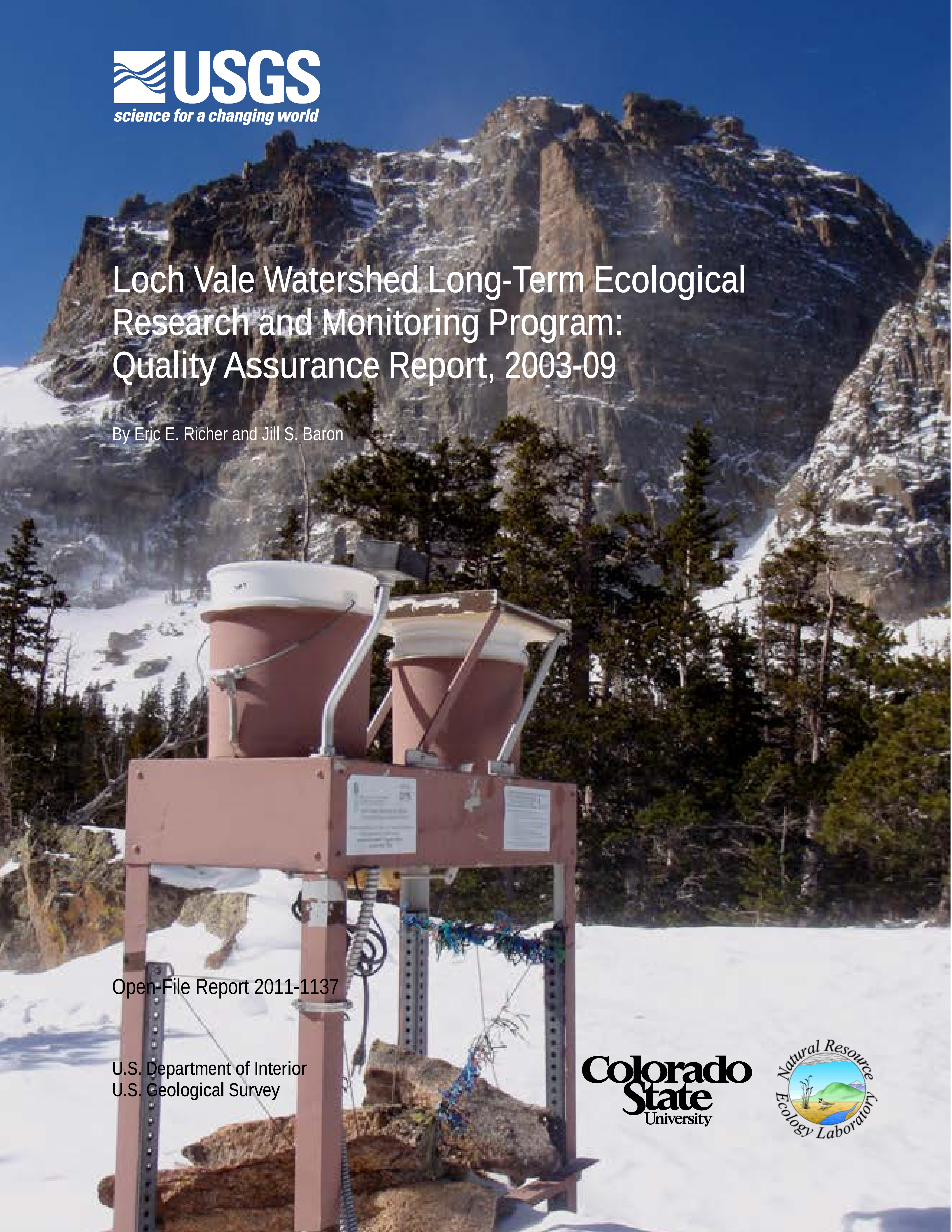

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Loch Vale Watershed Long-Term Ecological Research and Monitoring Program: Quality Assurance Report, 2003-09

By Eric E. Richer and Jill S. Baron

Open-File Report 2011-1137

U.S. Department of Interior
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Colorado State University

Natural Resource Ecology Laboratory

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km^2)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	264.2	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
	Flow rate	
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
	Pressure	
kilopascal (kPa)	0.01	bar

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C=(°F-32)/1.8
Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). Altitude, as used in this report, refers to distance above the vertical datum.
Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).
Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).
Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or microequivalents per liter (µeq/L).

Abbreviations

ANC	Acid neutralizing capacity
ARML	Air Resource Management Laboratory
Ca^{2+}	Calcium
CAL	Central Analytical Laboratory
Cl^-	Chloride
CPD	Conductance percent difference
CSU	Colorado State University
DI	Deionized
DOC	Dissolved organic carbon
F^-	Fluoride
IPD	Ion percent difference
K^+	Potassium
LVWS	Loch Vale Watershed
Mg^{2+}	Magnesium
Na^+	Sodium
NADP	National Atmospheric Deposition Program
NH_4^+	Ammonium as ammonium
NO_3^-	Nitrate as nitrate
NPS	National Park Service
NREL	Natural Resource Ecology Laboratory
PO_4^{3-}	Orthophosphate
QA	Quality assurance
QAP	Quality-assurance plan
QMP	Quality-management plan
RMNP	Rocky Mountain National Park
RMRS	Rocky Mountain Research Station
SC	Specific conductance
SiO_2	Dissolved silica as silicon dioxide
SO_4^-	Sulfate as sulfate
SRS	Standard reference sample
TDN	Total dissolved nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
USEPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
USGS	U. S. Geological Survey
WEBB	Water, Energy, and Biogeochemical Budgets
WMI	Western Mountain Initiative
WY	Water year

Loch Vale Watershed Long-Term Ecological Research and Monitoring Program: Quality Assurance Report, 2003-09

By Eric E. Richer[1] and Jill S. Baron[2]

Abstract

The Loch Vale watershed project is a long-term research and monitoring program located in Rocky Mountain National Park that addresses watershed-scale ecosystem processes, particularly as they respond to atmospheric deposition and climate variability. Measurements of precipitation depth, precipitation chemistry, discharge, and surface-water quality are made within the watershed and elsewhere in Rocky Mountain National Park. As data collected for the program are used by resource managers, scientists, policy makers, and students, it is important that all data collected in Loch Vale watershed meet high standards of quality. In this report, data quality was evaluated for precipitation, discharge, and surface-water chemistry measurements collected during 2003-09. Equipment upgrades were made at the Loch Vale National Atmospheric Deposition Program monitoring site to improve precipitation measurements and evaluate variability in precipitation depth and chemistry. Additional solar panels and batteries have been installed to improve the power supply, and data completeness, at the NADP site. As a result of equipment malfunction, discharge data for the Loch Outlet were estimated from October 18, 2005, to August 17, 2006. Quality-assurance results indicate that more than 98 percent of all surface-water chemistry measurements were accurate and precise. Records that did not meet quality criteria were removed from the database. Measurements of precipitation depth, precipitation chemistry, discharge, and surface-water quality were all sufficiently complete and consistent to support project data needs.

Introduction

The National Park Service (NPS) initiated the Loch Vale watershed (LVWS) project in 1982 with funding from the Aquatic Effects Research Program of the National Acid Precipitation Assessment Program. The LVWS is a 7-km^2 (square kilometer) basin located within Rocky Mountain National Park (RMNP) in the Colorado Front Range. The project is currently a cooperative effort of the NPS, U.S. Geological Survey (USGS), and Colorado State University (CSU). The long-term research and monitoring program addresses watershed-scale ecosystem processes, particularly as they respond to atmospheric deposition and climate variability.

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Monitoring of climate, hydrology, precipitation chemistry, and surface-water quality allows analysis of long-term trends and distinction between natural and human-caused disturbances. Research efforts are diverse, and include vegetation responses to nitrogen deposition, algal response to nitrogen availability, microbial activity in subalpine and alpine soils, hydrologic flow paths, and the response of aquatic organisms to disturbance. These research activities provide knowledge about the broad range of processes that influence high-altitude ecosystems in the Rocky Mountains.

Research Objectives

1. To understand and differentiate natural processes from unnatural, human-caused drivers of change.
2. To understand and quantify the effects of atmospheric deposition and climate change on high-altitude ecosystems.

Program Objectives

1. To share knowledge gained from research activities with the public, scientific community, and natural-resource managers.
2. To offer a program of graduate education and research that develops future scientists and knowledgeable resource managers.
3. To maintain the LVWS long-term ecological research project as a successful example of ecosystem-study design, interdisciplinary collaboration, long-term monitoring, and sustainable natural-resource management.

As results from the long-term monitoring and research program are used by resource managers, scientists, policy makers, and students, it is important that all data collected in LVWS meet high standards of quality. Therefore, the USGS must ensure the integrity of all data collected as part of the program.

Purpose and Scope

This report describes quality assurance (QA) procedures and results used in support of long-term data-collection efforts in the LVWS. Since 1982, all LVWS samples and data have been analyzed according to standard methods. This report addresses data collected from January 1, 2003, through December 31, 2009. Previous QA reports evaluated the quality of data collected during 1983-87 (Denning, 1988), 1989-90 (Edwards, 1991), 1991-94 (Allstott, 1995), 1995-98 (Allstott and others, 1999), and 1999-2002 (Botte and Baron, 2004). Variables addressed in this report include precipitation depth and chemistry, hydrologic measurements, and surface-water chemistry. Support for sampling in the LVWS is jointly provided by USGS Western Mountain Initiative (WMI) and Water, Energy, and Biogeochemical Budgets (WEBB) programs. The WMI supports LVWS personnel, which includes USGS employees, CSU employees, and NPS volunteers. LVWS personnel monitor precipitation depth, precipitation chemistry, and surface-water chemistry, which are the focus of this report. Meteorological, streamflow, and additional water-chemistry measurements are made within the LVWS and evaluated for data quality as part of the WEBB program.

Approach

Streamflow data were collected and processed by LVWS personnel during 1983-2006. In August 2006, responsibility for collection and QA of all discharge data in the LVWS was transferred from LVWS personnel to the WEBB program. Surface-water samples were collected weekly at the Loch Outlet and less frequently at many other sites in RMNP (fig. 1). Surface-water chemistry was determined according to U.S. Environmental Protection Agency (USEPA) protocols at the U.S. Forest Service Rocky Mountain Research Station (USFS-RMRS) Water Chemistry Laboratory and Natural Resource Ecology Laboratory (NREL) at CSU in Fort Collins, Colorado. Protocols for sampling and for measuring surface-water chemistry are documented in Richer and others (2011).

Precipitation depth and chemistry were monitored at the Loch Vale National Atmospheric Deposition Program (NADP) site, CO98 (fig. 1). Precipitation samples were collected according to NADP protocols (Dossett and Bowersox, 1999), and analyzed at the NADP Central Analytical Laboratory (CAL) in Champaign, Illinois. QA procedures for precipitation samples are outlined in the NADP Quality Assurance Plan (QAP; National Atmospheric Deposition Program, 2009a) and Quality Management Plan (QMP; National Atmospheric Deposition Program, 2009b). To further evaluate the quality of data collected at CO98, a colocated NADP site, CO89, was installed in October 2009.

LVWS data are available at multiple locations on the Internet (table 1), or by request from the Principal Investigator of the Loch Vale research program, U.S. Geological Survey, Fort Collins, Colorado.

Table 1. Summary of Loch Vale watershed data collected during 2003-09.

Web site	Available data
Loch Vale watershed: Water, Energy, and Biogeochemical Budgets (WEBB) *http://co.water.usgs.gov/lochvale/* *http://waterdata.usgs.gov/nwis*	• Hydrology: Andrews Creek, Icy Brook, and Loch Outlet • Surface-water chemistry: Andrews Creek, Icy Brook, and Loch Outlet • Meteorology: Main Loch Vale weather station, Andrews Meadow, and Sharkstooth
National Atmospheric Deposition Program *http://nadp.sws.uiuc.edu/*	• Precipitation depth and chemistry: Rocky Mountain National Park–Loch Vale (CO98 and CO89)
Natural Resource Ecology Laboratory: Loch Vale Watershed Research Project *http://www.nrel.colostate.edu/projects/lvws/pages/homepage.htm*	• Hydrology: Loch Outlet • Surface-water chemistry: Andrews Creek, Emerald Lake Outlet, Lake of Glass Outlet, Lake Haiyaha Outlet, Lake Husted, Loch Inlet, Loch Outlet, Lake Louise Inlet, Lake Louise Outlet, Sky Pond Inlet North, Sky Pond Inlet South, Sky Pond Outlet • Meteorology: Loch Vale remote area weather station

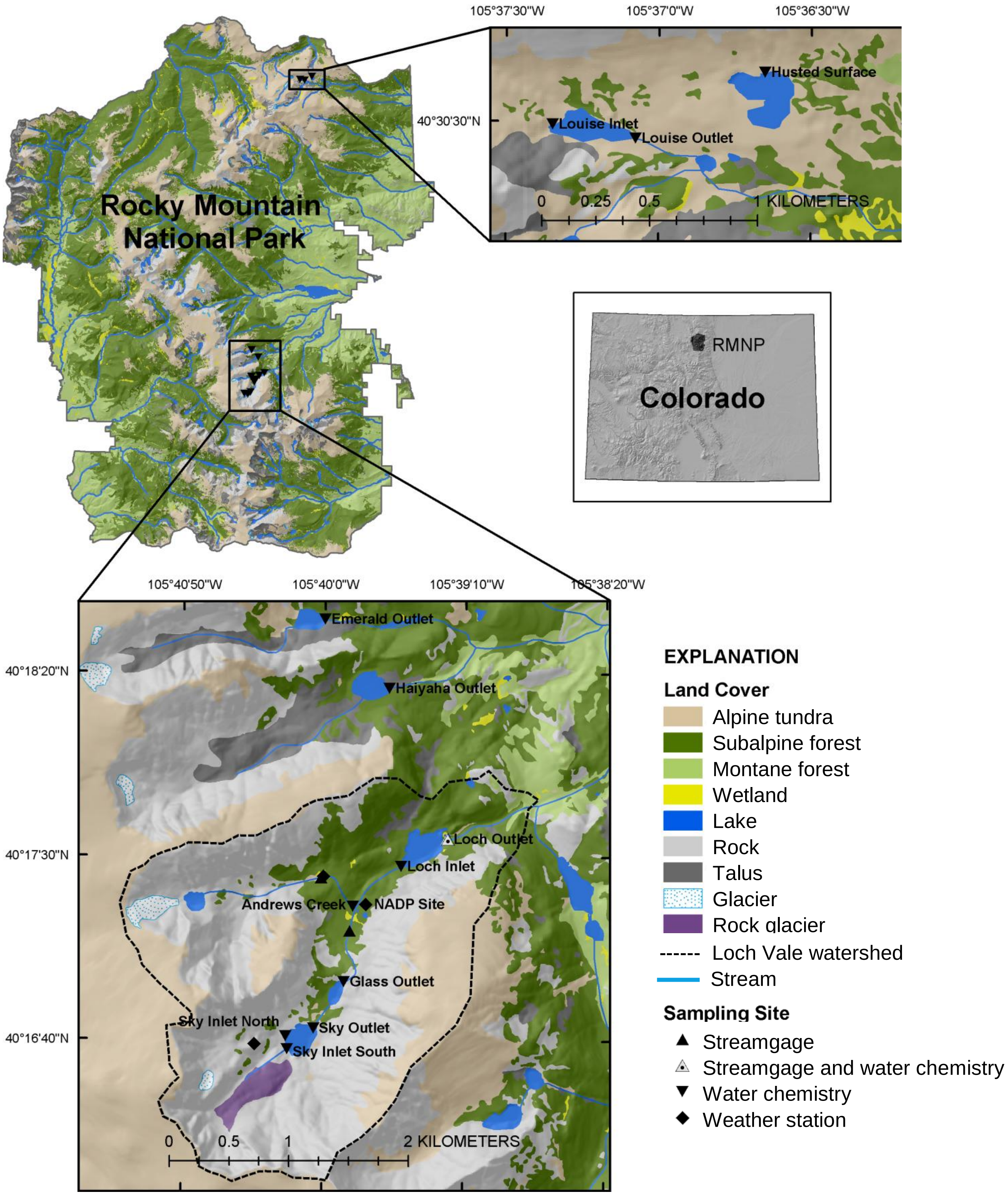

Figure 1. Loch Vale watershed project monitoring sites in Rocky Mountain National Park (RMNP) sampled during 2003-09. (NADP, National Atmospheric Deposition Program)

Precipitation Data

Precipitation was monitored at the Loch Vale NADP sites using rain gages and precipitation collectors. Cumulative precipitation depth was recorded to a data logger every 15 minutes, whereas precipitation samples were collected weekly. Precipitation depth was measured with an Alter shielded weighing bucket rain gage. Two types of rain gages were used at the Loch Vale NADP site during 2003-09. An Alter shielded Belfort Model 5-780 rain gage measured precipitation depth from August 1983 to August 2010. NADP resolved to upgrade all precipitation gages in 2006, and an Alter shielded ETI NOAH IV electronic rain gage (e-gage) was installed at the CO98 NADP site on June 18, 2007. After more than 2 years of colocated precipitation data collection, the Belfort rain gage was dismantled on August 9, 2010. Analysis of the colocated precipitation data for CO98 revealed that the NOAH IV captured approximately 7 percent more precipitation than the Belfort (fig. 2), which is within the expected margin of error associated with interpretation of Belfort strip charts. To compare variability in precipitation depth and chemistry between sites, a colocated NADP site, CO89, was installed in October 2009 but was not fully operational until January 2010. The Loch Vale NADP sites, CO98 and CO89, are located at an altitude of 3,160 m.

Aerochem Metrics Model 301 precipitation collectors were used at NADP sites to capture precipitation for chemical analysis. Although precipitation depth is reported for collector buckets, the catch efficiency of the Aerochem Metrics wet deposition sampler is limited because the sampler is not shielded, especially during winter months when precipitation falls as snow

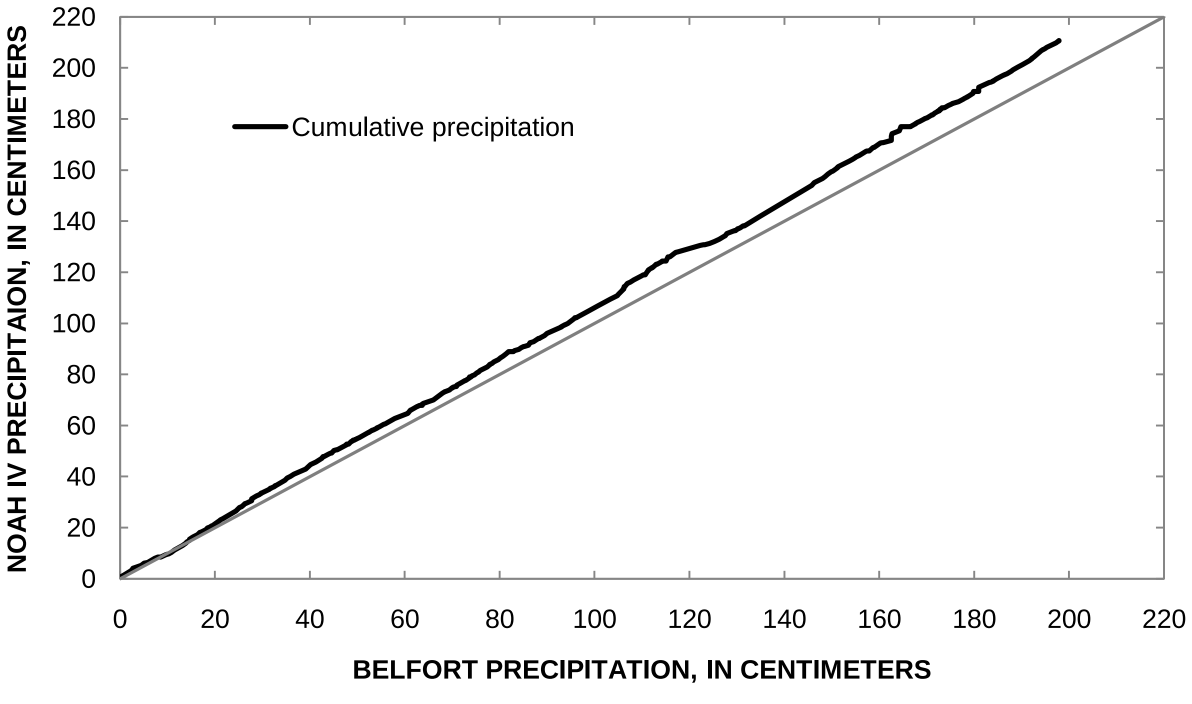

Figure 2. Cumulative precipitation measured at the colocated Belfort and NOAH IV rain gages at the Loch Vale CO98 National Atmospheric Deposition Program site during 2008-09. (The light grey line represents the 1:1 line.)

(table 2). Alter shielded rain gages are more effective than the Aerochem collectors for catching solid precipitation in wind-prone areas. The World Meteorological Organization reports that Alter shielded rain gages capture approximately 75 percent of winter precipitation, whereas unshielded gages similar to the Aerochem collector capture approximately 57 percent (Goodison and others, 1998). CO98 collector catch efficiency ranged from 99 percent in the summer to just 33 percent in the winter on average (table 2). Poor winter catch efficiency can invalidate samples as a result of inadequate sample volume for complete chemical analysis.

Table 2. Annual catch efficiency of the CO98 site Aerochem Metrics precipitation collector relative to the Alter shielded rain gage by season during 2003-09.

Season	Relative catch efficiency, in percent							
	2003	2004	2005	2006	2007	2008	2009	Average
Winter	51	27	25	27	47	29	22	33
Spring	44	66	62	50	58	56	57	56
Summer	99	100	97	107	101	96	98	99
Fall	50	68	40	66	86	62	61	62
Annual	57	70	62	62	73	61	54	63

Chemical analysis and quality assurance for all precipitation samples were conducted in accordance with NADP protocols (National Atmospheric Deposition Program, 2009a; 2009b). The quality-control program includes weekly blanks, check samples, blind network replicates, and internal blind audits with predetermined samples. The CAL was in compliance with the NADP QAP and QMP during 2003-09 (Rothert, 2008a; Rothert, 2008b; Rothert, 2009; Rothert, 2010; Dombek, 2011). Instruments used at CAL for chemical analysis of precipitation samples are listed in table 3. In 2004, CAL switched from a flame atomic absorption spectrometer to an inductively coupled plasma-optical emission spectrometer for analysis for calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+), and began using a Broadly-James electrode to measure pH. Detection limits for all ions measured at CAL are listed in table 4.

As part of the project, 363 precipitation samples were collected from CO98 for chemical analysis from December 31, 2002, to December 29, 2009. Of these 363 samples, 271 (75 percent) were considered valid according to NADP criteria. Only valid samples with adequate sample volume were used to calculate annual precipitation-weighted mean concentrations, deposition, and data completeness. Annual sample validity is summarized in table 5. Of the 92

Table 3. National Atmospheric Deposition Program Central Analytical Laboratory instrumentation for measuring concentrations of precipitation analytes during 2003-09.

[K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; Cl^-, chloride; NO_3^-, nitrate as nitrate; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as orthophosphate; SC, specific conductance; instrumentation data from Rothert (2010) and Dombeck (2011)]

Analyte	Instrument	Years of service
K^+, Na^+, Ca^{2+}, Mg^{2+}	Flame atomic absorption spectrometer	1978-2003
	Inductively coupled plasma-optical emission spectrometer	2004-2009
NH_4^+	Phenate (flow injection colorimetry)	1978-2009
Cl^-, NO_3^-, SO_4^{2-}	Ion chromatography, dionex	1985-2009
PO_4^{3-}	Ascorbic acid (flow injection colorimetry)	1978-2009
pH	Corning pH meter	1978-2003
	Broadly-James electrode	2004-2009
SC	YSI conductivity meter	2003-2009

Table 4. National Atmospheric Deposition Program Central Analytical Laboratory detection limits for precipitation analytes during 2003-09.

[K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; Cl^-, chloride; NO_3^-, nitrate as nitrate; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as orthophosphate; values from Rothert (2008a), Rothert (2008b), Rothert (2009), Rothert (2010), and Dombek (2011)]

	Detection limit (milligrams per liter)						
Analyte	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
K^+	0.003	0.001	0.001	0.002	0.001	0.001	0.001
Na^+	0.003	0.003	0.003	0.002	0.001	0.001	0.001
Ca^{2+}	0.009	0.002	0.002	0.002	0.002	0.006	0.006
Mg^{2+}	0.003	0.001	0.001	0.001	0.001	0.001	0.001
NH_4^+	0.020	0.020	0.005	0.003	0.004	0.006	0.003
Cl^-	0.005	0.005	0.008	0.005	0.003	0.004	0.004
NO_3^-	0.010	0.010	0.009	0.015	0.017	0.009	0.006
SO_4^{2-}	0.010	0.010	0.013	0.015	0.010	0.007	0.004
PO_4^{3-}	0.009	0.009	0.006	0.005	0.004	0.004	0.002

Table 5. Annual sample validity for National Atmospheric Deposition Program site CO98 during 2003-09.

Reason for invalidation	2003	2004	2005	2006	2007	2008	2009
Inadequate volume	1	3	3	6	7	5	8
Contaminated sample	5	4	0	4	7	6	4
Undefined sample	0	0	0	7	3	2	2
Bulk sample	0	0	0	0	0	7	4
Extended sampling interval	1	0	1	0	0	0	1
Field protocol departure	0	0	0	1	0	0	0
Number of invalid samples	**7**	**7**	**4**	**18**	**17**	**20**	**19**
Number of valid samples	**44**	**45**	**48**	**34**	**34**	**32**	**34**
Total number of samples	**51**	**52**	**52**	**52**	**51**	**52**	**53**
Percent valid samples	**86**	**87**	**92**	**65**	**67**	**62**	**64**

invalid samples, 33 were invalid because the sample volume was inadequate for analysis, 30 were contaminated, 14 were undefined (that is, the collector was open when no precipitation occurred), 11 were invalid because the collector was open continuously (that is, the sample was a bulk sample), 3 were invalid because the sampling interval was greater than 8 days, and 1 was invalid as a result of a departure from field protocol.

Inadequate sample volume was the most common reason for sample invalidation. There are three primary reasons for inadequate sample volume: (1) inadequate precipitation depth, (2) failure of the precipitation collector to open during snow storms due to insensitivity of the precipitation sensor, and (3) loss of sample when snow is blown back out of the collector bucket. Contamination was the second most common reason for sample invalidation. The most common types of contamination were dirt particles and plant matter. In the fall of 2009, approximately 20 trees around the Loch Vale NADP site were trimmed or felled to reduce sample contamination from plant matter. Cloudy or discolored samples, which may result from natural dust events, or the presence of insects in the collector bucket also contaminated samples. Of all precipitation samples sent to NADP during 2003-09, 7 percent were invalidated as a result of equipment malfunction (that is, bulk and undefined samples). Additional solar panels and batteries were installed in 2010 to reduce equipment malfunction from power loss.

Discharge Data

The Loch Outlet is located at the northeastern edge of the basin at an altitude of 3,105 m (fig. 1). Discharge at the Loch Outlet has been monitored with a Parshall flume and stilling well since 1983. Accuracy of the Parshall flume is estimated at ± 5 percent (Winter, 1981). In this section, discharge data for water years (WY) 2003-06 are evaluated. In August 2006, responsibility for collection and QA of discharge data at the Loch Outlet was transferred from LVWS personnel to the WEBB program. Stage was recorded with a Leupold and Stevens chart recorder through 2006. The chart recorder has since been replaced with a pressure transducer. As a quality check of flow data, stage height was recorded weekly from a staff gage located inside the flume, unless the flume was covered with snow.

Because stage records were incomplete as a result of a malfunctioning chart recorder, discharge data for the Loch Outlet from October 18, 2005, to August 17, 2006, were estimated from observed flows at the Andrews Creek streamgage. Discharge data for Andrews Creek and the Loch Outlet during 2000-09 were used to develop the simple linear model with an R^2 value of 0.89 (fig. 3). Qualitative analysis of hydrographs for 2003-06 shows that estimated discharge values agree with streamflow patterns observed in the watershed (figs. 4-7). These qualitative comparisons of discharge at the Andrews Creek, Icy Brook, and Loch Outlet streamgages show that runoff generally peaked within 1 week at the three sites. Discharge values were greatest at the Loch Outlet as a result of the larger contributing area, which includes both the Andrews Creek and Icy Brook subbasins. (Discharge data are available from the USGS National Water Information Web site at *http://waterdata.usgs.gov/nwis*.)

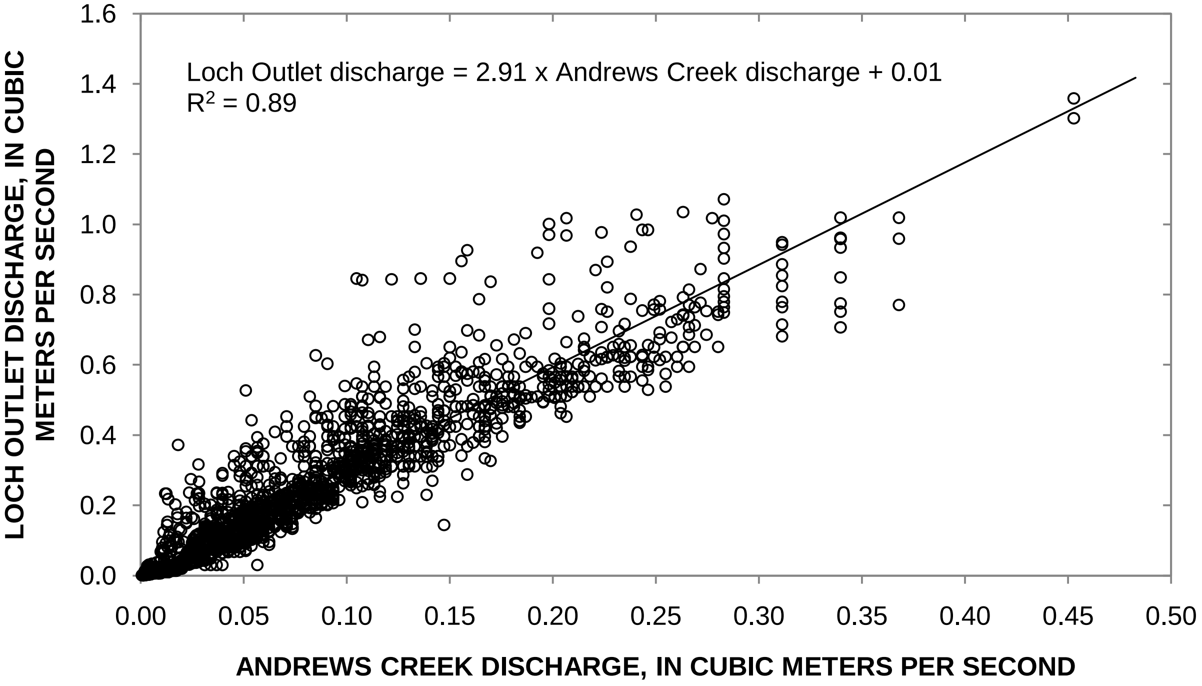

Figure 3. Relation between observed discharge at Andrews Creek and the Loch Outlet during 2000-09 used to estimate discharge for the Loch Outlet from October 18, 2005, to August 17, 2006.

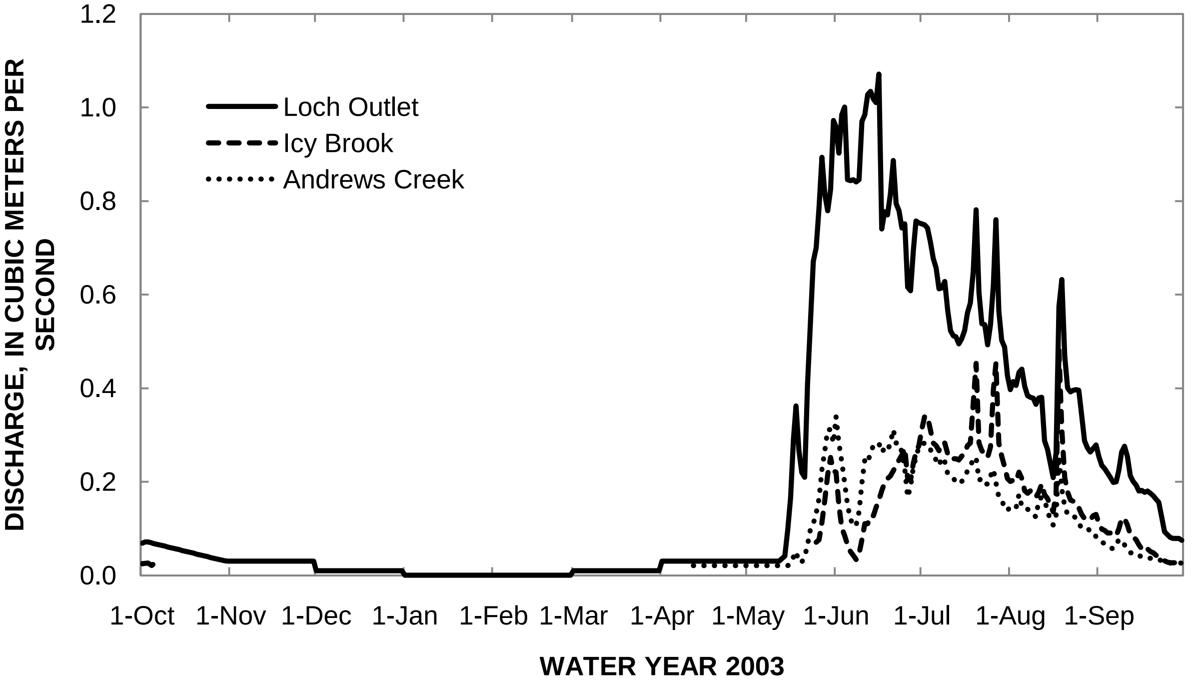

Figure 4. Discharge at three streamflow stations in the Loch Vale watershed during water year 2003.

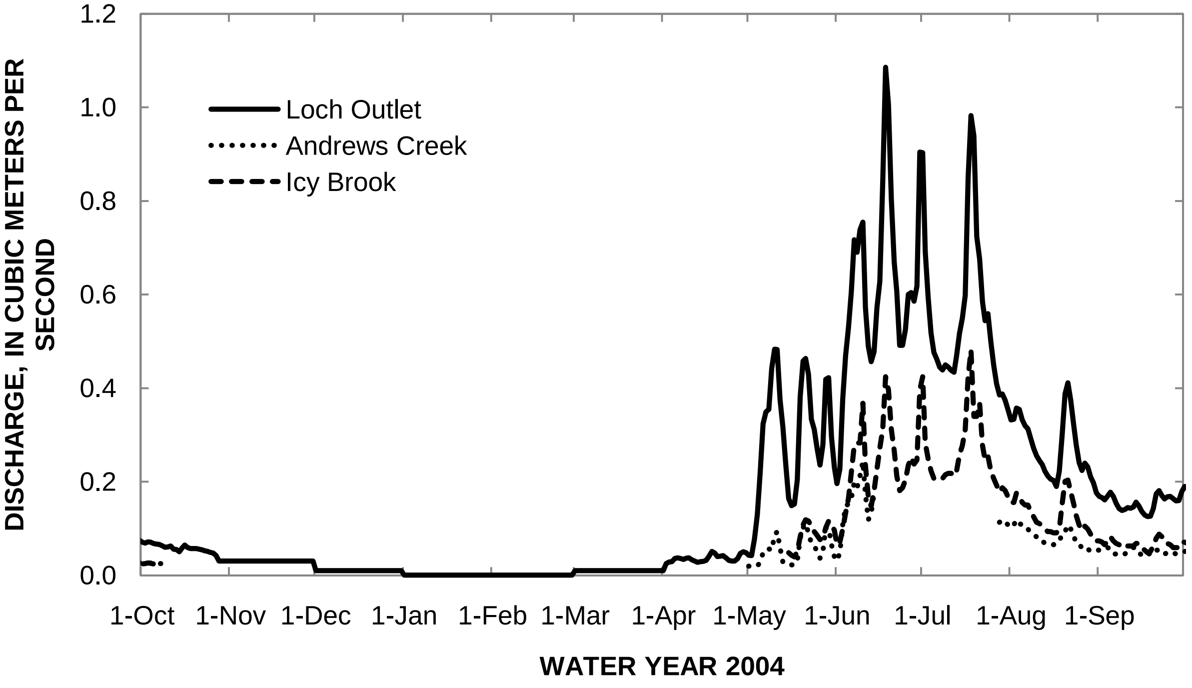

Figure 5. Discharge at three streamflow stations in the Loch Vale watershed during water year 2004.

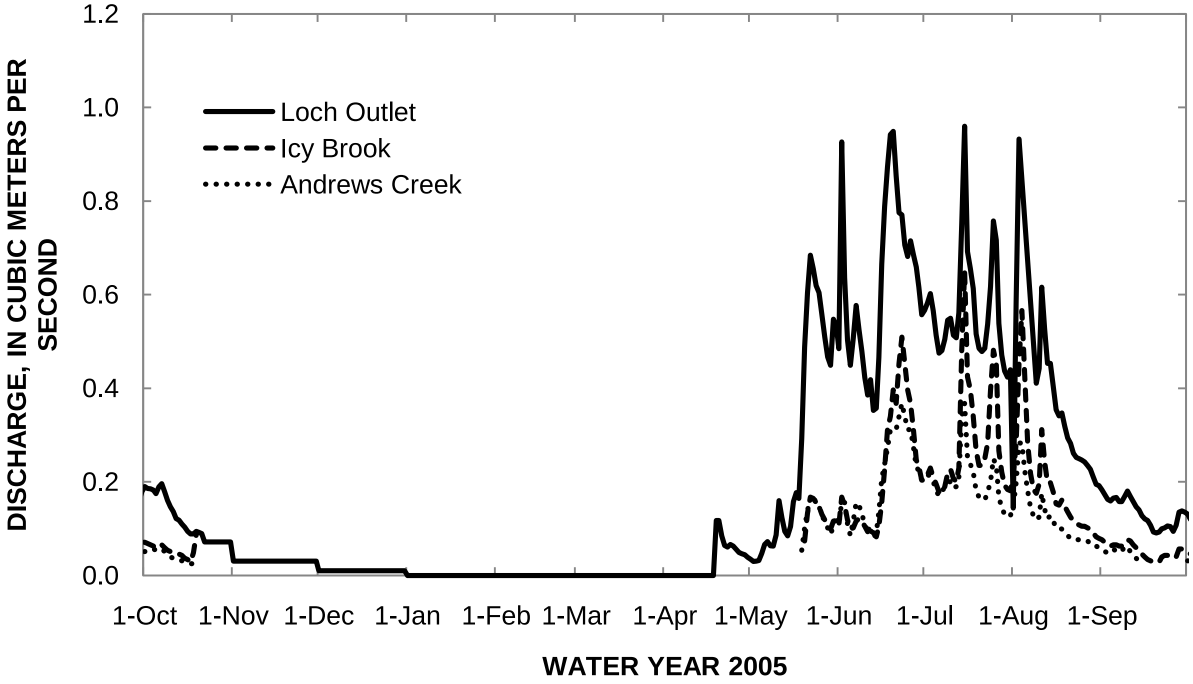

Figure 6. Discharge at three streamflow stations in the Loch Vale watershed during water year 2005.

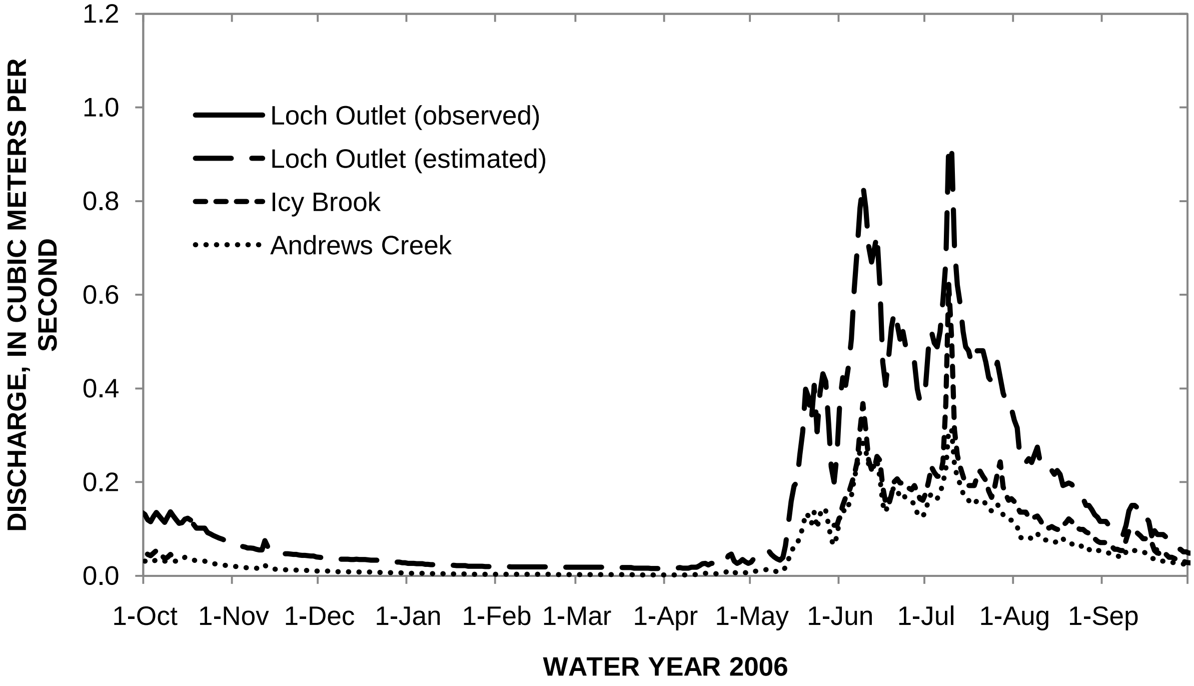

Figure 7. Discharge at three streamflow stations in the Loch Vale watershed during water year 2006. (Loch Outlet discharge data for October 18, 2005, to August 17, 2006, were estimated.)

Surface-Water Chemistry Data

Water samples from the Loch Outlet were collected and processed weekly; sample collection from the other sites was less frequent. During 2003-09, 565 samples were collected, 55 (10 percent) of which were QA samples. Data quality was evaluated using field blanks, field duplicates, charge balance calculations (that is, ion percent difference), and theoretical conductance (that is, conductance percent difference). Sample-collection and -processing procedures were assessed through the use of blank and duplicate samples. Field blanks were used to examine contamination from collection and processing procedures, whereas precision was evaluated with field duplicate samples. Differences in constituent concentrations in normal, blank, and duplicate samples highlight deficiencies in the analytical process. Quality-control check samples and laboratory blanks were analyzed every 10 samples to ensure internal quality control for each laboratory. All protocols used in the preparation, collection, processing, and shipment of samples are described in the LVWS methods manual (Richer and others, 2011). Changes in laboratory and field procedures during 2003-09 are summarized farther on in this report.

Natural Resource Ecology Laboratory

LVWS surface-water samples were processed at the NREL before delivery to the RMRS laboratory. Specific conductance at 25°C (that is, field conductivity) and water temperature were measured prior to sample collection with a Thermo Orion 105Aplus conductivity meter, which was checked against standard reference solutions weekly and calibrated as needed. Water samples were analyzed at the NREL for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) with a Schimadzu TOC-V CPN Total Organic Carbon Analyzer. The Schimadzu measures total organic carbon (TOC) and total nitrogen (TN) but, because the samples were filtered prior to analysis, the analytes measured are operationally defined as dissolved organic carbon (DOC) and total dissolved nitrogen (TDN). Dissolved silica (as SiO_2) was measured with a Thermo Spectronic 20D$^+$ spectrophotometer using the silicomolybdate method adapted from Clesceri and others (1998).

Detection limit is the lowest quantity of a substance that can be distinguished from the absence of that substance. This limit is defined as three times the standard deviation of signals produced by 10 nonconsecutive blank samples (U.S. Environmental Protection Agency, 1987). Detection limits for all analyses conducted at NREL were calculated in 2009 (table 6). Prior to 2009, detection limits were not evaluated annually. The calculated detection limits for DOC and TDN are below the required USEPA values (U.S. Environmental Protection Agency, 1987). The NREL detection limit for SiO_2 is just slightly higher than the estimated detection limit for the method, which is 0.3 mg SiO_2/L. Because phosphorus concentrations in LVWS waters were dilute, measurements of total phosphorus (TP) and orthophosphate (PO_4^{3-}) at NREL were suspended because detection limits have proved inadequate for these analyses (for example, greater than 0.001 mg/L for PO_4^{3-}). TP samples were acidified and stored at 4°C until analytical capabilities improve or another laboratory with a lower TP detection limit is identified. pH analyses at NREL were discontinued in January 2010 because they were redundant with pH measurements made at the RMRS laboratory.

Table 6. Detection limits for carbon, nitrogen, and silica at the Natural Resource Ecology Laboratory during 2009.

[mg/L, milligrams per liter; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; SiO_2, dissolved silica as silicon dioxide]

Analyte	Detection limit (mg/L)	Method of analysis
DOC	0.06	Oxidative combustion-infrared analysis
TDN	0.05	Oxidative combustion-chemiluminescence
SiO_2	0.4	Spectrophotometry-silicomolybdate

U.S. Forest Service Rocky Mountain Research Station Water Chemistry Laboratory

Major cations and anions were measured at the RMRS Water Chemistry Laboratory. Specific conductance at 25°C (that is, laboratory conductivity), pH, and acid neutralizing capacity (ANC) were also determined at the RMRS. Samples were delivered to the RMRS, where they were stored in a cold, dark environment, within 48 hours of collection and were processed in accordance with USEPA guidelines. Guidelines established in the Handbook of Methods for Acid Deposition Studies (U.S. Environmental Protection Agency, 1987) and the Standard Methods for the Examination of Water and Wastewater (Clesceri and others, 1998) were followed for all analyses at the RMRS laboratory. Control charts and control samples were utilized daily to monitor internal quality control. Field and laboratory blanks were analyzed as well as lab duplicates and check standards (every 10 samples). The lab manager, lab analyst, and data analyst checked, verified, and archived all data collected. The published detection limits for the RMRS laboratory, which was formerly affiliated with the Air Resource Management Laboratory (ARML), are listed in table 7. The detection limit for ANC is difficult to quantify as a result of the gran titration method used for the analysis and seasonality of the data, which vary widely throughout the year.

The performance of USGS, cooperator, and contractor analytical laboratories that measure chemical constituents in environmental samples is evaluated in the Standard Reference Sample (SRS) project. SRS testing is performed at the RMRS laboratory every 6 months to assess the quality of laboratory methods and procedures while evaluating analytical precision and

Table 7. Detection limits for U.S. Forest Service Rocky Mountain Research Station Water Chemistry Laboratory.

[mg/L, milligrams per liter; ANC, acid neutralization capacity; K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; F^-, fluoride; Cl^-, chloride; NO_3^-, nitrate as nitrate; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as orthophosphate; ND, no data; values from Air Resource Management Laboratory (2010)]

Analyte	Detection limit (mg/L)	Method of analysis
ANC	ND	Gran titration
K^+	0.01	Monovalent/divalent column
Na^+	0.02	Monovalent/divalent column
Ca^{2+}	0.04	Monovalent/divalent column
Mg^{2+}	0.01	Monovalent/divalent column
NH_4^+	0.01	Monovalent/divalent column
F^-	0.01	Ion chromatography with separator column
Cl^-	0.02	Ion chromatography with separator column
NO_3^-	0.03	Ion chromatography with separator column
SO_4^{2-}	0.04	Ion chromatography with separator column
PO_4^{3-}	0.04	Ion chromatography with separator column

accuracy. All pertinent SRS information and data are available at *http://bqs.usgs.gov/srs/.* SRS results for the RMRS laboratory (SRS lab #2) during 2003-09 are listed in table 8. The RMRS laboratory performed well for all SRS samples, with the exception of PO_4^{3-} and NH_4^+ measurements. Results for PO_4^{3-} have been variable over the years, and the RMRS laboratory has chosen not to report some values because they are typically below detection limit. NH_4^+ concentrations are generally very low for LVWS waters. In addition, high Na^+ concentrations make it difficult for the chromatography program to separate Na^+ and NH_4^+ peaks. As a result of the problem associated with determining NH_4^+ concentrations when Na^+ concentrations are high, the effective detection limit for NH_4^+ in LVWS surface waters is 0.05 mg/L (Derek Pierson, U.S. Forest Service, written commun., 2010). Therefore, NH_4^+ values less than 0.05 mg/L cannot be resolved.

Table 8. Analytical results for precipitation Standard Reference Samples analyzed at the U.S. Forest Service Rocky Mountain Research Station Water Chemistry Laboratory during 2003-09.

[SC, specific conductance; K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; F^-, fluoride; Cl^-, chloride; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as phosphorus; RV, reported value in milligrams per liter; MPV, most probable value in milligrams per liter; %Diff, percent difference between RV and MPV; ND, no data reported]

Period	Statistic	pH	SC	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	SO_4^{2-}	PO_4^{3-}
Fall	RV	3.950	57.9	ND	0.511	0.547	0.052	0.098	5.596	0.258	ND
2003	MPV	3.941	58.7	ND	0.480	0.550	0.054	0.107	5.878	0.320	ND
	%Diff	0.2	-1.4	ND	6.5	-0.5	-3.7	-8.4	-4.8	-19.4	ND
Spring	RV	3.932	65.7	0.331	0.313	0.499	0.048	0.112	5.821	0.283	ND
2004	MPV	3.900	63.2	0.325	0.304	0.495	0.048	0.110	6.120	0.344	ND
	%Diff	0.8	4.0	1.8	3.0	0.8	0.0	1.8	-4.9	-17.7	ND
Fall	RV	4.003	55.8	0.242	0.269	0.552	0.058	0.041	4.818	0.457	ND
2004	MPV	3.990	51.7	0.180	0.235	0.530	0.042	0.048	4.895	0.536	ND
	%Diff	0.3	7.9	34.4	14.5	4.2	39.4	-14.8	-1.6	-14.7	ND
Spring	RV	5.138	18.2	0.962	1.018	0.517	0.100	0.099	2.248	1.156	ND
2005	MPV	5.130	17.3	0.950	0.990	0.520	0.094	0.090	2.330	1.140	ND
	%Diff	0.2	5.2	1.3	2.8	-0.6	6.4	10.0	-3.5	1.4	ND
Spring	RV	4.143	39.9	0.459	0.703	0.464	0.073	0.136	4.375	0.517	ND
2006	MPV	4.160	42.4	0.445	0.652	0.452	0.050	0.140	4.380	0.555	ND
	%Diff	-0.4	-5.8	3.1	7.8	2.7	46.0	-2.9	-0.1	-6.8	ND
Fall	RV	6.696	20.2	0.174	1.777	1.496	0.123	0.071	3.924	0.172	ND
2006	MPV	6.650	20.0	0.190	1.760	1.450	0.123	0.080	3.630	0.190	ND
	%Diff	0.7	1.1	-8.4	1.0	3.2	0.0	-11.3	8.1	-9.5	ND
Fall	RV	6.870	15.2	0.121	0.543	1.585	0.095	0.192	1.096	0.625	ND
2007	MPV	6.870	15.9	0.130	0.540	1.920	0.100	0.180	1.120	0.600	ND
	%Diff	0.0	-4.6	-6.9	0.6	-17.5	-4.7	6.8	-2.2	4.1	ND
Spring	RV	6.330	12.8	0.302	0.605	0.890	0.227	0.114	1.586	0.857	0.047
2008	MPV	6.320	14.4	0.301	0.610	0.898	0.232	0.120	1.580	0.844	0.048
	%Diff	0.2	-10.9	0.5	-0.9	-0.9	-2.3	-5.4	0.3	1.6	-2.1
Fall	RV	6.180	12.8	0.234	1.270	0.332	0.297	0.173	1.174	1.910	0.000
2008	MPV	6.170	13.5	0.237	1.240	0.330	0.300	0.174	1.240	1.990	0.015
	%Diff	0.2	-5.2	-1.3	2.4	0.6	-1.0	-0.6	-5.3	-4.0	-100.0
Spring	RV	4.782	13.6	0.738	0.239	0.433	0.061	0.092	1.926	0.211	ND
2009	MPV	4.880	14.0	0.650	0.230	0.415	0.057	0.100	1.780	0.210	ND
	%Diff	-2.0	-2.7	13.5	3.9	4.3	7.0	-8.0	8.2	0.2	ND
Fall	RV	6.670	9.7	0.093	0.336	0.761	0.348	0.042	1.080	0.425	0.047
2009	MPV	6.700	10.0	0.080	0.321	0.741	0.340	0.040	1.050	0.418	0.026
	%Diff	-0.4	-3.0	15.8	4.6	2.7	2.4	3.8	2.9	1.7	80.8

Data Outliers

Outliers are defined as points that markedly deviate from all other data in the sample. Only two erroneous points were detected (table 9) from graphical analysis of the 2003-09 data. The low field conductance value reported on December 8, 2009, is indicative of a frozen probe. The NH_4^+ concentration reported on May 17, 2005, is an outlier. Although no other ion concentrations in this sample appear suspicious, the reported value is substantially higher than all other NH_4^+ concentrations. This result indicates possible sample contamination or an analytical error. Given the extremely low NH_4^+ concentrations in LVWS waters, a single breath can contaminate a sample for NH_4^+. Both of the outlying data points in table 9 were removed from LVWS data records and replaced as missing data.

Table 9. Data outliers removed from the Loch Vale watershed surface-water records for 2003-09.

[NH_4+, ammonium as ammonium; µS/cm, microsiemens per centimeter at 25° Celsius; mg/L, milligrams per liter]

Analyte	Units	Site	Date	Reported value	Mean value (2003-09)
Field conductivity	µS/cm	Loch Outlet	12/8/2009	0.7	18.3
NH_4^+	mg/L	Loch Outlet	5/17/2005	0.21	0.02

Ion and Specific Conductance Balances

Loch Vale surface-water samples were checked for ion percent difference (IPD) and specific conductance percent difference (CPD) (U.S. Environmental Protection Agency, 1987; Stednick and Gilbert, 1998; U.S. Environmental Protection Agency, 2004). Because all samples are electrically neutral, the sum of the measured cations should equal the sum of the measured anions, if it is assumed that all major ions are measured. The ion balance is expressed by the IPD, which is calculated as:

$$IPD = \frac{\sum cations - \sum anions}{\sum (cations + anions)} \times 100 \tag{1}$$

where

$$\Sigma\, cations = [Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}] + [NH_4^{+}] + [H^{+}],$$

$$\Sigma\, anions = [SO_4^{2-}] + [Cl^{-}] + [F^{-}] + [NO_3^{-}] + [HCO_3^{-}], \text{ and}$$

$$HCO_3^{-} = ANC + H^{+}$$

with all concentrations expressed in microequivalents per liter.

A negative IPD represents an excess of anions and a positive IPD represents an excess of cations. The IPD is an indicator of analytical accuracy and samples that fall outside criteria in table 11 are flagged and the analysis rerun. If the IPD is still outside the acceptable range after the sample has been reanalyzed, each sample is checked, ion by ion, for possible contamination. If one analyte is the obvious cause of the charge imbalance, it can be dropped from the record as long as the concentrations of the remaining analytes are normal for that time of year.

The theoretical conductance of a water sample is calculated by the formula:

$$\text{Theoretical conductance} = ([Ca^{2+}]59.47 + [Mg^{2+}]53.0 + [Na^{+}]50.08 + [K^{+}]73.48 + [NH_4^{+}]73.50 + [H^{+}]349.65 + [SO_4^{2-}]80.0 + [Cl^{-}]76.31 + [NO_3^{-}]71.42 + [HCO_3^{-}]44.5)/1000 \tag{2}$$

with all concentrations expressed in microequivalents per liter.

The CPD is calculated as:

$$CPD = \frac{\text{Theoretical conductance} - \text{Measured conductance}}{\text{Measured conductance}} \times 100 \tag{3}$$

CPD calculations were performed for all surface-water samples using the specific conductance measured at the RMRS laboratory (that is, laboratory conductivity). Positive CPD values indicate that theoretical conductance exceeds the laboratory measured value, and can indicate an analytical error in one or more of the solute measurements. Negative CPD values indicate an unmeasured or under measured ion. Deviations from zero also can result from errors in specific conductance measurements. CPD values that fall outside the ranges reported in table 10 are flagged and the sample reanalyzed.

Of the 534 non-blank environmental samples (that is, normal and duplicate samples) collected during 2003-09, no samples were flagged for IPD after reanalysis. Three samples, all of which had positive CPD values, did not meet quality criteria for CPD after reanalysis (table 11), which could indicate an analytical error in one of the measurements. However, none of the samples flagged for CPD were flagged for IPD, which indicates that the solute analyses were complete and balanced. Therefore, data associated with these samples (table 11) were not removed from the database, but are reported here for completeness.

Table 10. Surface-water sample reanalysis criteria for ion percent difference and conductance percent difference.

[ueq/L, microequivalents per liter; IPD, ion percent difference; µS/cm, microsiemens per centimeter at 25° Celsius; CPD, conductance percent difference; <, less than; ≥, greater than or equal to; criteria from U.S. Environmental Protection Agency, 1987]

Ion percent difference	
Total ionic strength (µeq/L)	**Maximum IPD (percent)**
<50	60
≥50<100	30
≥100	15
Conductance percent difference	
Measured specific conductance (µS/cm)	**Maximum CPD (percent)**
<5	50
≥5<30	30
≥30	20

Table 11. Samples that failed to meet quality criteria for conductance percent difference after reanalysis.

[µS/cm, microsiemens per centimeter at 25° Celsius; CPD, Conductance percent difference]

Site	Date	Sample type	Theoretical conductance (µS/cm)	Measured conductance (µS/cm)	CPD (percent)
Andrews Creek	09/23/03	Normal	19.7	14.5	35.9
Glass Outlet	09/23/03	Normal	25.9	18.5	40.1
Sky Inlet South	09/16/08	Normal	22.2	16.7	33.1

Measures of Contamination

Contamination of low-ionic-strength streamwater samples is quantified by measuring solute concentrations in field blank samples. Field blanks consist of deionized (DI) water that is processed with the same methods used for environmental water samples (that is, normal and field duplicate samples). Sources of contamination can include improper bottle-washing procedures, errors in the handling and processing of samples, and contamination of DI water columns. Twenty-seven field blanks were collected at the Loch Outlet during 2003-09. No known instances of contamination of the NREL DI water system occurred during 2003-09 (Dan Reuss, Natural Resource Ecology Laboratory, oral commun., 2010). The 25th- and 75th-percentile concentrations of each analyte for field blanks and environmental samples are listed in table 12.

The blank concentration values of most concern are those for DOC, as noted in previous QA reports (Allstott and others, 1999; Botte and Baron, 2004). Elevated DOC values are most likely caused by the inability of the DI water filtration system to effectively remove all organic carbon from the water. SiO_2 has also been detected in NREL DI water in the past (Allstott and others, 1999), but the concentrations reported in table 12 are well below the reported detection limit of 0.4 mg/L. SiO_2 concentrations greater than 11 mg/L were reported for three consecutive blank samples collected during December 2004-April 2005. As no instances of DI water contamination were reported at NREL during this time period, the abnormally high values are likely the result of operator error. Therefore, these three SiO_2 values were removed from the LVWS database and were not used in calculating values in table 12.

Measures of Precision

Analytical precision is quantified by determining differences between analyte concentrations in normal samples and field duplicates. Field duplicates are samples collected from the same location as normal samples, with identical methods and as close to the same time as possible. Twenty-eight duplicate samples were collected from the Loch Outlet during 2003-09. Duplicate samples are processed and analyzed exactly as are normal samples. Median absolute differences (MADs) for each analyte were calculated for paired normal and duplicate samples. Precision can be calculated by determining the ratio of MAD values for the normal/duplicate sample pairs to the 10th-percentile concentration value for the analyte in environmental samples from all sites. Analytical precision ranged from ±0.6 percent of the 10th-percentile value for fluoride to ±9.2 percent of the 10th-percentile value for DOC (table 13). Analytical precision for all analyses was acceptable at less than ±10 percent of the 10th-percentile value for all constituents.

Table 12. Analyte concentration percentiles for field blanks and environmental samples collected for the Loch Vale watershed project during 2003-09.

[P_{25}, 25th percentile; P_{75}, 75th percentile; n, sample size; NREL, Natural Resource Ecology Laboratory; RMRS, Rocky Mountain Research Station Water Chemistry Laboratory; ANC, acid neutralization capacity; K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; F^-, fluoride; Cl^-, chloride; NO_3^-, nitrate as nitrate; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as orthophosphate; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; SiO_2; dissolved silica as silicon dioxide; µS/cm, microsiemens per centimeter at 25° Celsius; ueq/L, microequivalents per liter; mg/L, milligrams per liter]

		Field blank samples			Environmental samples		
Analyte	**Units**	P_{25}	P_{75}	**n**	P_{25}	P_{75}	**n**
Field conductivity	µS/cm	0.8	1.3	26	12.1	21.8	525
Lab conductivity	µS/cm	1.00	1.39	27	13.00	22.60	532
NREL pH	Standard	5.30	5.80	25	6.40	6.84	525
RMRS pH	standard	5.49	5.69	27	6.56	6.74	532
ANC	ueq/L	-7.45	2.10	27	40.1	97.3	532
K^+	mg/L	0.00	0.00	27	0.17	0.25	532
Na^+	mg/L	0.00	0.02	27	0.52	1.04	532
Ca^{2+}	mg/L	0.00	0.02	27	1.45	2.47	532
Mg^{2+}	mg/L	0.00	0.00	27	0.22	0.38	532
NH_4^+	mg/L	0.00	0.01	27	0.00	0.03	531
F^-	mg/L	0.00	0.02	27	0.09	0.13	532
Cl^-	mg/L	0.01	0.02	27	0.11	0.24	532
NO_3^-	mg/L	0.00	0.00	27	1.04	1.88	532
SO_4^{2-}	mg/L	0.00	0.00	27	1.73	3.25	532
PO_4^{3-}	mg/L	0.00	0.00	27	0.00	0.00	532
DOC	mg/L	0.12	0.32	27	0.60	0.99	519
TDN	mg/L	0.02	0.05	27	0.34	0.51	519
SiO_2	mg/L	0.00	0.08	24	1.80	3.17	525

Table 13. Ratio of median absolute differences for normal/duplicate sample pairs to the 10th-percentile value for all environmental samples collected during 2003-09.

[MAD, median absolute difference; P_{10}, 10th percentile for environmental samples; NREL, Natural Resource Ecology Laboratory; RMRS, Rocky Mountain Research Station Water Chemistry Laboratory; ANC, acid neutralization capacity; K^+, potassium; Na^+, sodium; Ca^{2+}, calcium; Mg^{2+}, magnesium; NH_4^+, ammonium as ammonium; F^-, fluoride; Cl^-, chloride; NO_3^-, nitrate as nitrate; SO_4^{2-}, sulfate as sulfate; PO_4^{3-}, orthophosphate as orthophophate; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; SiO_2; dissolved silica as silicon dioxide; µS/cm, microsiemens per centimeter at 25° Celsius; ueq/L, microequivalents per liter; mg/L, milligrams per liter; BDL, below detection limit]

Analyte	Units	MAD	P_{10}	MAD/P_{10} (percent)
Field conductivity	µS/cm	0.1	10.2	1.0
Lab conductivity	µS/cm	0.20	11.14	1.8
NREL pH	Standard	0.06	6.27	1.0
RMRS pH	Standard	0.01	6.44	0.2
ANC	µeq/L	1.36	32.02	4.2
K^+	mg/L	0.010	0.140	7.1
Na^+	mg/L	0.020	0.450	4.4
Ca^{2+}	mg/L	0.030	1.201	2.5
Mg^{2+}	mg/L	0.010	0.177	5.6
NH_4^+	mg/L	BDL	BDL	BDL
F^-	mg/L	0.001	0.080	0.6
Cl^-	mg/L	0.007	0.090	8.1
NO_3^-	mg/L	0.010	0.709	1.4
SO_4^{2-}	mg/L	0.020	1.457	1.4
PO_4^{3-}	mg/L	BDL	BDL	BDL
DOC	mg/L	0.037	0.399	9.2
TDN	mg/L	0.009	0.271	3.4
SiO_2	mg/L	0.040	1.405	2.8

Changes in Field and Laboratory Procedures during 2003-09

Changes in the LVWS field operating procedures:

- Sky Outlet was not sampled during 2003-06.
- Louise Inlet was not sampled during 2005-07 and 2009.
- Sky Inlet North sampling was discontinued in 2006.
- A NOAH IV electronic rain gage was installed at Loch Vale NADP site CO98 on June 18, 2007.
- Colocated NADP site (CO89), with Aerochem Metric precipitation collector and NOAH IV electronic rain gage, was installed on September 29, 2009.

Changes in LVWS laboratory procedures:

- Orthophosphate and total phosphorus measurements at NREL were suspended in 2005. Samples are still collected, acidified, and stored at 4°C for measurement of total phosphorus concentrations until analytical capabilities improve or an alternate laboratory is identified.

- NADP discontinued support for field chemistry measurements (that is, pH and specific conductance) effective January 1, 2005. LVWS continued to measure pH of all precipitation and surface-water samples at NREL through December 2009.
- The Milton Roy Spectronic 301 Photo spectrometer was replaced with a Thermo Spectronic 20D$^+$ spectrometer in 2007.
- The ion chromatographs for Na^+ and NH_4^+ were modified in 2009 to improve detection of NH_4^+ in the presence of Na^+. Because of the influence of Na^+ on detection of NH_4^+, the effective detection limit for NH_4^+ is estimated at 0.05 mg/L.
- In 2010, all NREL pH measurements were discontinued because pH is also measured at the CAL and RMRS.

Summary

Measurements of precipitation depth, precipitation chemistry, discharge, and surface-water quality were all sufficiently complete and consistent to support project data needs.

Bias of new e-gages for precipitation-depth measurement at the Loch Vale National Atmospheric Deposition Program (NADP) site CO98 was approximately +7 percent. Annual average wet-deposition collector catch efficiency ranged from 54 to 73 percent. The percentage of valid weekly NADP wet-deposition samples ranged from 62 to 92 percent. Approximately 25 percent of precipitation samples collected during 2003-09 did not meet NADP criteria for valid samples. The primary reasons for sample invalidation were inadequate sample volume, contamination, and equipment malfunction.

Improvements were made to field instrumentation at the Loch Vale site CO98 and in the laboratories of the NADP Central Analytical Laboratory (CAL). In accordance with NADP site criteria, trees surrounding the CO98 site were trimmed or felled to reduce sample contamination from plant matter. Additional solar panels and batteries were installed to minimize equipment malfunction from power loss at the NADP site. Field instruments are now (2011) more reliable and provide more accurate precipitation measurements. A colocated site, CO89, was installed in 2009 to quantify the overall variability in NADP measurements of precipitation depth and chemistry at Loch Vale. Laboratory instruments currently used have lower detection limits to resolve low chemical concentrations in wet-deposition samples. The NADP CAL continues to produce accurate and precise data for the Loch Vale watershed (LVWS) long-term monitoring and research program.

As a result of equipment malfunction, discharge data for the Loch Outlet were estimated from October 18, 2005, to August 17, 2006. Discharge records are consistent among the three streamgaging stations for each water year during 2003-09.

More than 98 percent of all LVWS surface-water samplers met project quality criteria. Failures to meet quality criteria were attributable to sample contamination or analytical error. Rocky Mountain Research Station (RMRS) and Natural Resource Ecology Laboratory (NREL) data were quality assured using ion balance, specific conductance balance, blank samples, and duplicate samples. Quality-assurance results indicate all analyses were accurate and precise. The U.S. Forest Service (USFS)-RMRS Water Chemistry Laboratory and NREL continue to produce accurate and precise data for the LVWS long-term monitoring and research program.

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