl. Because of much higher pesticide concentrations in summer precipitation than in winter snow, between 80 to 90 percent of the annual pesticide deposition occurs during summer. Mercury deposition to Loch Vale was estimated at 7.1 µg/ha (micrograms per hectare) of which nearly 70 percent of the annual mercury deposition occurred during summer. Despite the fact that most precipitation at high-elevations falls during winter, these results emphasize the importance of monitoring precipitation chemistry during summer to improve estimates of contaminant deposition to high-elevation ecosystems in Rocky Mountain National Park.

Air-parcel back trajectories were calculated using an atmospheric transport model to identify potential source regions for contaminants reaching the park. The results indicate that during the winter, the most likely source of contaminants is from areas northwest of the park, but during summer, contaminants are most likely coming from sources to the southwest and east.

Introduction

The rapid growth of urban areas in the Rocky Mountain region has increased concern about the environmental effects of atmospheric contaminants on high-elevation ecosystems, particularly in protected areas such as National Parks and Class I wilderness areas. The atmospheric contaminant that perhaps poses the greatest threat to these ecosystems is nitrogen, which can cause increased nitrate concentrations in streams and changes in diatom and alpine vegetation communities (Baron and others, 1994; Burns, 2002). Rocky Mountain National Park (RMNP) in north-central Colorado (fig. 1) receives among the highest concentrations and loading rates of nitrogen in atmospheric deposition in the Rocky Mountain region (Burns, 2002). Because of the extremely low capacity of soils and biota at high elevations to assimilate high inputs of nitrogen, some alpine ecosystems in RMNP are at an advanced stage of nitrogen saturation (Baron and others, 1994; Campbell and others, 2000) that is similar to that of highly disturbed forested ecosystems in the Eastern United States (Burns, 2002). Nitrogen in precipitation primarily is derived from NOx gas from fossil fuel combustion and ammonium gas from agricultural production. The most likely sources of nitrogen contamination west of RMNP are large powerplants in northwestern Colorado, eastern Utah, and southwestern Wyoming. Because the moisture source for wintertime precipitation comes primarily from the Northern Pacific Ocean (Baron and Denning, 1993), these powerplants may be the most likely contributors of nitrogen in winter storms. To the east
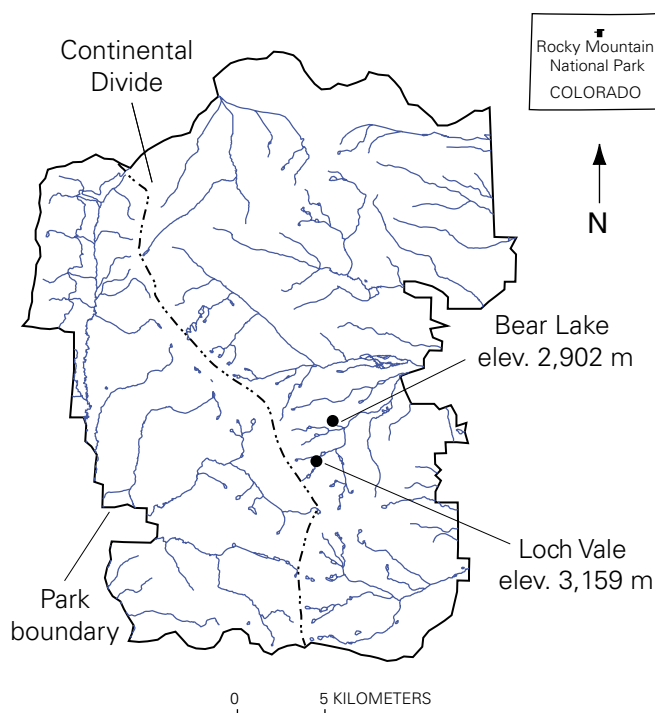
Figure 1. Location of precipitation sites in Rocky Mountain National Park, Colorado.

of RMNP, the Denver–Fort Collins–Colorado Springs urban corridor and agricultural areas and livestock operations in the plains are the most likely nitrogen sources (Burns, 2002).

In addition to being sources of nitrogen, areas to the east of RMNP also may be sources of pesticides. Pesticide deposition in remote areas is of concern because organic pollutants are suspected of disrupting the endocrine systems of aquatic organisms. High-elevation lakes in RMNP may be at risk from airborne pesticides due to high rates of precipitation and close proximity to agricultural and urban areas (Blais and others, 1998; Schindler, 1999). Pesticides become airborne through volatilization and wind erosion during and after application, so air concentrations are generally highest in spring and summer, coinciding with application times and warmer temperatures (Majewski and Capel, 1995). Although a number of studies have measured current-use pesticides in air and precipitation (Goolsby, 1997; Majewski and Capel, 1995), most of these have been conducted in or adjacent to major agricultural areas, and relatively little is known about long-range transport of these compounds to remote areas such as national parks and wilderness areas.

Mercury is another contaminant that reaches remote aquatic ecosystems through long-range transport and atmospheric deposition. Mercury primarily is released to the atmosphere by burning of fossil fuels and, once deposited, can accumulate in the tissues of aquatic organisms. High levels of mercury in fish pose health risks to humans and wildlife that consume large amounts of mercury-contaminated fish. Ecosystem-level effects are not well characterized, and additional study and data are needed to ascertain the effects of mercury at this scale. Although the Mercury Deposition Network (MDN) provides a consistent nationwide dataset for mercury in wetfall (*http://nadp.sws.uiuc.edu/mdn/,* accessed March 2003), few sites are located in remote locations and at high elevation. The only site with elevation similar to RMNP is Buffalo Pass in Colorado (3,234 m), about 100 km west of RMNP. Annual mercury deposition at Buffalo Pass is comparable in magnitude to sites in the Midwestern United States where fish-consumption advisories due to mercury contamination are common. In RMNP, snowpack samples have been analyzed for total mercury as part of the Rocky Mountain Snowpack Network (Ingersoll and others, 2002), but virtually no data exist for mercury concentrations in summer precipitation.

The U.S. Geological Survey (USGS), in cooperation with the National Park Service, began a study in 2002 to improve understanding of the type and magnitude of atmospheric contaminants being deposited in Rocky Mountain National Park during the summer. Although some research has been done on nitrogen deposition in the park (Campbell and others, 2002; Burns, 2002), relatively little information is available on the atmospheric deposition of mercury and pesticides, particularly during the summer months. This information is needed by land managers in RMNP to protect and preserve park resources from damage by atmospheric contaminants as required by the Clean Air Act Amendments of 1977 (*http://www2.nature.nps.gov/ard/,* accessed December 2003).

Purpose and Scope

The purpose of this report is to present baseline information on concentrations of nutrients, pesticides, and mercury in summer precipitation collected at two high-elevation sites in RMNP during 2002. In addition, data in this report were combined with previously collected snowpack data to estimate rates of contaminant deposition to the park throughout the year. The report also presents data for stable nitrogen and oxygen isotopes of the nitrate anions and discusses the use of these isotopic tracers to identify sources of atmospheric nitrogen. This report also attempts to identify potential source areas of contaminants reaching the park through the use of back trajectories computed using an atmospheric transport model.

Acknowledgments

Study Methods

Two bulk-deposition sites were established at different elevations on the east side of RMNP (fig. 1). The lower site was located in a small clearing near Bear Lake at an elevation of 2,902 m. Samples collected at this site were analyzed for nutrients, major constituents, nitrogen isotopes, and current-use pesticides. The second bulk-deposition site was established in the Loch Vale watershed at an elevation of 3,159 m. Samples collected at this site were analyzed for total mercury. Nutrient and major-constituent data from two other precipitation collectors operated in Loch Vale also are presented in this report. Weekly precipitation chemistry is collected for wet-only deposition at the Loch Vale National Atmospheric Deposition Program (NADP) station, and data are available at *http://nadp.sws.uiuc.edu/* (accessed March 2003). Weekly precipitation chemistry also is available for a bulk deposition site in Loch Vale operated by the USGS Water, Energy, and Biogeochemical Budgets (WEBB) program (*http://water.usgs.gov/webb/index.html*, accessed March 2003). All three precipitation monitoring sites in Loch Vale are located within 25 m of each other.

The bulk-deposition collector at Bear Lake consisted of an open bucket suspended on a rebar stand to elevate the bucket 2 m above the ground. Samples for nutrient, major constituent, and nitrogen isotope analyses were collected in a 20-L plastic bucket that was precleaned in the laboratory with deionized water. Rain samples were collected within 48 hours of each storm to minimize sample evaporation and contamination. The plastic bucket was replaced with a clean bucket during each sample collection or each Monday if no significant rain occurred during the previous week. Rain amount was recorded from a manual rain gage at the site. The plastic bucket was sealed and returned to the Colorado District laboratory in Denver, Colo., within 1 week of collection. At the laboratory, the sample was filtered through a 0.45-μm membrane filter and analyzed for major constituents and nutrients using methods described in Fishman (1993). Alkalinity and pH were determined in the laboratory by electrometric titration. Ammonium, nitrate, sulfate, and chloride were determined by ion chromatography, and calcium, magnesium, sodium, and potassium were determined by inductively coupled plasma spectroscopy. Samples for analysis of stable isotopes of nitrogen and oxygen in nitrate were frozen and shipped to the USGS Stable Isotope Laboratory in Menlo Park, Calif. The isotopic results are expressed as parts per thousand (per mil) relative to the standard mean ocean water (SMOW) standard for $\delta^{18}O$ and to atmospheric N_2 for $\delta^{15}N$.

Samples for pesticide analysis were collected at the Bear Lake site in a 40-L aluminum pot, which also was suspended on the rebar stand. Following each precipitation event, the sample was drained through a brass spigot at the base of the pot into prebaked 1-L amber glass bottles. The empty pot and spigot were then cleaned with three rinses of pesticide-grade deionized water, followed with three rinses of pesticide-grade methanol, and allowed to dry. The pot was cleaned each Mon-

day if no significant precipitation occurred during the previous week. All pesticide samples were stored unfiltered at 5°C and shipped to the laboratory within 1 week of collection. Pesticide analyses were conducted at the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., using a solid-phase extraction and gas chromatography/mass spectrometry with selected-ion monitoring (Zaugg and others, 1995).

The bulk-deposition collector in Loch Vale was designed for the collection of mercury samples and consisted of a precleaned polycarbonate funnel connected to a thermoplastic polyester (PETG) collection bottle with Teflon tubing (looped to minimize evaporation) similar to the system described by Landing and others (1998). All components of the bulk collector were soaked in 10-percent ultrapure hydrochloric acid for 24 hours, rinsed 6 times with deionized water, and allowed to dry in a dust-free hood. The PETG collection bottle was replaced weekly whether or not it contained measurable precipitation, and the funnel and tubing were replaced biweekly. The samples were returned unfiltered to the USGS District laboratory in Denver and were preserved in the PETG bottles by adding 10 mL of ultrapure 50-percent hydrochloric acid to each liter of sample. Samples were shipped to the USGS mercury laboratory in Madison, Wisconsin (*http://infotrek.er.usgs.gov/mercury/*, accessed March 2003), where they were analyzed for total mercury according to methods described in Olson and DeWild (1999).

Quality-control samples were used to assess data quality for the three types of analyses—pesticides, mercury, and nutrients and major constituents. Field blanks were collected to assess potential contamination of a sample from collection, processing, and cleaning procedures. One field blank for pesticides was collected during the study following the field cleaning procedure described previously by pouring 1 L of organic-free deionized water over the sides of the aluminum pot and collecting the sample from the spigot. The field blank had concentrations less than the method reporting limit for all 47 measured pesticides, indicating that the collection vessel was not a source of contamination and that the field cleaning procedure was effective in preventing contamination from one sample to the next. For mercury, one field blank was collected by pouring 1 L of mercury-free water through a clean precipitation collector installed in the field. The blank did not contain detectable mercury (less than 0.04 ng/L), indicating the potential for contamination during sample collection and processing was minimal. One field blank for nutrients and major constituents was collected from a clean plastic bucket and also had concentrations below the method reporting limit for all measured constituents.

Replicate samples were used to provide information on the precision of concentration values and the consistency in identifying the compounds of interest, particularly for pesticides. For this report, replicates were collected by splitting a single rain sample into two subsamples. The replicate samples were compared by calculating the relative percent difference as the difference in concentration between the two replicate samples divided by the mean concentration of the two repli-

cate samples. For the pesticide replicates, the same pesticides were detected in both samples and the relative percent differences in concentrations were less than 20 percent. Similarly for the nutrient and major constituent replicates, the relative percent differences in concentrations were less than 15 percent for all constituents, indicating variability introduced by the analytical measurements was small. A replicate was not collected for the mercury analysis due to insufficient sample volume.

a subset of 6 samples was analyzed for stable nitrogen and oxygen isotopes of the nitrate anion. Nine of the precipitation samples collected at the Bear Lake site also were analyzed for current-use pesticides. Seven weekly precipitation samples were collected at the Loch Vale site for analysis of total mercury. The samples were collected between July and October with precipitation amounts ranging from 0.19 to 2.91 cm. Chemical results for the two precipitation sites are discussed in the following sections of this report.

Atmospheric Deposition of Nutrients, Pesticides, and Mercury

Between May and September 2002, 14 precipitation samples were collected at the Bear Lake site with precipitation amounts ranging from 0.06 to 3.04 cm. All 14 samples were analyzed for nutrients and major dissolved constituents, and

Nutrients and Major Constituents

Nutrient and major constituent concentrations for the 14 bulk-deposition samples collected at Bear Lake are shown in table 1. The precipitation samples showed a wide range in chemistry with pH ranging from 4.71 to 7.18 and specific conductance ranging from 6.2 to 29.6 µS/cm. Concentrations of nutrients and major constituents in the June 3 sample were much higher than in other samples, probably due to the small

Table 1. Precipitation amounts and concentrations of nutrients and major constituents for bulk deposition at Bear Lake during summer 2002.

[Precipitation amount in centimeters; specific conductance in microsiemens per centimeter at 25°C; $CaCO_3$, calcium carbonate; constituent concentrations in milligrams per liter; —, not analyzed; <, less than]

Collection date	Precipitation amount	Specific conductance	pH	Alkalinity as CaCO$_3$	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Ammonium as N	Nitrate as N
5/14/02	1.82	18.6	7.18	6.15	2.50	0.12	0.14	0.13	0.13	0.77	0.22	0.32
5/20/02	0.62	29.6	6.65	2.13	2.68	.31	.32	.30	.48	2.66	.74	1.43
5/24/02	3.04	6.2	6.36	1.12	.57	.059	.025	.043	.039	.34	.14	.17
6/3/02	0.06	—	—	—	10.5	1.31	1.44	2.43	1.44	10.8	.71	4.59
6/5/02	1.21	7.6	5.26	<.025	.28	.040	.041	.082	.12	.59	.13	.23
6/20/02	0.73	17.9	6.68	4.04	1.43	.23	.23	1.81	.25	1.52	<.007	.41
7/8/02	0.84	17.9	6.19	3.16	1.17	.16	.15	.80	.26	1.42	.17	.55
7/11/02	1.21	16.0	5.77	.36	.61	.070	.062	.34	.11	1.65	<.007	.65
7/22/02	0.79	27.7	6.76	3.72	1.51	.18	.087	.78	.22	1.90	1.29	.95
7/24/02	0.15	27.5	4.71	<.025	.92	.13	.59	1.15	1.15	2.78	.94	.95
7/29/02	0.15	—	5.42	1.79	2.80	.53	.42	4.37	1.13	4.94	1.20	2.53
8/5/02	0.58	21.6	5.54	.39	1.71	.15	.12	.37	.21	2.11	.55	1.06
8/6/02	0.95	9.1	4.87	<.025	.20	.019	.028	.12	.084	.50	.11	.29
9/12/02	1.75	6.6	4.96	<.025	.070	.010	.009	.043	.042	.28	.10	.19

amount of precipitation that fell during the collection period (0.06 cm). In precipitation samples collected at Bear Lake in 2002, calcium and ammonium were the dominant cations. Nitrate and sulfate were the dominant anions in low-pH samples (pH less than 6.0), whereas bicarbonate was the dominant anion in high-pH samples. Ammonium concentrations ranged from less than 0.007 to 1.29 mg N/L, and nitrate concentrations ranged from 0.17 to 4.59 mg N/L.

The volume-weighted mean (VWM) summer concentrations at the Bear Lake site were compared with VWM summer concentrations at the Loch Vale bulk-deposition site and the Loch Vale NADP station (table 2). At the Bear Lake and Loch Vale bulk-deposition sites, most constituent concentrations were 2 to 4 times higher than concentrations measured at the Loch Vale NADP station. The most likely explanation for this difference is that bulk collectors capture both wet and dry deposition whereas the NADP collector captures wet deposition only. VWM concentrations at the Bear Lake bulk-deposition site were very similar to VWM concentrations at the Loch Vale bulk-deposition site in 2002 with the exception of ammonium, which was higher at Loch Vale, and potassium, which was higher at Bear Lake. In 2002, several constituents were elevated at the Loch Vale and Bear Lake bulk-deposition sites relative to previous years (1999–2001) at the Loch Vale site. The higher VWM concentrations may simply result from lower amounts of precipitation in 2002. For example, precipitation amount at the Bear Lake SNOTEL (Snowpack Telemetry) site was 50 percent of average during the sum-

mer months in 2002 (*http://www.wcc.nrcs.usda.gov/snow/*, accessed March 2003) and 55 percent of average at the Loch Vale NADP station. Another possible explanation is that there were higher levels of dust in the atmosphere due to drought conditions during 2002. Table 1 shows high levels of alkalinity in some Bear Lake samples (precipitation in Loch Vale is normally acidic), which indicates that carbonate-rich dust perhaps from soil ablation was a potential source of the excess calcium and magnesium in precipitation during 2002. The VWM concentrations of ammonium and nitrate at both bulk-deposition sites in 2002 also were elevated compared to 1999–2001 at Loch Vale. Similar to calcium, the excess nitrogen may have been related to higher amounts of dust that was derived from drought-affected agricultural areas to the east of RMNP. Alternatively, higher nitrogen (and potassium) concentrations may have been due to several large wildfires that burned in mountainous areas of Colorado during 2002. Smoke from fires commonly contains elevated levels of nitrogen as well as potassium, which can be used as atmospheric tracers of smoke (Tanner and others, 2001),

The VWM concentration data for the Bear Lake and Loch Vale bulk-deposition sites were used to estimate annual and seasonal deposition of nitrogen during 2002 (table 3). Precipitation volume from Bear Lake was taken from the Bear Lake SNOTEL site (*http://www.wcc.nrcs.usda.gov/snow/*, accessed March 2003), and precipitation amounts for Loch Vale were determined from the Loch Vale NADP station (*http://nadp.sws.uiuc.edu/*, accessed March 2003). The sum-

Table 2.   Volume-weighted mean concentrations of nutrients and major constituents in bulk and wet deposition during summer at Bear Lake and Loch Vale.

[Chemical concentrations are in units of milligrams per liter; N, nitrogen; NADP, National Atmospheric Deposition Program]

| Site | Type | Period | pH | Volume-Weighted Mean Concentration | | | | | | | |
				Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Ammonium as N	Nitrate as N
Bear Lake[1]	Bulk	2002	5.44	1.00	0.10	0.094	0.34	0.15	1.01	0.25	0.46
Loch Vale[2]	Bulk	2002	5.61	0.92	0.095	0.085	0.18	0.13	1.27	0.40	0.55
Loch Vale[2]	Bulk	1999–2001	4.93	0.43	0.044	0.064	0.070	0.12	0.95	0.18	0.35
Loch Vale NADP[3]	Wet	2002	5.27	0.45	0.042	0.032	0.043	0.067	0.57	0.26	0.28

[1]This study.

[2]David W. Clow, U.S. Geological Survey, unpublished data, 1999–2002.

[3]Data from *http://nadp.sws.uiuc.edu*

Table 3.   Precipitation amount and nitrogen deposition at Bear Lake and Loch Vale in 2002.

[Summer is May through October; winter is November through April; cm, centimeter; kg, kilogram; N, nitrogen; ha, hectare; NADP, National Atmospheric Deposition Program]

Period	Precipitation amount (cm)	Ammonium (kg N/ha)	Nitrate (kg N/ha)
Bear Lake bulk deposition			
Annual	49	0.76	1.52
Summer	18	0.44	0.83
Winter	31	0.32	0.69
Loch Vale bulk deposition			
Annual	61	1.26	2.09
Summer	26	1.05	1.42
Winter	35	0.22	0.67
Loch Vale wet deposition (NADP Station)			
Annual	61	1.08	1.32
Summer	26	0.68	0.72
Winter	35	0.40	0.60

mer period was defined as May through October and the winter period was defined as November through April. The VWM concentration of ammonium and nitrate during summer is listed in table 2. Winter nitrogen concentrations at both sites were determined from bulk-snowpack samples collected just before the onset of snowmelt (Ingersoll and others, 2002). The VWM ammonium concentrations were 0.10 mg N/L at Bear Lake and 0.062 mg N/L at Loch Vale, and VWM nitrate concentrations during winter were 0.23 mg N/L at Bear Lake and 0.19 mg N/L at Loch Vale (Ingersoll and others, 2002). Annual ammonium deposition was 0.76 kg N/ha (kilograms of nitrogen per hectare) at Bear Lake and 1.26 kg N/ha at Loch Vale, and annual nitrate deposition was 1.52 kg N/ha at Bear Lake and 2.09 kg N/ha at Loch Vale in 2002. Total annual nitrogen deposition (ammonium plus nitrate) in 2002 was 2.28 kg/ha at Bear Lake and 3.35 kg/ha at Loch Vale. Higher nitrogen deposition in Loch Vale compared to Bear Lake was due to the combination of higher summer concentrations and higher annual precipitation in Loch Vale. At Bear Lake, summer deposition was similar to winter deposition whereas in Loch Vale, summer deposition was considerably higher than winter

deposition. Wet-only deposition of nitrate and ammonium also was calculated for the Loch Vale NADP station in 2002 (table 3). Annual wet deposition measured at Loch Vale was 86 percent of annual bulk deposition for ammonium, and 63 percent of annual bulk deposition for nitrate, indicating that dry deposition of nitrogen species may be an important component of total atmospheric nitrogen deposition in the park. Seasonal differences between wet and bulk nitrate deposition at Loch Vale indicate that dry deposition of nitrogen was minimal during winter but accounted for nearly one-half of the nitrogen deposition during the summer, indicating dry deposition is a larger component of deposition during summer. This conclusion is consistent with a study of throughfall collected from an area of subalpine forest in Loch Vale, which indicated that 56 percent of annual nitrogen deposition consisted of dry deposition during the growing season (Arthur and Fahey, 1993). On an annual basis during 2002, dry deposition accounted for 28 percent of total nitrogen deposition in Loch Vale, which is similar to the estimate of 32 percent by Burns (2002) for the east side of Rocky Mountain National Park.

Nitrate Isotopes

Stable isotopes of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) of the nitrate anion were measured in six samples collected at Bear Lake to determine if nitrate isotopes could be used to trace sources of atmospherically deposited nitrogen. The summer values for $\delta^{15}N$ ranged from –4.0 to –0.8 per mil, and values for $\delta^{18}O$ ranged from +67.3 to +76.8 per mil (table 4). These isotopic values are similar to those measured in precipitation in the Loch Vale watershed by Campbell and others (2002), where rain and snow samples ranged from –6.0 to +3.6 per mil for $\delta^{15}N$ and from +40.3 to +67.7 per mil for $\delta^{18}O$ (table 4).

Table 4. Stable nitrogen and oxygen isotopes of nitrate in bulk precipitation at Bear Lake during summer 2002 and from Loch Vale during 1995–97

Collection date	Period	$\delta^{15}N$ (per mil)	$\delta^{18}O$ (per mil)	Reference
5/14/02	summer	–4.0	+76.1	this study
5/20/02	summer	–1.9	+73.2	this study
6/5/02	summer	–3.9	+71.3	this study
7/8/02	summer	–0.8	+71.2	this study
7/22/02	summer	–2.8	+67.3	this study
8/5/02	summer	–1.8	+76.8	this study
10/5/95	summer	–2.6	+60.0	Campbell and others, 2002
7/30/96	summer	–3.3	+58.3	Campbell and others, 2002
8/22/96	summer	–2.5	+47.4	Campbell and others, 2002
9/11/96	summer	–2.6	+51.4	Campbell and others, 2002
9/11/96	summer	–2.0	+50.2	Campbell and others, 2002
5/16/97	summer	–0.1	+54.2	Campbell and others, 2002
6/17/97	summer	–0.3	+53.5	Campbell and others, 2002
6/17/97	summer	–2.8	+60.0	Campbell and others, 2002
8/8/97	summer	–6.0	+42.9	Campbell and others, 2002
9/24/97	summer	–4.3	+40.3	Campbell and others, 2002
4/11/95	winter	0.8	+60.2	Campbell and others, 2002
4/11/95	winter	1.0	+59.3	Campbell and others, 2002
4/11/95	winter	2.1	+67.7	Campbell and others, 2002
4/12/95	winter	2.2	+64.4	Campbell and others, 2002
4/12/95	winter	3.6	+56.7	Campbell and others, 2002
4/10/96	winter	0.4	+59.8	Campbell and others, 2002
4/10/96	winter	1.8	+53.6	Campbell and others, 2002

The $\delta^{18}O$ of summer precipitation at Bear Lake measured for this report was higher (+67.3 to +76.8 per mil) than in summer precipitation collected at Loch Vale (+40.3 to +60.0 per mil) by Campbell and others (2002). The cause of the difference in $\delta^{18}O$ between the two sites is not known but might be related to differences in location or period of study. Alternatively, the differences could be accounted for by a change in analytical method that occurred in 2002 (Scott Wankel, U.S. Geological Survey, written commun., 2002).

The $\delta^{15}N$ of summer precipitation at Bear Lake (–4.0 to –0.8 per mil) was similar to summer precipitation collected in Loch Vale (–6.0 to –0.1 per mil; Campbell and others, 2002) but was lower than that found in the winter precipitation (+0.4 to +3.6 per mil; Campbell and others, 2002) at Loch Vale. Campbell and others suggested that the shift in isotopic values between summer and winter precipitation might be caused by seasonal differences in storm types and sources of nitrogen oxide emissions. Winter precipitation is associated with synoptic weather systems with westerly airflow and is affected by regional nitrogen emissions. Summer precipitation is affected by the same regional emissions plus an easterly flow component that carries a mixture of sources from the east that includes substantial vehicle emissions and agricultural sources. Thus, it appears that the $\delta^{15}N$ of nitrate may be a promising tool for discrimination of seasonal sources of nitrate, although additional isotopic and meteorological data for individual precipitation events would be needed to assess this possibility.

Current-Use Pesticides

Nine precipitation samples were collected at the Bear Lake site between May 14 and August 6 and were analyzed for the 47 current-use pesticides listed in table 5. Although few of the pesticide compounds were detected, at least one compound was detected in each precipitation sample (table 5). Atrazine, a triazine herbicide, was detected in seven of the nine samples at concentrations ranging from less than 0.0147 to 0.0604 µg/L. Deethylatrazine (DEA), a breakdown product of atrazine, was detected in one sample, and metolachlor, another herbicide, was detected in one sample. The detection of atrazine was not unexpected because it is one of the most commonly used pesticides in the United States and is the most heavily used pesticide on irrigated lands in eastern Colorado (Kimbrough and Litke, 1997). Atrazine is the pesticide most often detected in surface water throughout the United States and also has been detected in precipitation and air samples collected in several Midwestern and Northeastern States, sometimes at

Table 5. Concentrations of 47 current-use pesticides in bulk deposition at Bear Lake during summer 2002.

[Concentrations in units of micrograms per liter; <, less than; values shown in bold for concentrations above the method reporting level; —, not reported]

Compound	05/14/02	05/20/02	05/24/02	06/05/02	06/20/02	07/08/02	07/11/02	07/22/02	08/06/02
2,6-Diethylaniline	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600
Acetochlor	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600	<.00600
Alachlor	<.00450	<.00450	<.00450	<.00450	<.00450	<.00450	<.00450	<.0100	<.00450
alpha-HCH	<.0046	<.0046	<.0046	<.0046	<.0046	<.0046	<.0046	<.0046	<.0046
Atrazine	**0.0197**	**0.0252**	**0.0154**	<.0070	**0.0262**	**0.0147**	**0.0501**	**0.0604**	<.0070
Azinphos-methyl	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500	<.0500
Benfluralin	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100
Butylate	<.00200	<.00200	<.00200	<.00200	<.00200	<.00200	<.00200	<.00200	<.00200
Carbaryl	**0.0096**	**0.0262**	**0.0123**	**0.0079**	**0.0319**	**0.0206**	**0.0952**	**0.0317**	<.0410
Carbofuran	<.0200	<.04	<.0200	<.0200	<.0200	<.0200	<.0200	<.0200	<.0200
Chlorpyrifos	<.0100	<.0050	<.0050	<.0050	<.0050	<.0050	**0.0081**	<.0050	<.0050
cis-Permethrin	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060
Cyanazine	<.0180	<.0180	<.0180	<.0180	<.0180	<.0180	<.0180	<.0180	<.0180
Dacthal	**0.0089**	**0.0093**	**0.003**	**0.0052**	**0.0067**	**0.0068**	**0.0068**	**0.0055**	**0.0031**
Deethylatrazine	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	**0.01**	<.0060

Table 5.   Concentrations of 47 current-use pesticides in bulk deposition at Bear Lake during summer 2002.—Continued

[concentrations in units of micrograms per liter; <, less than; values shown in bold for concentrations above the method reporting level; —, not reported]

Compound	05/14/02	05/20/02	05/24/02	06/05/02	06/20/02	07/08/02	07/11/02	07/22/02	08/06/02
Diazinon	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050
Dieldrin	<.0048	<.0048	<.0048	<.0048	<.0048	<.0048	<.011	<.0048	<.0048
Disulfoton	<.0210	<.0210	<.0210	<.0210	<.0210	<.0210	<.0210	<.0210	<.0210
EPTC	<.0020	<.0020	**0.0312**	<.0020	<.0020	<.0020	<.0020	<.0020	<.0020
Ethalfluralin	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090
Ethoprophos	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050	<.0050
Fonofos	<.0027	<.0027	<.0027	<.0027	<.0027	<.0027	<.0027	<.0027	<.0027
Lindane	<.0040	<.0040	<.0040	<.0040	<.0040	<.0040	<.0040	<.0040	<.0040
Linuron	<.0350	<.0350	<.0350	<.0350	<.0350	<.0350	<.0350	<.0350	<.0350
Malathion	<.0270	<.0270	<.0270	<.0270	**0.0658**	<.0270	<.0270	<.0270	<.0270
Metolachlor	<.0130	<.0130	**0.0068**	<.0130	<.0130	<.0130	<.0130	<.0130	<.0130
Metribuzin	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060
Molinate	<.0016	<.0016	<.0016	—	<.0016	<.0016	<.0016	<.0016	<.0016
Napropamide	<.0070	<.0070	<.0070	<.0070	<.0070	<.0070	<.0070	<.0070	<.0070
p,p'-DDE	<.0025	<.0025	<.0025	<.0025	<.0025	<.0025	<.0025	<.0025	<.0025
Parathion	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100
Parathion-methyl	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060	<.0060
Pebulate	<.00410	<.00410	<.00410	<.00410	<.00410	<.00410	<.00410	<.00410	<.00410
Pendimethalin	<.0220	<.0220	<.0220	<.0220	<.0220	<.0220	<.0220	<.0220	<.0220
Phorate	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110
Prometon	<.0150	<.0150	<.0150	<.0150	<.0150	<.0150	<.0150	<.0150	<.0150
Propachlor	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100	<.0100
Propanil	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110	<.0110
Propargite	<.0230	<.24	<.0230	<.0230	<.0230	<.0230	<.0230	<.0230	<.0230
Propyzamide	<.0041	<.0041	<.0041	<.0041	<.0041	<.0041	<.0041	<.0041	<.0041
Simazine	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500	<.00500
Tebuthiuron	<.0160	<.0160	<.0160	<.0160	<.0160	<.0160	<.0160	<.0160	<.0160
Terbacil	<.0340	<.0340	<.0340	<.0340	<.0340	<.0340	<.0340	<.0340	<.0340
Terbufos	<.0170	<.0170	<.0170	<.0170	<.0170	<.0170	<.0170	<.0170	<.0170
Thiobencarb	<.0048	<.0048	<.0048	<.0048	<.0048	<.0048	<.0048	<.0048	<.0048
Tri-allate	<.0023	<.0023	<.0023	<.0023	<.0023	<.0023	<.0023	<.0023	<.0023
Trifluralin	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090	<.0090

relatively high concentrations (Goolsby and others, 1997). Although atrazine was detected in most of the Bear Lake precipitation samples, the concentrations were much lower than in precipitation in the Midwest where atrazine concentrations commonly exceed 0.30 µg/L (Goolsby and others, 1997). In addition, all concentrations in Bear Lake samples were 2 orders of magnitude lower than the water-supply standard of 3.0 µg/L for surface waters in the State of Colorado (Colorado Department of Public Health and Environment, 2001) and the freshwater aquatic-life criterion of 1.8 µg/L in Canada (Environment Canada, 1999).

Another herbicide, dacthal (DCPA), was detected in all nine precipitation samples in concentrations ranging from 0.0030 to 0.0093 µg/L. Dacthal is a general-use broadleaf herbicide that is used for fruit and vegetable crops as well as on sod farms, golf courses, and residential lawns. In eastern Colorado, dacthal is among the 10 most commonly used agricultural herbicides on irrigated land and primarily is used for cultivation of onions (Kimbrough and Litke, 1997). Dacthal has been detected in precipitation at Isle Royale National Park in Michigan, indicating it can be transported by air currents over long distances (Majewski and Capel, 1995). There currently are no established water-supply- or aquatic-life-based criteria for this pesticide.

Carbaryl and malathion, which are insecticides, were detected in eight samples and one sample, respectively. These insecticides are more common in urban streams than in agricultural streams because they are used extensively for lawn care in urban environments (Majewski and Capel, 1995). In the South Platte River Basin, carbaryl was the most frequently detected pesticide in surface water at urban sites in Denver (Kimbrough and Litke, 1997). Carbaryl was measured in rain in the Mississippi River Valley, where it was detected more frequently at urban sites than at agricultural sites (Majewski and others, 2000). Concentrations of carbaryl in summer precipitation at Bear Lake, which ranged from 0.0079 to 0.0952 µg/L, were lower than the freshwater aquatic-life criterion of 0.2 µg/L in Canada (Environment Canada, 1999). There currently are no water-supply standards in the State of Colorado for this pesticide.

Preliminary data also are available for selected pesticide concentrations in snow samples collected in RMNP in spring of 2001 (Mast and others, 2001b). Atrazine and dacthal were detected in many of the snow samples but at concentrations an order of magnitude lower than in the Bear Lake summer precipitation samples. Carbaryl, which was detected in all but one of the Bear Lake samples, was not detected in any of the snow samples. This result is not surprising considering that pesticide concentrations in air and precipitation generally are highest in spring and summer, coinciding with pesticide application times and warmer temperatures (Majewski and Capel, 1995).

Combining the results from summer precipitation and winter snowpack, it is possible to make preliminary estimates of pesticide deposition at Bear Lake in 2002. Volume-weighted mean concentrations of atrazine, dacthal, and carbaryl in summer precipitation were 0.022, 0.006, and 0.027 µg/L,

respectively. Average concentrations of atrazine and dacthal in snow during 2001 were 0.002 and 0.0009 µg/L, respectively. Because carbaryl was below detection in 2001 snowpack samples, the concentration in snow was estimated at one-half the method reporting limit of 0.0041 µg/L. Using the precipitation amounts in table 3 and assuming that concentrations in snow were similar in 2001 and 2002, annual deposition rates for Bear Lake in 2002 were estimated as 45.8 mg/ha atrazine, 14.2 mg/ha dacthal, and 54.8 mg/ha carbaryl. Because of the much higher concentrations in summer precipitation than winter snow, between 80 and 90 percent of the pesticide deposition to Bear Lake occurred during the summer months. Assuming that pesticide concentrations in Loch Vale were similar to those at Bear Lake, deposition would have been 25 percent higher in Loch Vale during 2002 due to the higher amount of precipitation. To improve estimates of pesticide deposition rates in Loch Vale and other high-elevation areas of RMNP, additional data is needed to determine how pesticide concentrations in precipitation vary with elevation, particularly during summer.

Mercury

Seven weekly bulk-deposition samples were analyzed for total mercury concentrations in the Loch Vale watershed during July through October 2002 (table 6). Concentrations of total mercury in summer precipitation ranged from 2.6 to 36.2 ng/L, and the volume-weighted mean concentration was 21.6 ng/L. A single snow sample collected in Loch Vale on April 5, 2002and analyzed at teh USGS mercury laboratory, had a concentration of 6.4 ng/L (George Ingersoll, U.S. Geological Survey, unpub. data, 2002). Because the snow sample was collected over the entire snowpack depth just before the onset of snowmelt, it should represent the average mercury concentration in precipitation during winter. Although some mercury in precipitation could come from natural sources, a recent study shows that current mercury loading to sediment in alpine lakes in RMNP is elevated 4 times above preindustrial levels (Manthorne, 2002), indicating that most mercury in precipitation is derived from anthropogenic sources. The concentrations measured in Loch Vale were similar to those reported at the Buffalo Pass Mercury Deposition Network (MDN) station near Steamboat Springs, Colo., the only high-elevation station in the Rocky Mountains (*http://nadp.sws.uiuc.edu/mdn/*, accessed April 2003). Volume-weighted mean concentrations of mercury at Buffalo Pass for 1999–2002 were 12.2 ng/L during summer months and 6.4 ng/L during winter months. Mercury concentrations in precipitation at both these sites exhibit similar seasonal patterns with higher concentrations in summer than winter, which generally is attributed to washout of suspended dust by rainfall. Multiplying the annual volume-weighted mean mercury concentration at Loch Vale (11.6 ng/L) by the annual precipitation amount (61 cm) yields an annual mercury deposition of 7.1 µg/m^2 in 2002 at Loch Vale. By comparison, annual deposition at Buffalo Pass

Table 6. Precipitation amounts and total mercury concentrations in bulk deposition at Loch Vale during summer 2002.

[ng/L, nanograms per liter; cm, centimeters]

Date	Precipitation amount (cm)	Total mercury (ng/L)
7/16/02	0.38	12.3
7/23/02	1.51	36.2
7/30/02	0.82	23.3
8/6/02	2.91	16.8
8/27/02	0.51	16.2
10/1/02	1.34	22.2
10/20/02	0.19	2.6

was 8.5 $\mu g/m^2$ in 2000, 6.3 $\mu g/m^2$ in 2001, and 5.9 $\mu g/m^2$ in 2002. These estimates of deposition at Loch Vale and Buffalo Pass are similar to areas in the upper Midwest and Northeast (*http://nadp.sws.uiuc.edu/mdn/*, accessed March 2003) where statewide fish-consumption advisories are common, indicating that mercury deposition rates to RMNP are high enough to be of concern depending on the rate of methylation once mercury is introduced into aquatic ecosystems (Hurley and others, 1995). The relatively high rates of deposition at both sites results from moderate mercury concentrations in precipitation combined with high amounts of precipitation that are typical of high-elevation areas in the Rocky Mountains. Higher concentrations in rain than snow result in nearly 70 percent of the annual mercury deposition occurring during summer months despite the fact that snow accounts for most of the annual precipitation at high elevations. Because mercury deposition during summer appears to exceed deposition during winter, year-round monitoring of mercury deposition may be warranted. Although mercury is measured routinely in snowpack samples in RMNP as part of Rocky Mountain Snowpack Network (Ingersoll and others, 2002) and the Western Airborne Contaminant Assessment Project (National Park Service, 2002), this report describes the only measured mercury concentrations in summer precipitation available to date (2003) for RMNP.

Back Trajectory Models

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) atmospheric transport model (Draxler and Hess, 1997) was used to compute back trajectories, which show the path that an air parcel took to reach RMNP. These trajectories may be useful in determining the potential source regions of contaminants reaching the park. The HYSPLIT model was run interactively on the internet at *http:*

//www.arl.noaa.gov/ready/hysplit4.html (accessed March 2003) using meteorological data sets available on the Web site. One back trajectory was computed for each day starting at noon during June, July, and August 2002. Trajectories were started at a height of 2,000 m above the ground level and were run over the previous 36-hour period. Daily trajectories also were computed for February 2002 to compare trajectory paths during winter with trajectory paths during the summer study period. Figure 2 shows the daily trajectories plotted for the four modeled months on maps of the Western United States. As expected, air masses that reach the park predominantly originate from the west, although distinct seasonal differences in the direction of the trajectories are evident. During winter months, mountainous areas of Colorado are dominated by storms from the northwest that are driven by cyclones sweeping across the Pacific Ocean (Baron and Denning, 1993). This pattern is illustrated by the back trajectories for February, which show that about two-thirds of the air parcels reaching RMNP originated from the north and northwest. During summer, precipitation is associated with convective instability of air masses originating primarily from the southwest and southeast (Baron and Denning, 1993). Trajectories for June, July, and August show a greater percentage of air parcels originating from the southwest and east compared to trajectories during February. For example, in June 2002, nearly two-thirds of the air parcels passed through Utah and Arizona, and only a few trajectories originated from the northwest. In July 2002, there was a notable shift away from the southwest with nearly one-half the air parcels originating to the east of RMNP. This shift reflects an increase in thunderstorm activity resulting from diurnal heating and cooling along the Front Range of Colorado. In August, there was a shift back to southwesterly trajectories with a few trajectories coming from the southeast. This change in pattern likely reflects strengthening of monsoonal flow from the tropical Pacific into the Southwestern United States, which is a common weather pattern during late summer in Colorado.

Although trajectories were computed only for 4 months of the year, some generalizations can be made about the potential source regions and preferred transport pathways of contaminants reaching RMNP in 2002. In winter, contaminants likely were transported from the northwest and perhaps even from more distant trans-Pacific sources such as Asia. A relatively large number of the February trajectories tracked through northwestern Colorado, where two large, coal-fired powerplants are located (Turk and Campbell, 1997). In summer, potential source regions shifted more to the Western and Southwestern States and eastern plains. The most likely sources of contaminants from the West and Southwest are powerplants in southwestern Wyoming, northwestern Colorado, eastern Utah, northern New Mexico and Arizona (Mast and others, 2001a; Peterson and others, 1998). The main contaminant sources to the east are the Front Range urban corridor and agricultural areas on the eastern plains. Because the trajectories were computed only once per day and at a relatively high elevation (2,000 m above ground level), they
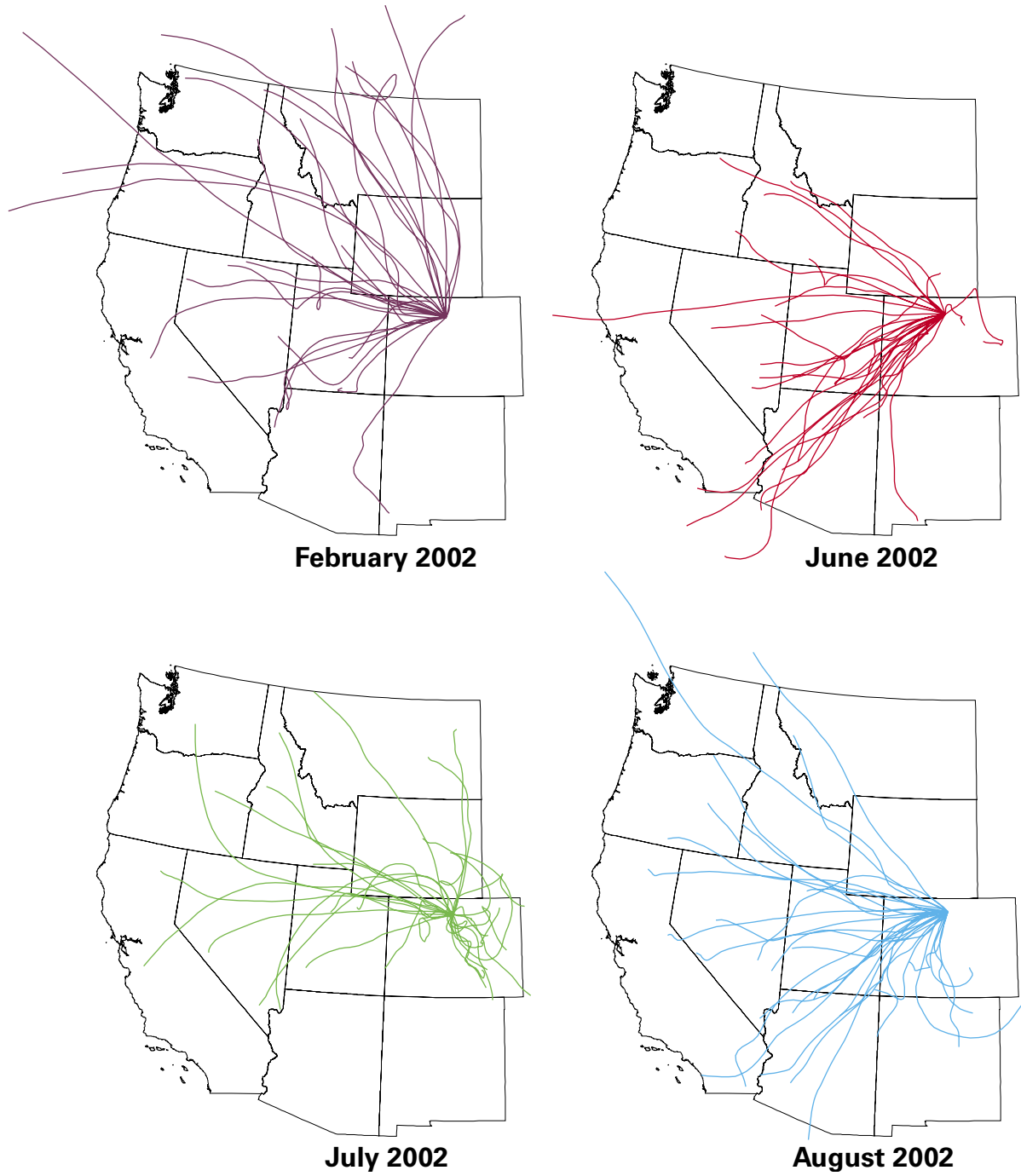
Figure 2.   Daily 36-hour back trajectories at Rocky Mountain National Park during February, June, July, and August.

probably tend to reflect the high-level regional flow from the west and underepresent the frequency of low-level air parcels arriving from east of RMNP. This underrepresentation is probably more pronounced during summer months when localized thunderstorm activity has the potential to carry contaminated air parcels on upvalley winds from the eastern plains into the mountains on nearly a daily basis (Parrish and others, 1990).

Summary and Conclusions

This report presents baseline information on concentrations of nutrients, pesticides, and mercury in summer precipitation collected on the east side of Rocky Mountain National Park in Colorado during 2002. Samples for nutrient and pesticide analyses were collected at a site near Bear Lake (elevation 2,902 m), and samples for mercury analyses were collected at a site in the Loch Vale watershed (elevation 3,159 m). Drought conditions persisted during the study period with summer precipitation amounts at 50 percent of normal at Bear Lake and 55 percent of normal at Loch Vale.

Concentrations of nutrients in summer precipitation at Bear Lake ranged from less than 0.007 to 1.29 mg N/L for ammonium and 0.17 to 4.59 mg N/L for nitrate and were similar to those measured at the Loch Vale NADP station, where nitrogen concentrations in precipitation are among the highest in the Rocky Mountains. Concentrations in summer precipitation were combined with snowpack data from a USGS study to estimate annual deposition of nitrogen in 2002 at Bear Lake and Loch Vale. Annual bulk nitrogen deposition in 2002 was 2.28 kg N/ha at Bear Lake and 3.35 kg N/ha at Loch Vale. Annual wet deposition of nutrients at the Loch Vale NADP collector was 28 percent lower than bulk deposition at Loch Vale, indicating that dry deposition is an important source of nutrients to the park. Although wet deposition is monitored routinely at two NADP sites in the park, additional monitoring of bulk deposition, particularly during summer, is needed to better define dry-deposition inputs of contaminants.

Stable nitrogen and oxygen isotopic data for nitrate collected at Bear Lake were similar to data collected in a 1995–97 USGS study in the Loch Vale watershed. Variations in $\delta^{15}N$ indicate that nitrate isotopes might be useful for distinguishing sources of nitrogen oxide emissions. Additional information on variations in nitrogen isotopes could be gained by collecting isotopic and meteorological data for specific precipitation events.

Current-use pesticides were detected in all nine of the precipitation samples collected at Bear Lake, although concentrations were very low. Atrazine, dacthal, and carbaryl were the most frequently detected pesticides at Bear Lake. Atrazine, a commonly used agricultural herbicide, was detected in seven of nine samples, and dacthal, another herbicide, was detected in all nine samples. Carbaryl, an insecticide used primarily in urban areas, was detected in eight samples. Carbaryl was present at the highest concentrations (0.0079 to 0.0952 µg/L, fol-

lowed by atrazine (0.014 to 0.0604 µg/L), and dacthal (0.0030 to 0.0093 µg/L). Annual deposition rates for 2002 were calculated at Bear Lake for atrazine, carbaryl, and dacthal. Because concentrations in summer precipitation were an order of magnitude higher than in snow, between 80 and 90 percent of the annual pesticide deposition at Bear Lake occurred during summer months. Improved estimates of the magnitude of pesticide deposition in Rocky Mountain National Park would require additional monitoring of pesticide concentrations in precipitation at other high-elevation areas, especially during the late spring and summer when pesticide application is greatest.

Mercury concentrations were measured in all seven weekly samples collected during 2002 in the Loch Vale watershed in concentrations ranging from 2.6 to 36.2 ng/L. The volume-weighted mean concentration of mercury in summer precipitation was 21.6 ng/L, which was more than 3 times higher than the average concentration in snow. Annual mercury deposition in Loch Vale in 2002 was estimated at 7.1 µg/ha, which was similar to deposition at locations in the Midwestern United States where fish-consumption advisories are common. Because mercury deposition during summer appears to exceed deposition during winter, year-round monitoring of mercury deposition is warranted. Although mercury is measured routinely in snowpack samples in RMNP, this report describes the only measured mercury concentrations in summer precipitation available to date (2003) for RNMP.

Back trajectories of air parcels were computed by using the atmospheric transport model HYSPLIT to help identify potential source regions for contaminants reaching the park. Air masses that reach the park predominantly originate from the west, although distinct seasonal differences exist in the direction of the trajectories and, therefore, presumably in the source regions of contaminants. During winter, contaminants probably come from areas to the north and west of Rocky Mountain National Park including an area in northwest Colorado where two large powerplants are located. During summer, contaminants most likely originate from the southwest and southeast from a mixture of sources including powerplants, urban centers, and agricultural areas. The back-trajectory modeling, however, may have underestimated the importance of contaminant sources to the east of Rocky Mountain National Park particularly during the summer thunderstorm season.

References Cited

Arthur, M.A., and Fahey, T.J., 1993, Throughfall chemistry in an Engelmann spruce-subalpine fir forest in north-central Colorado: Canadian Journal of Forest Research, v. 23, p. 738–742.

Baron, Jill, and Denning, A.S., 1993, The influence of mountain meteorology on precipitation chemistry at low and high elevations of the Colorado Front Range, USA: Atmospheric Environment v. 27, p. 2337–2349.

Baron, J.S., Ojima, D.S., Holland, E.A., and Parton, W.J., 1994, Analysis of nitrogen saturation potential in Rocky Mountain tundra and forest—Implications for aquatic ecosystems: Biogeochemistry, v. 27, p. 61–82.

Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., and Rosenberg, B., 1998, Accumulation of persistent organochlorine compounds in mountains of western Canada: Nature, v. 395, p. 585–588.

Burns, D.A., 2002, The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming—A synthesis and critical assessment of published results: U.S. Geological Survey Water-Resources Investigations Report 02–4066, 36 p.

Campbell, D.H., Baron, J., Tonnessen, K.A., Brooks, P.D., and Schuster, P.F., 2000, Controls on nitrogen flux in alpine/subalpine watersheds of Colorado: Water Resources Research, v. 36, p. 37–47.

Campbell, D.H., Kendall, C., Chang, C.Y., Silva, S.R., and Tonnessen, K.A., 2002, Pathways for nitrate release from an alpine watershed—Determination using $\delta^{15}N$ and $\delta^{18}O$: Water Resources Research, v. 38, no. 5, p. 10–1.

Colorado Department of Public Health and Environment, 2001, Regulation No. 31—The basic standards and methodologies for surface water: Colorado Department of Public Health and Environment, Water Quality Control Commission, accessed May 2003, at URL *http://www.cdphe.state.co.us/op/regs/waterregs/100231.pdf*

Draxler, R.R., and Hess, G.D., 1997, Description of the Hysplit_4 modeling system, NOAA Tech Memo ERL ARL–224, December, 24 p.

Environment Canada, 1999, Canadian water-quality guidelines for the protection of aquatic life, Summary tables: Environment Quality Branch, Guidelines and Standards Division, accessed May 2003, at URL *http://www.ec.gc.ca*

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Goolsby, D.A., and others, 1997, Herbicides and their metabolites in rainfall—Origin, transport, and deposition patterns across the Midwestern and Northeastern United States, 1990–1991: Environmental Science and Technology, v. 31, p. 1325–1333.

Hurley, J.P., Benoit, J.M., Babiarz, C.L., Shafer, M.M., Andren, A.W., Sullivan, J.R., Hammond, R., Webb, D.A., 1995, Influences of watershed characteristics on mercury levels in Wisconsin rivers: Environmental Science and Technology, v. 29, no. 7, p. 1867–1875.

Ingersoll, G.P., Turk, J.T., Mast, M.A., Clow, D.W., Campbell, D.H., and Bailey, Z.C., 2002, Rocky Mountain Snowpack Chemistry Network—History, methods, and the importance of monitoring mountain ecosystems: U.S. Geological Survey Open-File Report 01–466, 14 p.

Kimbrough, R.A., and. Litke, D.W., 1997, Pesticides in surface water in agricultural and urban areas of the South Platte River Basin, from Denver, Colorado, to North Platte, Nebraska, 1993–94, 98: U.S. Geological Survey Water-Resources Investigations Report 97–4230.

Landing, W.M., Guentzel, J.L., Gill, G.A., Pollman, C.D., 1998, Methods for measuring mercury in rainfall and aerosols in Florida: Atmospheric Environment, v. 32, p. 909–918.

Majewski, M.S., and Capel, P.D., 1995, Pesticides in the atmosphere—Pesticides in the hydrologic system: Chelsea, Mich., Ann Arbor Press, v. 1, 214 p.

Majewski, M.S., Foreman, W.T., and Goolsby, D.A., 2000, Pesticides in the atmosphere of the Mississippi River Valley, Part I—Rain: The Science of the Total Environment, v. 248, p. 201–212.

Manthorne, D.J., 2002, An inventory of atmospheric mercury enrichment to alpine lakes in Colorado: Boulder, University of Colorado, Master's thesis, 76 p.

Mast, M.A., Turk, J.T., Ingersoll, G.P, Clow, D.W., and Kester, C.L., 2001a, Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpack: Atmospheric Environment, v. 35, p. 3303–3313.

Mast, M.A., Ingersoll, G.P., Clow, D.W., and Foreman, W.T., 2001b, Accumulation of pesticides in a Rocky Mountain snowpack and influence of an Asian dust storm: Society of Environmental Toxicology and Chemistry, Annual Meeting, November 2001, Knoxville, Tenn.

National Park Service, 2002, Western Airborne Contaminant Assessment Project: National Park Service Fact Sheet, URL *http://www2.nature.nps.gov/ard/aqmon/air_toxics/wacap.htm*, accessed March 2003.

Olson, M.L., and DeWild, J.F., 1999, Low-level collection techniques and species-specific analytical methods for mercury in water, sediment, and biota: U.S. Geological Survey Water Resources Investigations Report 99–4018b, 11 p.

Parrish, D.D., Hahn, C.H., Fahey, D.W., Williams, E.J., Bollinger, M.J., Hibler, G., Buhr, M.P., Murphy, P.C., Trainer, M., Hsie, E.Y., Liu, S.C., and Fehsenfeld, F.C., 1990, Systematic variations in the concentration of NOx at Niwot Ridge, Colorado: Geophysical Research, v. 95, no. D2, p. 1817–1836.

Peterson, D.L., Sullivan, T.J., Eilers, J.M., and Brace, S., 1998, Assessment of air quality and air pollutant impacts in National Parks of the Rocky Mountains and Northern Great Plains. Denver: Report NPS/CCSOUW/NRTR–-98/19, U.S. Department of the Interior, National Park Service, Air Resources Division.

Schindler, D., 1999, From acid rain to toxic snow; Ambio, v. 28, no. 4, p. 350–355.

Tanner, R.L., Parkhursta, W.J., Valentea, M.L., Humesa, K.L., Jones, K., and Gilbert, J., 2001, Impact of the 1998 Central American fires on PM2.5 mass and composition in the southeastern United States: Atmospheric Environment, v. 35, no. 36, p. 6539–6547.

Turk, J.T., and Campbell, D.H., 1997, Are aquatic resources of the Mt. Zirkel Wilderness Area in Colorado affected by acid deposition and what will emissions reductions at the local powerplants do?: U.S. Geological Survey Fact Sheet 043–97, 4 p.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C–18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 60 p.