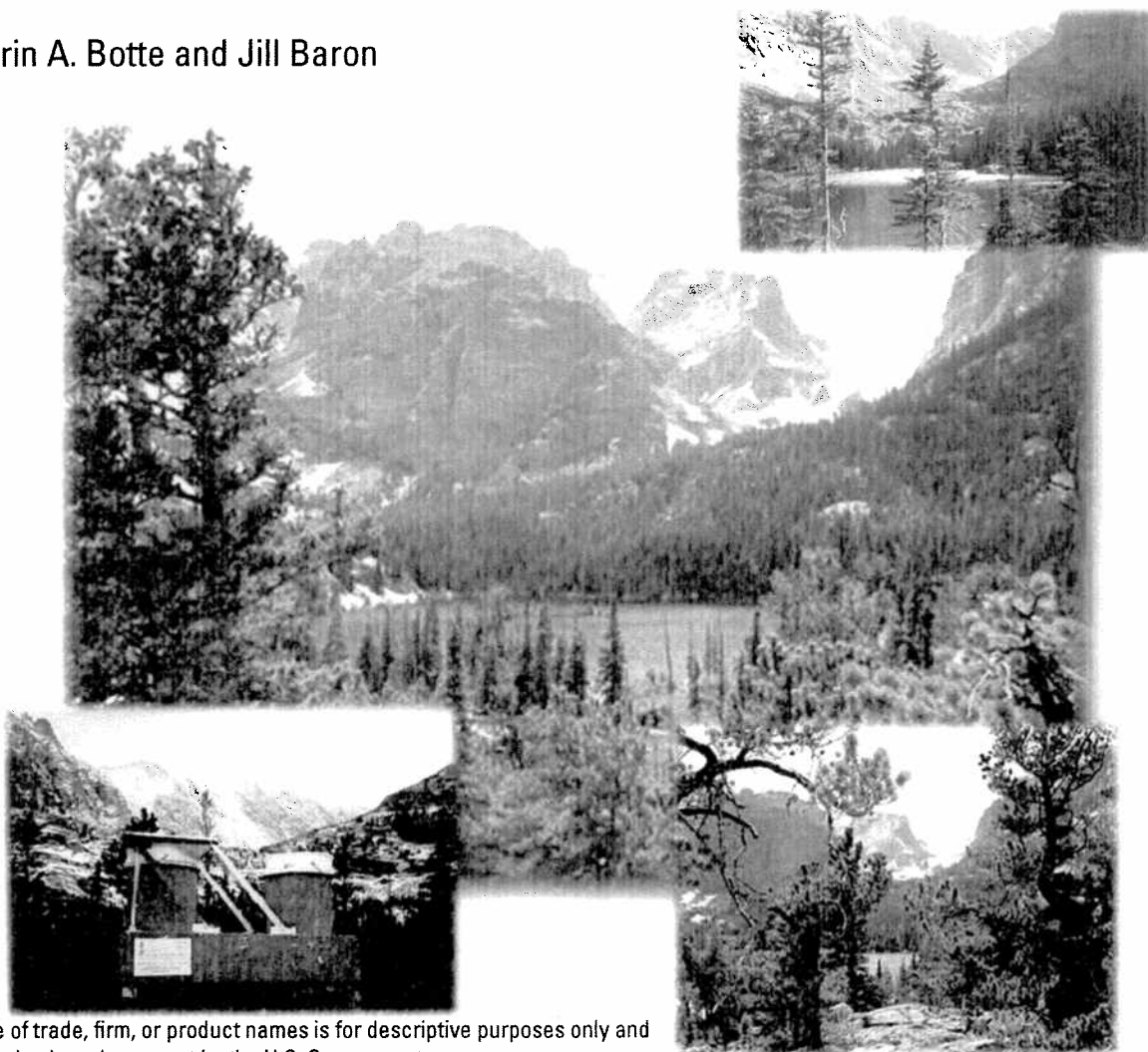




Quality Assurance Report –Loch Vale Watershed, 1999–2002

By Jorin A. Botte and Jill Baron



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Introduction

The National Park Service initiated the Loch Vale Watershed (LVWS) project in 1980 with funding from the Aquatic Effects Research Program of the National Acid Precipitation Assessment Program. Long-term ecological research and monitoring address watershed-scale ecosystem processes, particularly as they respond to atmospheric deposition and climate variability. Monitoring of meteorological, hydrologic, precipitation chemistry, and surface water quality parameters enable us to use long-term trends to distinguish natural from human-caused disturbances. Research into snow distribution, hydrologic flowpaths, vegetation responses to N deposition, isotopic transformations of N by forest and soil processes, trace metals, and aquatic ecological responses to disturbance enable us to understand processes that influence high elevation ecosystems.

Research Objectives

1. To observe and differentiate natural biogeochemical and biological variability from human-caused disturbance in alpine and subalpine ecosystems through intensive long-term study.
2. To understand and better quantify the role of climatic variability, particularly changes in precipitation and temperature, on alpine and subalpine processes.
3. To apply new and better methods to address the role of climate on winter snow accumulation, redistribution, and melt processes.
4. To estimate potential ecosystem damage induced by changes in climate due to regional land use change and/or globally increasing greenhouse gases.

Program Objectives

1. To share results and information on real and potential threats to natural alpine and subalpine resources with the public, scientific community, and air, water, and land managers.
2. To apply information gained in Rocky Mountain National Park (RMNP) to other National Park Service (NPS) and federally managed lands in Colorado, nationwide, and worldwide.
3. To offer a program of graduate education and research that develops future scientists and knowledgeable resource managers.
4. To continue the LVWS long-term ecological research project as a successful example of ecosystem study design, interdisciplinary collaboration, long-term continuity of quality-assured data collection, data base management, and better applied natural resource management.

It is important for all data collected in Loch Vale to meet the high standards of quality set forth in previous LVWS Quality Assurance/Quality Control (QA/QC) reports and LVWS Methods Manuals. Given the ever-widening usage of data collected in Loch Vale, it is equally important to provide users of that data with a report assuring that all data are sound. Parameters covered in this report are meteorological measurement, precipitation chemistry, hydrologic measurements, and surface water chemistry.

Purpose and Scope

This report describes QA/QC procedures used by the U.S. Geological Survey (USGS) in support of long-term data collection efforts in Loch Vale. This quality assurance report addresses data collected from January 1, 1999 through December 31, 2002. Previous quality assurance reports include: 1983–1987 (Denning, 1987); 1989–1990 (Edwards, 1991); 1991–1994 (Allstott, 1995); and 1995–1998 (Allstott and others, 1999).

Since 1982, all LVWS samples and data have been analyzed according to standard methods. Meteorological data were collected, analyzed, and stored by LVWS project personnel from 1982–1998. The U.S. Geological Survey-Water Resources Discipline (USGS-WRD) has collected meteorological data since 1992 and is responsible for QA/QC of the meteorological data since the decommissioning of the U.S. Geological Survey-Biological Resources Discipline (USGS-BRD) weather station (11/24/1998). Methods for handling the BRD meteorological data are documented in Denning (1988), Edwards (1991), Newkirk (1995), and Allstott (1995).

Precipitation chemistry data are collected according to National Atmospheric Deposition Program (NADP) protocol (Bigelow, 1988), and analyzed at the Central Analytical Laboratory (CAL) of the Illinois State Water Survey in Champaign, Illinois <http://nadp.sws.uiuc.edu/>. QA/QC procedures of the NADP are documented in Rothert and others (2002).

Stream flow data are collected and calculated according to standard LVWS methods (Allstott and others, 1999). Protocols for sampling surface waters are documented in Allstott and others (1999). Analysis of surface-water chemistry has been performed using standard Environmental Protection Agency (EPA) protocols at the U.S. Department of Agriculture's U.S. Forest Service's Rocky Mountain Research Station (USFS-RMRS) Biogeochemistry Laboratory since 1993.

All LVWS (BRD) data are reviewed and stored in a relational database (Microsoft Access) on the Natural Resource Ecology Laboratory (NREL) computer network at Colorado State University. Data are available at <http://www.nrel.colostate.edu/projects/lvws/pages/homepage.htm>.

Meteorological Data

The USGS-WRD operates the main weather station in LVWS at an elevation of 3,159 m. The station takes readings every 15 seconds and calculates average hourly and daily values. The average hourly and daily values are recorded to a storage module that is downloaded every two to three months. The data are quality assured by the USGS-WRD using standard methods and are available upon request at <http://co.water.usgs.gov/lochvale/>. The following are a list of QC procedures performed by the USGS-WRD for their meteorological station data.

1. Sensors are scanned for complete operation. If there is a failure of a sensor, or if it appears there are intermittent gaps in data (such as wind speed), they are evaluated on a case-by-case basis. Data are rejected as needed when it appears there are sensor problems.
2. Sets of minimum, average, and maximum values are plotted for consistency and logical patterns. Outliers are then easily identified and rejected.
3. Sensor performance is evaluated using these sets of values over time with respect to the season.
4. Logical extremes or exceedance of physical limits (e.g. humidity >100%) are checked, and unreasonable values are investigated.
5. WRD meteorological data are downloaded bimonthly and scrutinized using time-series plots prior to being appended to existing flat files stored on Unix machines (George Ingersoll, USGS-WRD, written commun., 2003).

The USGS-BRD operated a Remote Area Weather Station (RAWS) colocated (30 m apart) in the Loch Vale Watershed from 1983–1998. The BRD station was decommissioned on November 24, 1998 due to failing station sensors, growing equipment costs, and the need for more standardized climate data. Common climate parameters measured for both stations are: solar radiation, 2 m air temperature, relative humidity, 6 m wind speed, and 6 m wind direction. Requests for Loch Vale climate data will be filled with BRD data from September 8, 1983–December 31, 1994 and WRD data after January 1, 1995. See Table 1 for a complete list of weather parameters measured by both stations. For both stations, sensors are located at 2 heights (2 m and 6 m).

Table 1. Meteorological parameters recorded by WRD-BRD weather stations.

[WRD, Water Resources Discipline; BRD, Biological Resources Discipline; QS, short wave radiation; QA, long wave radiation; avg., average; min., minimum; max., maximum; mph, miles per hour; m/sec., meters per second.]

WRD variables	Units	BRD variables	Units
Daily Avg. QS radiation in	Langleys/hour	Daily avg. QS radiation	Watts/m ²
Daily Avg. QS radiation out	Langleys/hour		
Daily Avg. QA radiation in	Langleys/hour		
Daily Avg. QA radiation out	Langleys/hour		
Daily Avg. net radiation	Langleys/hour		
Min. 2&6-m air temperature	°C	2-m air temperature	°C
Avg. 2&6-m air temperature	°C		
Max. 2&6-m air temperature	°C		
Min. 2&6-m relative humidity	%	Relative humidity	%
Avg. 2&6-m relative humidity	%		
Max. 2&6-m relative humidity	%		
Max. 2&6-m wind speed	mph	6-m wind speed	m/sec.
2&6-m EPA wind speed	mph		
2&6-m Campbell wind speed	mph		
2&6-m Campbell vector magnitude	mph		
2&6-m EPA UT vector direction	360°		
2&6-m EPA vector direction sd	360°	6-m wind direction	360°
2&6-m Camp. vector direction	360°		
2&6-m Camp. vector direction sd	360°	Barometric pressure	Millibars

Discharge Data

Discharge at the outlet of the Loch, located at the northeastern edge of the basin at an elevation of 3,050 m, has been gauged with a Parshall flume and stilling well since 1983. The accuracy of a Parshall flume is $\pm 5\%$ (Winter, 1981). Frequent inspection of the LV flume's condition reveals that as much as 5% of stream flow is not measured by the flume due to water flowing around or under the flume structure. A low-water inspection of the inside of the flume on September 2002 revealed that it is still of its original dimensions (extremely important when calculating flow volumes and rates), and that it is structurally sound.

As a quality spot-check of flow data, weekly manual readings of actual stage height are recorded by observing a staff gauge located just inside the flume as flow and snow permits. Stage height (ft) is converted to flow rate (m³/sec) using a rating formula provided by the Thompson Pipe and Steel Co., Denver, Colorado, and compared to the mechanically collected values.

Stage is recorded automatically using a Leupold and Stevens chart recorder. Two independent methods are used to confirm these measurements. Discharge is checked periodically by making manual measurements of flow using a pygmy meter. Discharge is also checked by comparison of flow records at other locations higher in the watershed (see Figures 1 and 2). While the pygmy meter is an attempt at a quantitative comparison of flow at the Loch outlet, the use of other flow records in the watershed allows only qualitative peak flow comparisons.

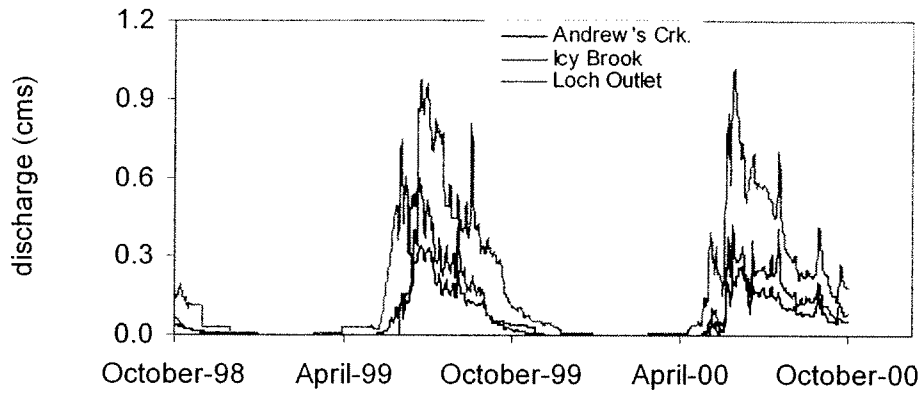


Figure 1. Comparison of discharge at three stream flow stations in the Loch Vale Watershed for water years 1999 and 2000.

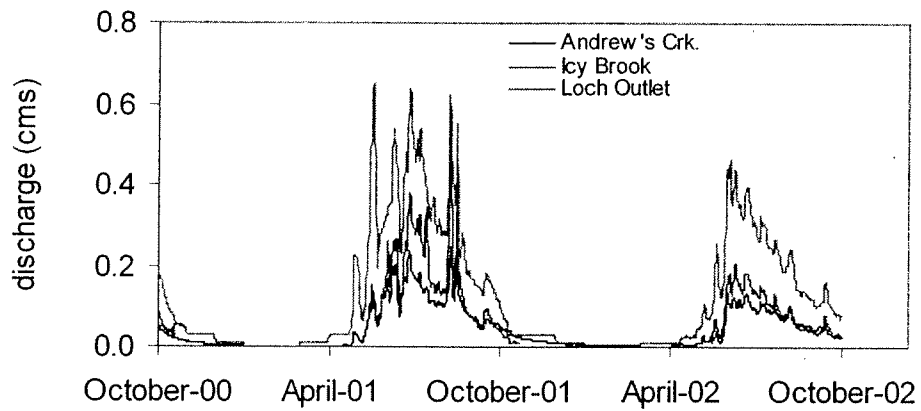


Figure 2. Comparison of discharge at three stream flow stations in the Loch Vale Watershed for water years 2001 and 2002.

There are two main tributaries in Loch Vale: Andrew's Creek, which drains the northern sub-basin, and Icy Brook, which drains the southern sub-basin. These two creeks join approximately 1 km above the Loch. Stream gauges are operated by the USGS-WRD on Andrew's Creek and Icy Brook. Discharge data at these tributaries are processed by field office personnel according to standard U.S. Geological Survey procedures (George Ingersoll, USGS-WRD, written commun., 2003). Results from qualitative comparisons of discharge at Andrew's Creek, Icy Brook, and the Loch outlet show that timing of snowmelt peaks generally occur within a week of each other. We expect to see greater discharge values from the Loch outlet compared to Andrew's Creek and Icy Brook because the Loch gauge is at the lowest point in the basin. Discharge data are stored in the USGS WATSTORE (Water Data Storage and Retrieval System) and can be found at <http://waterdata.usgs.gov/nwis/>.

Precipitation Chemistry Data

Weekly precipitation chemistry in LVWS is collected at the Loch Vale NADP site adjacent to the main weather station. Chemical analysis and quality assurance at the NADP station are conducted as part of the NADP protocol. Details of the NADP quality control plan and the quality assurance protocol at the Central Analytical Laboratory (CAL) are presented in Rothert and others (2002) and Gordon and others (2003). Detection limits and precision of analytes measured at CAL are summarized in Table 2.

Table 2. NADP Data Quality Goals for Precipitation Chemistry (Rothert and others, 2002).

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH₄, ammonium; SO₄, sulfate; NO₃, nitrate; PO₄, phosphate; Cl, chloride; mg/l, milligram per liter; μS/cm, microsiemen per centimeter.]

Analyte	Units	Bias	Detection limit
Ca	mg/l		.009
Mg	mg/l	100% at detection limit	.003
Na	mg/l		.003
K	mg/l	20% at 10 times detection limit	.003
NH ₄	mg/l		.02
SO ₄	mg/l	10% at 100 times detection limit	.010
NO ₃	mg/l		.010
PO ₄	mg/l		.009
Cl	mg/l		.005
pH<5.0		±0.1(bias)/±0.03(precision)	
pH>5.0		±0.3/±0.1	
Specific Conductance			
10–100	μS/cm	±10% / ±3%	
>100	μS/cm	±6% / ±2%	

The most recent CAL QA report covers data from 1999–2002 and states that the CAL has been meeting these goals through a quality control program of weekly blanks, check samples, blind network sample replicates, and an internal blind audit with predetermined samples (Rothert and others, 2002).

The NADP provides operators at each station with an annual summary of sample validity. This summary shows that 209 samples from the Loch Vale station were sent to the CAL for analysis between January 1, 1999 and December 31, 2002. Of these 209 samples, 148 (71%) were considered valid according to NADP standards. Of the 61 invalid samples, 13 were due to contamination, 7 were undefined samples due to the collector being open to dry deposition for more than 6 hours, 39 were a result of inadequate volume for analysis, 1 was due to the collector being open continuously, and 1 was due to an unknown precipitation amount (National Atmospheric Deposition Program [NADP], 2003). Therefore, ~10% of the samples sent to NADP from 1999–2002 were not valid due to contamination and equipment errors. Contamination of NADP Loch Vale precipitation samples typically results from the samples being cloudy or discolored or having high particulate matter.

Precipitation amount is measured by two techniques at the NADP station, the wet/dry collector and the Belfort gauge with Alter shield. There is a persistent problem with the catch efficiency of the AeroChem-Metrics wet deposition sampler used by NADP. Alter and Nipher shielded rain gauges are more effective devices for

catching precipitation in wind-prone areas than is the sample bucket. Allstott and others (1999) showed that weekly winter precipitation amounts recorded by the Alter and Nipher shielded rain gauges are usually one-and-a-half to two times greater than that of the amount recorded by the NADP AeroChem-Metrics sample bucket. Summer precipitation amounts from the rain gauge and sample bucket typically match each other more closely, but rarely fall within the $\pm 5\%$ desired by NADP (Allstott, 1995).

LVWS field personnel are responsible for measuring pH and specific conductance of the weekly precipitation samples as a check on NADP analyses. Each analysis is accompanied by measurement of a quality control check sample. If pH is not within ± 0.15 pH units and specific conductance within ± 2 $\mu\text{S}/\text{cm}$ of the check sample values, the equipment is recalibrated and the sample is reanalyzed. LVWS field technicians also participate in a biannual intersite comparison quality assurance program sponsored by the USGS <http://btdqs.usgs.gov/srs/>. As part of the program, an artificial sample is sent to each NADP site operator for measurement of pH and conductivity. Results must be within the acceptance criteria calculated from the network-wide median value for that sample. If they are not, the problem area within the analysis is identified and the necessary adjustments in procedure, equipment, or personnel are made. From 1999–2002 laboratory results met with NADP quality assurance criteria (Table 3).

Surface–Water Chemistry Data

This section details the QC procedures used by the LVWS project to minimize errors in the estimates of surface water chemical solute composition. Data quality is evaluated using field blanks, co-located field duplicates, charge balance calculations (ion percent difference), and comparisons of theoretical conductance (conductance percent difference).

Surface-water samples for chemical analysis are routinely collected throughout the entire Loch Vale Watershed. Major cations and anions measured include: calcium, magnesium, sodium, potassium, ammonium, sulfate, nitrate, chloride, fluoride, and phosphate. Loch Vale waters are also examined for specific conductance, pH, dissolved organic carbon (DOC), total nitrogen (TN), dissolved organic nitrogen (DON), total phosphorus (TP), dissolved organic phosphorous (DOP), silica, and alkalinity. pH, specific conductance, and major ions are processed and analyzed on a weekly basis. Silica, TN, DON, TP, DOP, and DOC are processed (filtered and/or preserved) weekly and held for analysis until early fall of each year. Loch Vale methods adhere to established protocol for low ionic strength waters (Lockheed, 1989) and all analytical laboratories that LVWS participates with conduct their own internal quality assurance procedures according to standards for the analysis of low ionic strength natural waters (Friedman, 1982). Further details can be found in Loch Vale Watershed Methods Manual 2000 (Allstott and others, 1999).

Field and laboratory sample treatment procedures are assessed through the implementation of blank and duplicate samples. At least 10% of the total number of samples collected from the Loch are QC samples. Bias and contamination due to field processing procedures are examined through the use of field blank samples. Precision is estimated by incorporating field duplicate samples. All QA/QC protocols required in the preparation, collection, processing, and shipping of samples are described in detail in the Loch Vale Watershed Methods Manuals (Allstott and others, 1999). Differences in the results between normal, blank, and duplicate samples will highlight any deficiencies in the analytical process.

The focus of this section is on QA/QC samples collected from the outlet of the Loch. Of the 256 samples taken from this outlet from 1999–2002, 18% of those were QC samples, including 9% field blanks and 9% field duplicates. QA/QC data collected prior to 1999 can be found in earlier reports by Allstott (1995), Allstott and others (1999), Edwards (1991), and Denning (1988). Small procedural, lab, and field changes will be detailed at the end of this report.

Table 3. U.S. Geological Survey intersite comparison program results for C098 (Loch Vale Watershed).

Comp #	Date	Target pH	Measured pH	Met goal?	Target conductance	Measured conductance	Met goal?
#43	July-99	4.85	4.92	Yes	17.5	18.0	Yes
#44	June-00	4.53	4.56	Yes	30.7	30.4	Yes
#45	Dec-00	4.08	4.12	Yes	38.4	36.5	Yes
#46	July-01	4.98	5.00	Yes	26.1	25.7	Yes
#47	Jan-02	5.06	5.25	Yes	15.7	15.3	Yes
#48	Apr-02	4.91	5.05	Yes	23.8	25.4	Yes
#49	Nov-02	4.72	4.80	Yes	8.9	8.1	Yes

Analytical Laboratories

Chemical analysis of stream water samples were performed at the USDA Forest Service, Rocky Mountain Research Station Biogeochemistry Laboratory, in Fort Collins, Colorado. QA/QC guidelines established in the Handbook of Methods for Acid Deposition Studies (EPA 600/4-87/026, September 1987) and the Standard Methods for the Examination of Water and Waste Water (19th edition) are followed for analytical activities in the biogeochemistry laboratory.

Loch Vale samples are processed at the NREL and sent to the USFS laboratory within 48 hours of field collection. All samples received are immediately computer archived, stored in a cold, dark environment, and processed as quickly as dictated by EPA guidelines. Control charts and control samples are utilized daily to monitor internal quality control. Appropriate field and laboratory blanks are analyzed as well as duplicates and check standards (every 10 samples). The lab manager, lab analyst, and data analyst check, verify, and archive all collected data.

Table 4 lists the detection limits posted for the USFS-RMRS and the USGS. Detection limit is a numerical boundary below which the level of accuracy in the measurement of a particular analyte declines severely. This limit is defined as three times the standard deviation of signals produced by replicated blank analyses. Detection limits for ANC are difficult to quantify due to the use of the Gran Titration method. ANC limits are not available since the values range widely due to the seasonality of the data.

Standard reference materials are certified by the National Institute of Standards and Technology. The Rocky Mountain Research Station laboratory also participates in laboratory exchange and analytical evaluation programs. Exchange programs involve sharing samples with other analytical laboratories for comparison of results. Analytical evaluation programs include the U.S. Geological Analytical Evaluation Program (Standard Reference Samples) and the USDA Forest Service North Central Round Robin. These programs assess the quality of laboratory methods and procedures along with information about analytical precision and accuracy. Table 5 lists evaluation program results for 1999-2002.

Table 4. Detection limits for USFS/USGS water and soils laboratory.

[ANC, acid neutralizing capacity; Na, sodium; NH₄, ammonium; K, potassium; Mg, magnesium; Ca, calcium; F, fluorine; Cl, chloride; NO₃, nitrate; SO₄, sulfate; PO₄, phosphate; mg/L, milligram per liter.]

Analyte	Detection limit (mg/L)	Method of analysis
ANC	na	Gran Analysis Technique
Na	0.01	Ion Chromatograph w/ separator column for
NH ₄	0.01	
K	0.02	anions
Mg	0.02	and
Ca	0.02	
F	0.01	monovalent/divalent
Cl	0.01	column for
NO ₃	0.02	cations
SO ₄	0.05	
PO ₄	0.015	

NREL Water Quality Laboratory

The NREL Loch Vale water chemistry laboratory participates in the USGS Intersite Comparison Program in which pH and specific conductivity measurements are routinely tested on samples with known chemical indices. Results from the past 4 years are presented in Table 3. The laboratory has achieved all accuracy goals since 1999. We continue to use the NADP approved VWR Model 8000 pH meter in conjunction with NADP supplied probes for all sample analyses.

Preliminary QA/QC Checks

All Loch Vale water quality analyses are checked using two methods: the ion percent difference (IPD) and the conductance percent difference (CPD). Since all samples are electrically neutral, the sum of the measured cations should equal the sum of the measured anions, assuming all major ions are measured. This is shown by the IPD, which is calculated as:

$$IPD = \frac{(\sum cations - \sum anions) * 100}{\sum cations + \sum anions}$$

where all constituents are expressed in micro equivalents per liter. A negative IPD represents an excess of negative charge and a positive IPD represents an excess of positive charge. The IPD is an indicator of analytical accuracy and samples that fall outside the $\pm 15\%$ range are flagged and rerun. If the IPD is still outside the acceptable range after being rerun, each sample is checked ion by ion for possible contamination. If one analyte is the obvious cause of the charge imbalance, it may be dropped from the record (as long as the remainder of the analytes looks normal for that time of year). In 1999–2002, 5 of the 404 Loch Vale stream samples fell outside of the 15% IPD criteria. These samples were just outside of the $\pm 15\%$ cut-off and are most likely the result of contamination introduced in the field and laboratory.

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

$$[(H)(350) + (ANC)(43.6) + (Ca)(52) + (Cl)(75.9) + (Mg)(46.6) + (K)(72) + (Na)(48.9) + (NO_3)(71) + (SO_4)(73.9) + (NH_4)(74.5)] / 1000$$

where all concentrations are expressed in microequivalents per liter. This calculation is performed on all samples sent to the USFS and the results are compared to the specific conductance measured at the USFS laboratory. Conductance percent difference is calculated for each sample as a percentage of the measured specific conductance. Positive CPD values indicate that calculated conductance exceeds the laboratory 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 may also result from errors in specific conductance measurements. In 1999–2002, 2 of the 404 Loch Vale stream samples fell outside of the acceptable $\pm 30\%$ CPD range. The most obvious reason for these differences is due to differences in the field versus laboratory specific conductance meters used from 1999–2002.

Table 5. Results of USGS Standard Reference Sample (USDA Forest Service, Rocky Mountain Research Station Biogeochemistry Laboratory; lab #2). Rating: 4 = Excellent, 3 = Good, 2 = Satisfactory, 1 = Marginal, 0 = Unsatisfactory. Supplemental information and SRS Round Robin results can be viewed at <http://btdqs.usgs.gov/srs/> (taken from USFS laboratory website).

[Ca, calcium; Cl, chloride; F, fluorine; K, potassium; Mg, magnesium; Na, sodium; SO₄, sulfate; mg/L, milligrams per liter; MPV, most probable value.]

Date	Constituent	Reported Value (mg/L)	MPV	Rating
Spring 1999	Ca	1.37	1.40	4
	Cl	1.58	1.64	4
	F	.215	.216	4
	K	.335	.399	4
	Mg	.380	.378	4
	Na	2.08	1.75	0
	SO ₄	1.77	1.88	4
	pH	4.41	4.42	4
Fall 1999	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	.242	.322	1
	Cl	1.79	2.38	0
	F	.112	.105	4
	K	.112	.110	4
	Mg	.119	.100	2
	Na	1.93	1.42	0
	SO ₄	1.42	1.41	4
Spring 2000	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	1.77	1.63	1
	Cl	4.63	4.18	0
	F	.164	.161	4
	K	.212	.238	3
	Mg	.624	.592	3
	Na	.474	.450	3
	SO ₄	.459	.437	4
Fall 2000	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	.551	.541	4
	Cl	4.651	5.31	1
	F	.239	.238	4
	K	.177	.184	4
	Mg	.096	.090	4
	Na	3.096	3.00	4
	SO ₄	.702	.673	4
pH	5.112	4.89	3	

Date	Constituent	Reported Value (mg/L)	MPV	Rating
Spring 2001	Ca	.603	.590	4
	Cl	3.719	3.47	3
	F	.098	.109	3
	K	.191	.170	2
	Mg	.076	.076	4
	Na	.398	.380	4
	SO ₄	.661	.655	4
	pH	4.09	4.19	4
Fall 2001	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	1.029	1.03	4
	Cl	3.167	3.10	4
	F	.102	.103	4
	K	.516	.500	4
	Mg	.509	.506	4
	Na	.857	.800	3
	SO ₄	1.467	1.44	4
Spring 2002	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	6.472	6.40	4
	Cl	--	8.37	--
	F	.037	--	--
	K	.854	.830	4
	Mg	1.158	1.15	4
	Na	1.915	1.80	3
	SO ₄	3.086	2.99	4
Fall 2002	Constituent	Reported Value (mg/L)	MPV	Rating
	Ca	9.013	8.65	3
	Cl	2.196	2.07	2
	F	.630	.650	4
	K	1.609	1.57	4
	Mg	.843	.812	3
	Na	6.391	6.19	3
	SO ₄	29.961	29.3	4
pH	3.628	3.66	4	

Measures of Bias and Contamination

Bias and contamination of low ionic strength stream water samples are quantified by measuring solute concentrations in field blank samples. Field blanks consist of deionized water that is processed according to the same methods as routine water samples. Sources of bias and contamination may include contamination of deionized water columns, improper bottle washing procedures, errors in the handling and processing of samples, analytical bias in the laboratory, and errors with data management. Field blanks were taken once every other month. Mean concentrations of each analyte from field blank samples are presented in Table 6.

Table 6. Loch Vale stream chemistry field blank sample mean concentrations.

[us/cm, microsiemens per centimeter; ueq/l, microequivalents per liter; mg/l, milligrams per liter.]

Analyte	Units	Mean concentration	Standard deviation	N
Field conductivity	us/cm	0.745	0.540	22
Lab conductivity	us/cm	1.504	1.712	23
Field pH	pH	5.818	0.335	22
Lab pH	pH	5.455	0.150	23
Alkalinity	ueq/l	-1.754	3.797	23
Calcium	mg/l	0.017	0.019	23
Magnesium	mg/l	0.000	0.001	23
Sodium	mg/l	0.006	0.020	23
Potassium	mg/l	0.005	0.011	23
Ammonium	mg/l	0.009	0.023	23
Sulfate	mg/l	0.002	0.008	23
Nitrate	mg/l	0.002	0.005	23
Phosphate	mg/l	0.000	0.000	23
Chloride	mg/l	0.024	0.041	23
Fluorine	mg/l	0.000	0.002	23
Silica	mg/l	0.107	0.551	23
Dissolved organic carbon	mg/l	0.338	0.224	23

There has been no known source of contamination to the DI water system at the NREL since the last reported spike in the summer/fall of 1996. The blank samples in Table 6 are from 1999–2002 and concentrations are expressed in microequivalents per liter (alkalinity) and milligrams per liter. The blank concentration values of most concern are SiO₂ and DOC, as noted in the 1999 QA report. These elevated values are most likely due to the fact that the DI system is unable to effectively remove all of the SiO₂ and DOC from the water.

Measures of Precision

Analytical precision is measured by quantifying differences between field duplicates. Field duplicates are pairs of samples collected by identical methods at the same sampling location, as close to one another in time as possible. Duplicate samples are collected every other month and processed exactly as normal samples.

Because precision often varies with concentration, the mean concentration of duplicate pairs is plotted against its standard deviation (SD) to help determine problems in precision (U.S. Environmental Protection Agency, 1980). A deficiency in precision would be indicated by a relationship between all paired means and their respective standard deviations. The lack of relationship in the majority of the regressions of duplicate pair means versus duplicate pair standard deviations indicates robust analytical precision at varying sample concentrations. Table 7 shows the R-square values for each regression and Figure 3 shows the actual regressions.

The only two analytes that show any relationship between duplicate pair mean concentrations and duplicate pair standard deviations are sulfate (SO₄) and phosphate (PO₄). The R² of SO₄ (.30) may indicate a lack of analytical precision while the R² of PO₄ (.99) is a result of the extremely low concentration of phosphate in Loch Vale sample waters (a mean of 0.0 produces a SD of 0.0 which contributes to a high R² value). The majority of PO₄ samples collected in Loch Vale are at or near a concentration of 0.0 mg/l.

Table 7. R² values for duplicate pair means versus duplicate pair standard deviations.

Analyte	Units	R ² value	N
Field conductivity	us/cm	0.0624	23
Lab conductivity	us/cm	0.1423	24
Field pH	pH	0.0648	24
Lab pH	pH	0.0021	24
Alkalinity	ueq/l	0.0114	24
Calcium	mg/l	0.0020	24
Magnesium	mg/l	0.0006	24
Sodium	mg/l	0.0796	24
Potassium	mg/l	0.1868	24
Ammonium	mg/l	0.0696	24
Sulfate	mg/l	0.3005	24
Nitrate	mg/l	0.1221	24
Phosphate	mg/l	0.9889	24
Chloride	mg/l	0.0298	24
Fluorine	mg/l	0.0648	24
Silica	mg/l	0.0698	23
Dissolved organic carbon	mg/l	0.0026	23

Another method for examining analytical precision is to calculate the statistical difference between normal and duplicate sample pairs. Paired two-tailed t-tests were applied to the Loch outlet normal and duplicate sample pairs to highlight inconsistencies in precision. Table 8 shows the results of these tests.

The majority of sample pairs are statistically similar with t-test p values greater than $\alpha = 0.05$ level. Field pH and field conductivity show significant differences in their paired measurements. These differences are most likely attributed to the quality of LVWS field pH and conductivity meters compared to the instruments employed by the USFS laboratory. As similarly reported in 1999 for field pH measurements, the USFS laboratories pH and conductivity measurements are more accurate and reproducible than Loch Vale field measurements.

The slight differences in duplicate pairs of sodium (Na), sulfate (SO₄) and nitrate (NO₃) are most likely the result of one or two samples with elevated standard deviations. These are identified in the precision plots and can have a strong influence on the paired average estimates.

Precision Plots

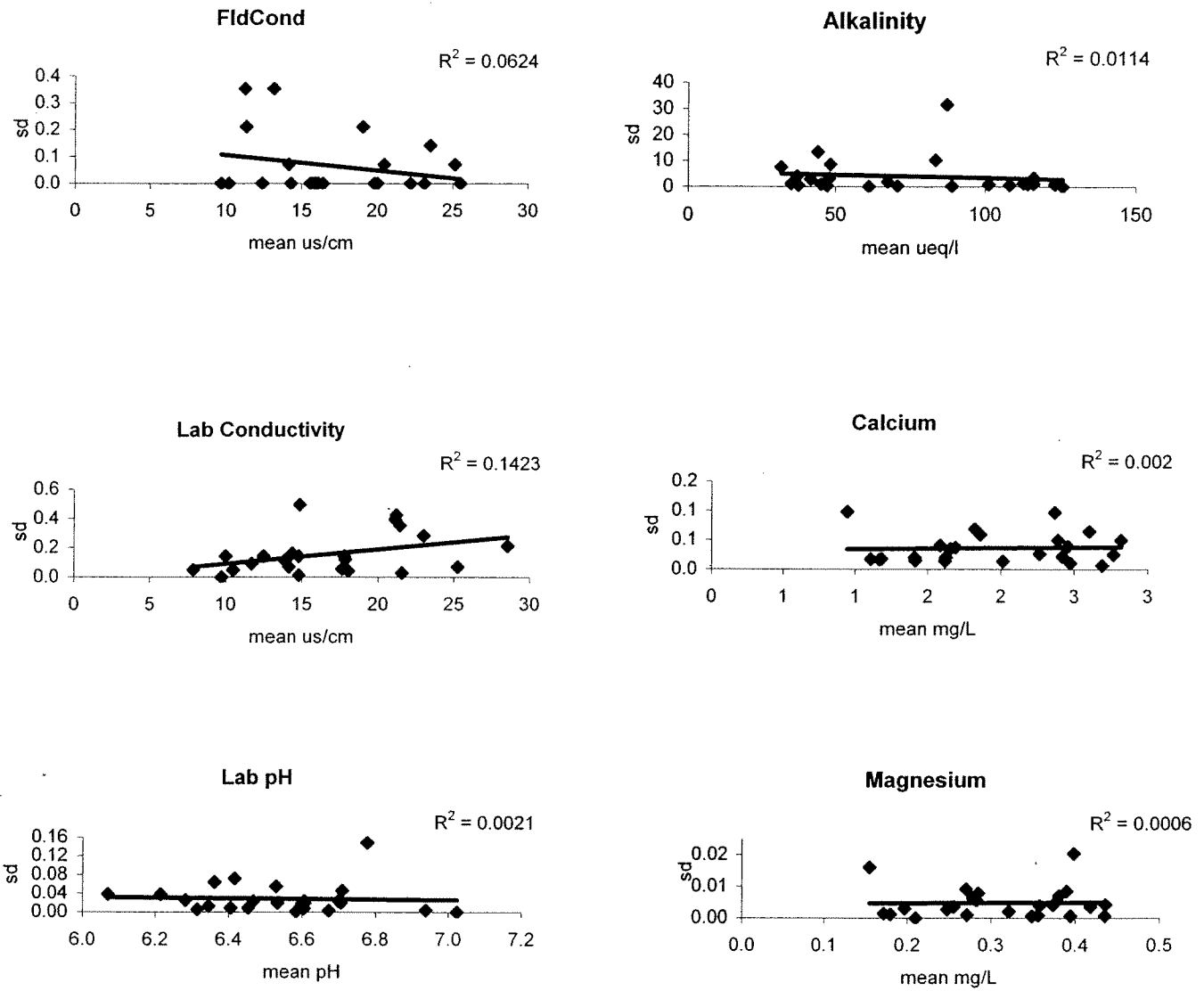


Figure 3. Precision plots for duplicate paired samples. Standard deviation versus paired mean concentration.

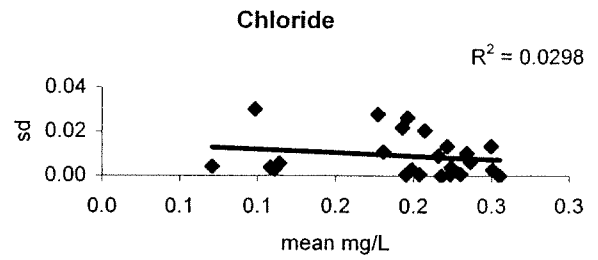
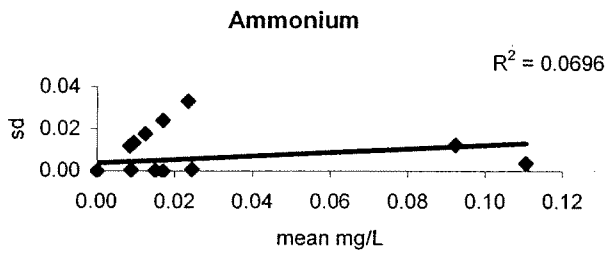
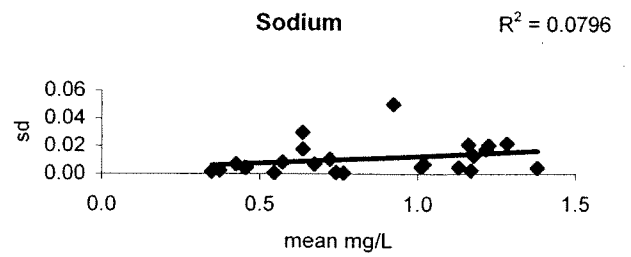
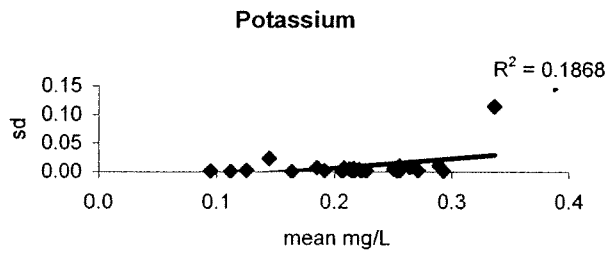
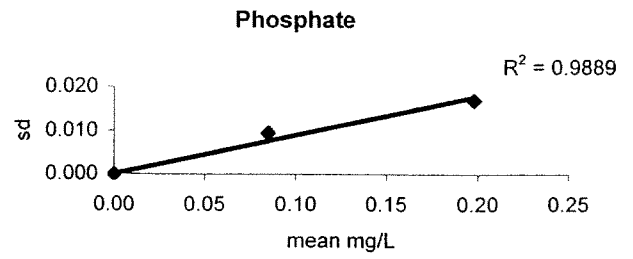
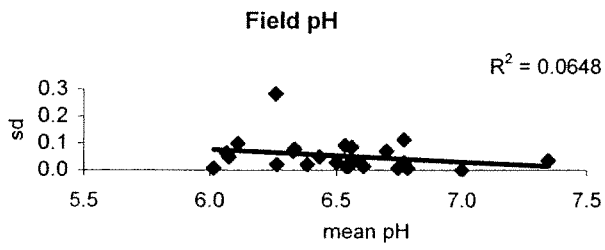


Figure 3. Concluded.

Table 8. Paired two-tailed t-test differences between Loch Outlet normal and duplicate samples.

Analyte	Units	Normal mean	Dupe mean	N	Pearson correlation	T-test P
Field conductivity	us/cm	17.31	17.23	23	0.999	0.0470*
Lab conductivity	us/cm	16.53	16.53	24	0.998	0.9728
Field pH	pH	6.47	6.55	24	0.966	0.0003*
Lab pH	pH	6.53	6.55	24	0.965	0.1616
Alkalinity	ueq/l	73.94	75.40	24	0.945	0.5292
Calcium	mg/l	1.93	1.94	24	0.994	0.5437
Magnesium	mg/l	0.31	0.31	24	0.994	0.8415
Sodium	mg/l	0.83	0.84	24	0.998	0.0124*
Potassium	mg/l	0.21	0.22	24	0.853	0.3392
Ammonium	mg/l	0.014	0.015	24	0.875	0.7676
Sulfate	mg/l	2.27	2.29	24	0.999	0.0378*
Nitrate	mg/l	1.16	1.17	24	0.999	0.0135*
Phosphate	mg/l	0.011	0.013	24	1.000	0.1792
Chloride	mg/l	0.19	0.19	24	0.938	0.9450
Fluorine	mg/l	0.104	0.105	24	0.996	0.1541
Silica	mg/l	2.32	2.24	23	0.997	0.9364
Dissolved Organic Carbon	mg/l	1.29	1.27	23	0.990	0.4492

After charting the Loch Outlet stream chemistry data from 1999 through 2002, there appeared to be a few points that were unrealistic. The five erroneous data points occurred between the months of May –July. The data that were flagged are presented in Table 9.

Table 9. Unrealistic data points for Loch Outlet stream chemistry from 1999–2002.

Analyte	Date	Reported Conc.	Mean Conc. 99–02
NO ₃	5/9/2000	3.92 mg/l	1.28 mg/l
NO ₃	5/19/2000	2.96 mg/l	1.28 mg/l
K	7/2/2002	0.78 mg/l	0.21 mg/l
NH ₄	7/2/2002	0.18 mg/l	0.01 mg/l
Cl	7/23/2002	0.68 mg/l	0.20 mg/l

After reviewing the original data, only one of those five points was flagged by the USFS (for conductance percent difference). These points were possibly a result of field/laboratory contamination or equipment errors. The above trend plots have been corrected for the five suspect data points.

Field and Laboratory Changes

Major Changes in the LVWS Field Operating Procedures from 1999–2002

- NADP site replaced batteries (Jan. 2002)
- NADP site rewired (March 2002)
- trace metal sampling ended (Summer 2002)
- lake synoptic reduced to 6 sites (Fall 2002)
- winter lake sampling ended (Dec. 2002)
- syringe pH ended (Jan. 2003)

Major Changes in LVWS Laboratory/Database Procedures from 1999–2002

- new pH meter (VWR 8000) (Jan. 1999)
- pH electrode changed (April 2000)
- pH electrode changed (April 2001)
- new conductivity meter (Orion 105A+) (Sept. 2001)
- ended DOC analysis in Boulder (Aiken) (Nov. 2001)
- new conductivity probe (Orion 013010D) (Oct. 2002)
- moved LVWS Excel database to Access (Fall 2002)
- new Shimadzu TC/TN analyzer (in-house DOC) (Winter 2002)

General Conclusions

In conclusion, overall quality of LVWS data was good for the period 1999–2002 compared to all other previous years. The quality of stream discharge measurements are difficult to ensure due to the lack of an accurate reference comparison, but general trends between Andrew's Creek and Icy Brook display no obvious discrepancies. It is prudent to point out that the accuracy of the Parshall flume is rated $\pm 5\%$. An additional 5% uncertainty should be added to this figure during high flow events when water can flow around and under the frame structure.

Meteorological data are quality assured by the USGS-WRD. Communication with George Ingersoll reveals that weather data entered in the database have been quality checked and erroneous entries removed prior to releasing the data to cooperating agencies.

NADP precipitation data are carefully scrutinized by Central Analytical Laboratory personnel before being posted on the NADP website. Routine LVWS laboratory checks reveal no problems with our methods or equipment to date.

LVWS water quality data are checked by the USFS laboratory and again by the database manager before any values are published. While there appear to be minor discrepancies with the precision of normal/duplicate pairs for Na, SO₄, and NO₃, the main reason is traced back to 1–2 duplicate pairs with inflated standard deviations. These findings are similar to those found by Denning (1987) and appear to be due to minor field/laboratory contamination. Low ratings from the USGS Analytical Evaluation Program are a result of the variation in the number of sites participating for any test period along with the range of the measurements and fit of the data. No problems in the lab were reported.

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