Ecosystems Mission Area

Quality Assurance Report for Loch Vale Watershed, 2010–19

Techniques and Methods 1–D9

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

Cover. Loch Vale, Colorado. Photograph by U.S. Geological Survey.

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Contents

Figures

Tables

Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
	Area	
square kilometer (km^2)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	33.81402	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)
liter (L)	61.02	cubic inch (in^3)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
microgram (µg)	0.000000035	ounce, avoirdupois (oz)

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.

Supplemental Information

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 micrograms per liter (µg/L).

Abbreviations

ACM	Aerochem Metrics Model 301wet-dry precipitation collector
AMoN	National Atmospheric Deposition Program Ammonia Monitoring Network
ANC	acid neutralizing capacity
APD	absolute percent difference
CAL	National Atmospheric Deposition Program Central Analytical Laboratory
CPD	conductance percent difference
CSU	Colorado State University
EPA	U.S. Environmental Protection Agency
HSWL	High Sierra Water Laboratory
IPD	ion percent difference
IQ	Rinterquartile range
LVWS	Loch Vale Watershed
MAP	Dmedian absolute percent difference
MDL	method detection limit
NADP	National Atmospheric Deposition Program
NH_3	ammonia
NH_4^+	ammonium
NH_4-	Nnitrogen as ammonium
NO_3	nitrate
NO_3-N	nitrogen as nitrate
NREL	Colorado State University Natural Resources Ecology Laboratory
NWIS	U.S. Geological Survey National Water Information System
PO_4^{3-}	phosphate
QA	quality assurance
QC	quality control
RMNP	Rocky Mountain National Park
RMRS	Rocky Mountain Research Station Biogeochemistry Laboratory
RSD	relative standard deviation or coefficient of variation
SD	standard deviation
SiO_2	silica
USGS	U.S. Geological Survey
USU	Utah State University Watershed Sciences Laboratory
WEBB	Water, Energy, and Biogeochemical Budgets

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Abstract

The Loch Vale Watershed Research and Monitoring Program collects long-term datasets of ecological and biogeochemical parameters in Rocky Mountain National Park to support both (1) management of this protected area and (2) research into watershed-scale ecosystem processes as those processes respond to atmospheric deposition and climate variability. The program collects data on precipitation depth and atmospheric deposition chemistry—as well as surface water biogeochemistry—within the watershed and in other areas of the park. These data are used by resource managers, scientists, policy makers, and students, so it is important that all collected data meet high quality standards. This report presents an evaluation of data quality for precipitation, atmospheric ammonia, and surface water quality samples collected from 2010 to 2019. This report also presents changes made to the monitoring and laboratory equipment used during the study period and describes new data streams added to the project, including atmospheric ammonia, surface water chlorophyll-a, and dissolved oxygen in two lakes: The Loch and Sky Pond.

Quality-assurance procedures looked at the accuracy and precision of measurements made over the study period and found that precipitation and surface water chemistry data were 99 percent accurate and precise. Records that failed to meet quality standards were removed from published databases. From 2010 to 2014, a colocated precipitation gauge and deposition collector were installed on site as quality checks. From 2014 to 2018, power loss at the site resulted in significant loss of precipitation data records during the snow seasons. Those problems were addressed by installing new solar-power equipment in 2019. Measurements of deposition chemistry, atmospheric ammonia deposition, and surface water biogeochemistry were all sufficiently complete and consistent to support project data needs.

Introduction

The Loch Vale Watershed (LVWS) Research and Monitoring Program was established in 1982. The program has operated continually since then, currently as a cooperative effort of the U.S. Geological Survey (USGS), National Park Service (NPS), and Colorado State University (CSU). The historical and contemporary purpose of the program is (1) to gather and interpret data to determine the effects of atmospheric deposition and climate change on Rocky Mountain National Park (RMNP) alpine and subalpine ecosystems and (2) to differentiate natural changes from those caused by humans. The program addresses ecosystem processes at the watershed scale by examining weather, hydrology, deposition chemistry, and surface water quality in the 7 square kilometer (km^2) catchment. Measures of lake algal productivity represented by chlorophyll-a have been monitored since 2016.

In addition to monitoring services, research efforts in LVWS have included both observational and experimental studies. Observational studies have examined geochemical weathering rates, sulfur biogeochemistry, trace gas fluxes from soils and waters, microbial activity and carbon composition from glaciers and rock glaciers, and hydrologic flow paths. Experimental studies have considered vegetation responses to nitrogen deposition, algal responses to nutrient availability and warming, microbial activity and carbon storage in subalpine forest soils under elevated nitrogen, and the response of aquatic organisms to disturbance. These research activities build an understanding of the processes that control alpine and subalpine ecosystems in the Rocky Mountains.

Research and Program Objectives

Research efforts in LVWS are focused on two main objectives, and the research and monitoring program is organized to meet three objectives.

Research Objectives

1. To understand and differentiate natural variation in ecosystem processes like biogeochemical cycling, ecological community dynamics, and geochemical weathering rates, from unnatural, human-caused drivers of change.
2. To understand and quantify the effects of atmospheric deposition and climate change on alpine and subalpine ecosystems.

Program Objectives

1. To share knowledge with the public, scientific community, and natural-resource managers.
2. To offer a program of undergraduate and graduate education and research through CSU, as well as other institutions, 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.

Meeting these objectives requires data that conform to high standards of quality. To ensure that these high standards are met, the LVWS program implements regular quality assurance (QA) protocols and periodically releases reports of QA measures related to the long-term monitoring program.

The QA approach described in this report uses statistical analysis of data collected in LVWS as well as analysis of quality control (QC) samples such as field blanks and duplicates. Evaluation of measurements for which LVWS staff are directly responsible are presented in this report, and they include precipitation volume and inorganic solutes from National Atmospheric Deposition Program (NADP) site CO98, atmospheric ammonia samples from site CO98, surface water chemical measurements, and lake productivity represented by chlorophyll-a measurements. Continuous weather and discharge data are collected in LVWS by researchers from the USGS Colorado Water Science Center, who perform QA procedures on these data.

The precipitation catch and wet solute deposition data were quality checked by comparing colocated precipitation gauges, evaluating completeness of the data record, and conducting a comparison of precipitation catch—or accumulation—by different instruments (see “Precipitation”). QA protocols for atmospheric ammonia sampling included travel blank and field triplicate samples. This method allowed for a measure of contamination bias and the calculation of the proportional difference between multiple measurements made over the same period (see “Atmospheric Ammonia”). Surface water sampling was augmented by the collection of field blanks and duplicate samples of all water chemistry analytes. Statistical tests were used to determine outliers and biased samples among the data, as well as to evaluate the variance among duplicates. The completeness of the dissolved ion profile was also determined with charge balance equations between cations and anions (see “Surface Water Chemistry”). A record of changes made to the monitoring program over the study period is included (see “Changes in Field and Laboratory Procedures, 2010–19”).

Purpose and Scope

This report describes the QA procedures and results supporting long-term monitoring and data collection in LVWS from January 1, 2010, through December 31, 2019. Samples have been collected and analyzed according to standard methods since 1982 (Bowker and Baron, 2017), and data quality were evaluated in previous QA reports dating from 1983 to 1987 (Denning, 1988), from 1989 to 1990 (Edwards, 1991), from 1991 to 1994 (Allstott, 1995), from 1995 to 1998 (Allstott and others, 1999), from 1999 to 2002 (Botte and Baron, 2004), and from 2003 to 2009 (Richer and Baron, 2011). Data reported on here include precipitation depth and chemistry, ammonia deposition, and surface water biogeochemistry. Other monitoring data from LVWS include climatological records (Akie and others, 2020) and stream discharge (https://waterdata.usgs.gov/nwis/uv?site_no=401733105392404) that are supported by the USGS Climate Research and Development Program (Ecosystem Mission Area) and maintained by the USGS Colorado Water Science Center.

Surface water samples and measurements were collected from three lakes and two streams within LVWS. Stream discharge was measured at Andrews Creek, Icy Brook, and the Loch outlet, the point at which the Loch drains into Icy Brook. Grab samples for water chemistry analysis were collected in the lakes Sky Pond, Andrews Tarn, and the Loch, as well as in Andrews Creek. Samples from Sky Pond were collected at the inlet (where runoff first enters the lake), lake surface, hypolimnion (the lowest layer in a lake’s water column), and the outlet (the point at which Sky Pond drains into Icy Brook). Samples from the Loch were also collected at the inlet (where Icy Brooke enters the Loch), lake surface, hypolimnion, and the outlet. Samples from Andrews Tarn were collected at the inlet, where runoff from Andrews Glacier enters the lake, and the outlet, where the lake drains into Andrews Creek. Samples from Andrews Creek were collected just above the confluence of Andrews Creek with Icy Brook. Additional grab samples were collected from lakes outside LVWS, in Emerald Lake, Lake Haiyaha, Lake Louise, and Lake Husted, all located within RMNP.

Stream discharge data were collected and processed by LVWS personnel prior to August 2006, when responsibility for collection and QA of LVWS discharge data was transferred to the USGS Colorado Water Science Center. Those data, along with stream chemistry and meteorological data from LVWS, are publicly available through the USGS National Water Information System (NWIS). Table 1 presents the web locations of all LVWS data.

Staff with the LVWS collect weekly surface water samples at the Loch outlet and less frequently at other sites in RMNP. Surface water chemistry samples are analyzed according to U.S. Environmental Protection Agency (EPA) protocols at the

Table 1. Summary of Loch Vale Watershed (LVWS) monitoring data, 2010–19.

[USGS, U.S. Geological Survey; NADP, National Atmospheric Deposition Program; NREL, Natural Resource Ecology Laboratory]

Website	Available data
Water, Energy, and Biogeochemical Budgets: Loch Vale Watershed, at https://co.water.usgs.gov/lochvale/ (USGS, 2004)	Hydrology: Andrews Creek, Icy Brook, and Loch outlet Surface water chemistry: Andrews Creek, Icy Brook, and Loch outlet
Climatological data for LVWS in Rocky Mountain National Park, Colorado, water years 1992–2019, at https://www.sciencebase.gov/catalog/item/5dd80882e4b069579765be28 (Akie and others, 2020)	Meteorology: Main LVWS Weather Station, Andrews Meadow, and Sharkstooth
National Atmospheric Deposition Program, at https://nadp.slh.wisc.edu (NADP, 2021)	Precipitation depth and chemistry: Rocky Mountain National Park—Loch Vale (CO98 and CO89) Ammonia deposition: CO98
USGS Water Data for the Nation, at https://waterdata.usgs.gov/nwis/ (USGS, 2021)	Hydrology: Loch outlet Surface water chemistry: Andrews Creek, Andrews Tarn, Emerald Lake outlet, Lake of Glass outlet, Lake Haiyaha outlet, Lake Husted, Loch hypolimnion, Loch inlet, Loch outlet, Loch surface, Lake Louise inlet, Lake Louise outlet, Sky Pond hypolimnion, Sky Pond inlet, Sky Pond outlet, Sky Pond surface
Natural Resource Ecology Laboratory:Loch Vale Watershed: Long-term Ecological Research and Monitoring Program, at https://www2.nrel.colostate.edu/projects/lvws/data.html (NREL, 2011)	Research data Spatial data Historical data Links to surface water chemistry and hydrology Quality assurance reports and methods manual

U.S. Department of Agriculture Forest Service, Rocky Mountain Research Station Biogeochemistry Laboratory (RMRS) and the Natural Resource Ecology Laboratory (NREL) at CSU. Protocols for sampling and analyzing surface water chemistry are documented in the LVWS Methods Manual (Bowker and Baron, 2017).

Precipitation depth and inorganic chemistry have been measured since 1983 at the LVWS NADP site CO98. Precipitation and ammonia samples are collected by LVWS personnel according to NADP protocols (National Atmospheric Deposition Program [NADP], 2019a, 2019b) and analyzed at the National Atmospheric Deposition Program Central Analytical Laboratory (CAL). The CAL was in Champaign, Illinois, until May 2018, when the facilities transferred to the Wisconsin State Laboratory of Hygiene at the University of Wisconsin. To further evaluate the quality of data collected at CO98, a colocated NADP site, CO89, was installed in October 2009, and a report on 5 years (2010–14) of colocation data was published (Wetherbee, 2016). The colocation study ended after 5 years in September 2014, but the CO89 precipitation gauge was left in place to provide a backup precipitation depth record.

In 2011, LVWS joined the NADP Ammonia Monitoring Network (AMoN). Personnel with LVWS regularly deploy and collect passive atmospheric ammonia samplers according to standard protocols (NADP, 2019b). QA procedures for precipitation and ammonia samples are outlined in the NADP Quality Assurance Plan (Central Analytical Laboratory, 2016a) and Quality Assurance Report (Central Analytical Laboratory, 2016b).

Precipitation Depth and Chemistry

Precipitation depth and wet-deposition chemistry were monitored in LVWS at NADP site CO98 and at a colocated site 6.5-meters (m) east, CO89. Precipitation depth was recorded every 15 minutes onto Campbell CR 1000 dataloggers in two alter-shielded ETI NOAH-IV2 electronic precipitation gauges (CO98 and CO89). Cumulative depth data were downloaded weekly from the loggers in the field. From the start of the study period, January 2010, until April 2019, data were downloaded using a Hewlett-Packard iPAC personal digital assistant (Hewlett Packard, Fort Collins, Colo.). Since April 2019, data have been downloaded onto a bluetooth-enabled Android device via the LoggerLink application (Campbell Scientific, https://www.campbellsci.com/loggerlink). Wet precipitation samples were collected weekly from an Aerochem Metrics Model 301 (ACM) wet-dry precipitation collector according to NADP protocols (NADP, 2019a). Buckets containing weekly wet precipitation samples were transported to NREL at CSU where they were weighed to determine sample volume. Precipitation samples were decanted to 1-liter (L) Nalgene bottles and shipped to the CAL for chemical analysis. All equipment (Aerochem Metrics wet precipitation collector and two NOAH-IV electronic precipitation gauges CO98 and CO89) was powered by on-site solar power systems.

Comparison of CO89 and CO98, 2010–14

From October 2009 through May 2014, a second set of precipitation depth and chemistry data were collected from CO89. The colocated CO89 site included an ACM wet-dry precipitation collector and an ETI NOAH-IV precipitation gauge with an Alter Shield. The colocated data were analyzed to determine bias and variability of precipitation catch data and nitrogen (N) deposition data. Results of that comparison were published and are summarized in figure 1 (Wetherbee, 2016). The difference in median weekly precipitation depth between CO89 and CO98 ranged from 0.00 to 0.25 millimeters (mm) over the study period. More variability in depth occurred during weeks when all precipitation fell as snow compared with weeks when all precipitation fell as rain. Differences in the median ion concentrations of ammonium (NH_4^+) ranged from 0.005 to 0.016 milligrams per liter (mg/L), whereas differences in nitrate (NO_3^+) concentrations ranged from 0.004 to 0.025 mg/L. The greatest difference in N deposition between collectors occurred in 2014, when the difference in NO_3^- measurements between collectors was 0.056 mg/L. In all years except 2012–13, median weekly precipitation and precipitation-weighted mean N concentrations were greater at CO98 than CO89 by 0 to 25 percent (Wetherbee, 2016).

At the conclusion of the study in 2014, the CO89 ACM was dismantled, but the NOAH-IV precipitation gauge remained in place as a backup to the CO98 precipitation depth record. Between 2014 and 2018, equipment failures and power outages led to downtime on the CO98 collector, and CO89 data were substituted to maintain completeness in the precipitation record. Figure 1 shows the cumulative precipitation recorded by CO89 and CO98 from 2014 to 2018. Where the curve is flat, only one precipitation collector was operational. From late 2018 through 2019, both collectors experienced significant interruptions, which is discussed further under “Precipitation Record 2014–19.”

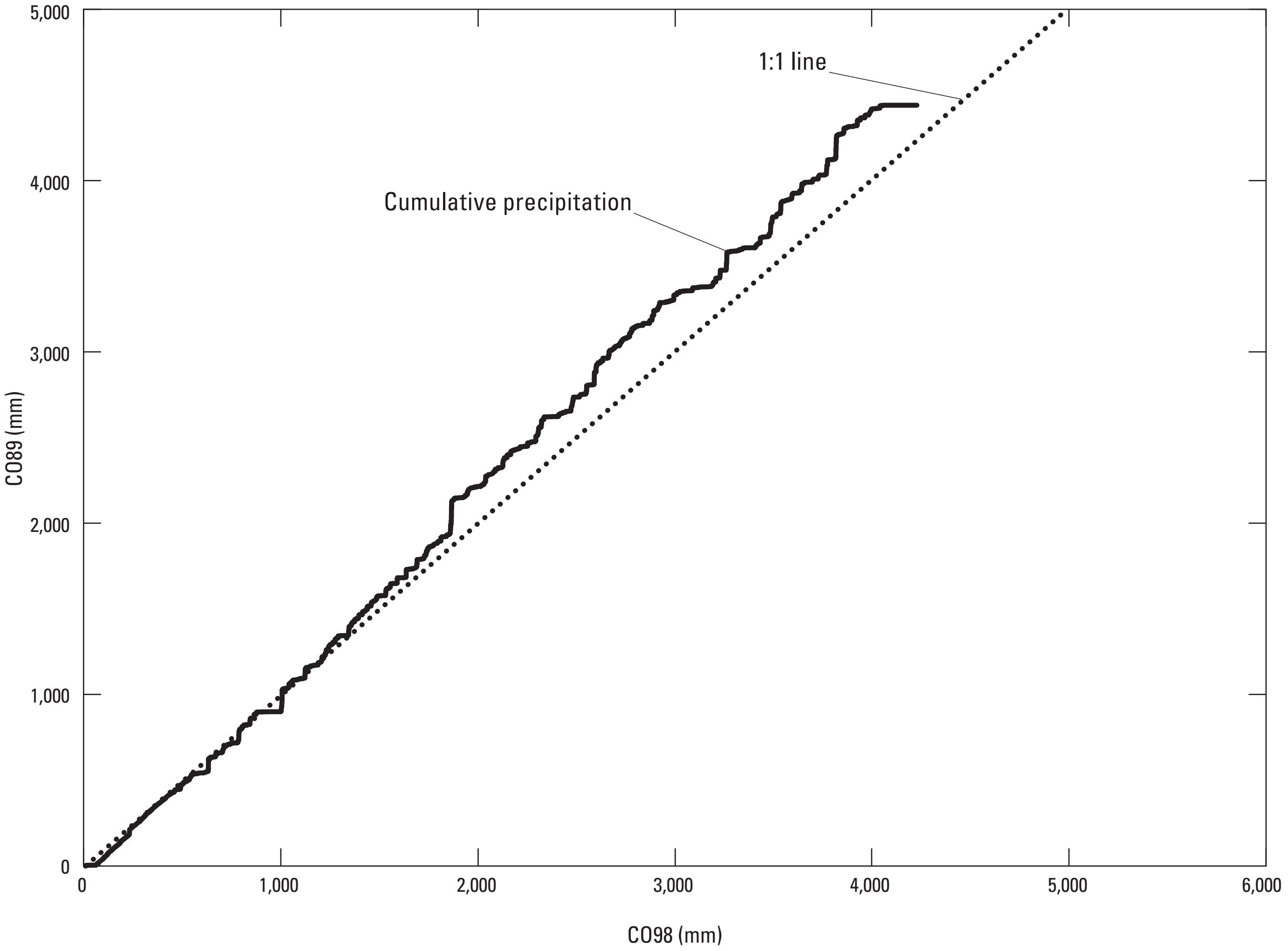

Figure 1. Comparison of cumulative precipitation depths recorded at National Atmospheric Deposition Program (NADP) sites CO89 and CO98, 2014–18. (mm, millimeters)

Precipitation Record 2014–19

Beginning in 2014, periodic loss of power occurred at CO98 because of equipment failure in the solar power system (table 2). Samples were not collected from the ACM, and precipitation-depth data were not recorded during power outages. From 2014 through 2017, the data losses occurred during intervals in December and January and amounted to gaps in the data record of 35.75–155.5 hours per year (table 2). Power losses occurred during winter storms characterized by snow, cold temperatures, and limited daylight hours. Gaps in the data record from CO98 were filled by data collected from CO89 when such data were available.

In 2018 and 2019, simultaneous losses of power occurred at both CO89 and CO98, resulting in an incomplete data record for those years. Loss of power was observed outside the months of December and January in 2018 and 2019 (table 2). A faulty solar controller was subsequently replaced, and the electrical connection to CO89 was rewired to mitigate power and data losses going forward. As specified by NADP procedure, missing precipitation collector records are to be replaced by estimated depth calculated using the deposition bucket catch (NADP, 2019a). However, the precipitation catch efficiency at CO98 is low during much of the year (see “Catch Efficiency and Sample Validity”), so the deposition collector is not an ideal replacement for the Alter-shielded NOAH-IV. Schichtel and others (2019) developed a bootstrapping method for imputing missing weekly concentrations that accounts for their seasonal and precipitation dependence. This method reduced the errors in annual deposition rates by about 30 percent compared to the NADP protocol, and the biases were near zero. Schichtel and others (Bret Schichtel, National Park Service, written commun., 2020) developed a modeling method to account for missing data. The method uses PRISM estimates to replace invalid records in precipitation depth. PRISM data are modeled climatological data (including precipitation depth) developed by regressing point measurements across a modeled land surface, which accounts for important factors like elevation and terrain (Daly and the National Center for Atmospheric Research, 2002).

Catch Efficiency and Sample Validity

The fraction of total measured precipitation depth (measured by the NOAH-IV gauge) captured by the ACM collector is called the catch efficiency, and this efficiency is often lower than 90 percent in LVWS (table 3). The annual catch efficiency ranged from a low of 36 percent in 2013 to a high of 57 percent in 2015 and averaged 47 percent during the study period. Seasonal catch efficiency was highest from July through September (89 percent during 2010–19), when

Table 2. Periods of missing precipitation depth record data at National Atmospheric Deposition Program (NADP) site CO98, 2014–19.

[Dates shown as month and day (mm/dd)]

Year	Date range	Missing hours	Annual missing hours
2014	12/29–12/31	50.5	50.5
2015	12/21–12/31	155.5	155.5
2016	12/22–12/29	35.75	35.75
2017	1/13–1/18	73.75	147.25
	12/7–12/24	73.5	
2018	2/1–2/16	129	644
	10/31–12/31	515	
2019	1/7–1/28	191.5	772
	2/6–2/23	119.5	
	3/2–3/20	232.5	
	4/11–5/3	158.25	
	12/14–12/30	70.25	

Table 3. Annual and seasonal catch efficiencies for the National Atmospheric Deposition Program (NADP) site CO98 Aerochem Metrics model 301 precipitation collector compared with the Alter-shielded ETI Noah-IV precipitation gauge, 2010–19.

Period	Catch efficiency (percent)										
	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	Average
Winter	15	10	31	22	16	32	17	9	23	29	20
Spring	31	42	40	26	45	58	28	39	56	43	41
Summer	86	99	85	85	96	84	90	94	84	92	89
Fall	58	68	78	25	49	61	53	78	80	52	60
Annual	49	44	56	36	44	57	38	42	56	52	47

precipitation occurs as rain, and was lowest for January through March (20 percent) when precipitation occurs as snow. When both rain and snow occur, the catch efficiency was moderate: 41 percent for April through June and 60 percent for October through December.

Low catch efficiency stems from the shallow, unshielded buckets of ACM collectors compared with deeper, Alter-shielded precipitation gauges, and low efficiencies are exacerbated by high winds and blowing snow in LVWS. As Richer and Baron (2011) reported, unshielded precipitation collectors capture approximately 57 percent of precipitation (Goodison and others, 1998), whereas shielded gauges capture up to 50 percent more total precipitation, especially during snow events (Kochendorfer and others, 2017). Low catch efficiency can bias the precipitation record if ACM collector samples are used as estimates of precipitation depth or can lead to invalid samples from insufficient sample volume.

Weekly sample collection in LVWS from 2010–19 resulted in 357 valid precipitation samples, representing 77 percent of the study period. Samples are invalidated because of numerous reasons, including contamination from dust or plant material, sample handling or protocol error, overlong sampling periods, site equipment malfunction, and, most commonly, low sample volume (Richer and Baron, 2011). Sample validity varied by season, with 64 percent valid samples in winter, 77 percent in spring, 81 percent in summer, and 87 percent in fall. Annually, sample validity varied from a low of 60 percent in 2014 to a high of 91 percent in 2015.

The NADP reports on the total measured precipitation depth represented by valid samples (https://nadp.slh.wisc.edu). Seasonal variance in this measure of completeness tracked closely with sample validity, with 65 percent of precipitation depth represented by valid samples in winter, 72 percent in spring, 92 percent in summer, and 88 percent in fall. Annually, the total measured precipitation depth represented by valid samples varied from a low of 56 percent in 2016 to a high of 93 percent in 2019. The number of valid samples collected during the study period and the percentage of total precipitation depth represented by valid samples are shown in table 4.

Precipitation Chemistry Instruments and Detection Limits

The CAL performed all chemical analyses and QA procedures on the CO98 precipitation samples in accordance with NADP protocols (Danielson, 2020). The CAL implements internal QC procedures that include weekly blanks, check samples, blind network replicates, and internal blind audits. The CAL also participates in external QA programs implemented by the World Meteorological Organization, Environment and Climate Change Canada, and the USGS (Wetherbee and others, 2021). The CAL published QA reports during the study period, and the LVWS program complied with the NADP QA protocols during the period (Gartman, 2016; Danielson, 2020). For each QA report, CAL staff determined the method detection limit (MDL) for all analytes (table 5). Base cations were measured using an Inductively Coupled Plasma–Optical Emission Spectrometer (Agilent 5100). Anions were measured by ion chromatography (Dionex Integrion), and NH_4^+ and ortho-phosphate (PO_4^{3-}) were measured using flow injection analysis (Lachat Quik Chem 8500 S2). Acidity was measured by pH meter, and conductance was measured using a Mettler S700 probe (Danielson, 2020).

Atmospheric Ammonia

The AMoN is a component of NADP that has measured ambient ammonia (NH_3) concentrations near ground level since 2010. Loch Vale Watershed initiated NH_3 sampling in 2011. The AMoN sampler is attached to the LVWS weather station, approximately 20-m northeast of the CO98 site. Radiello passive NH_3 samplers are deployed inside a closed-top, open-bottom shelter 2 m above the ground (Radiello 120-1). The deployed sampler is collected every 2 weeks and shipped in a sealed glass jar to the CAL for extraction and chemical analysis according to NADP methods (Danielson, 2020) and in compliance with NADP QA protocols (Gartman, 2016; Danielson, 2020).

During the study period, 217 AMoN samplers were deployed in LVWS, resulting in 214 valid samples: a 99 percent rate of success (table 6). There has never been more than one invalid AMoN sample per year in LVWS. The sampler deployed on February 28, 2012, broke in the field, and the inner core was lost, resulting in an invalid sample. The sampler intended for deployment on December 27, 2017, was mistakenly not installed by the technician. The sampler deployed on January 15, 2019, could not be collected on time because of RMNP closure during a Federal government shutdown.

Valid AMoN samples may have minor issues that were noted in the NADP data files but did not require invalidation of the sample. The most common minor issue noted from 2011–19 was concentrations below the MDL (87 samples). The remaining minor issues observed were delayed laboratory analysis (23 samples), long sample time (16 samples, usually caused by weather hazards preventing timely access to the site), local sources of NH_3 present during sample period (10 samples, caused by burning of slash piles by RMNP), and sample handling issues (8 samples, usually breakage of the plastic spool that holds the sampler or by the presence of dust inside the sample container). A total of 51 percent of the samples had at least one minor issue, whereas 48 percent had no issues and 1 percent had invalidating issues.

Table 4. Annual sample validity at National Atmospheric Deposition Program site CO98, 2010–19.

[The count represents the number of samples collected over each 13-week season (or 52-week year). Columns showing the percent of precipitation give the percentage of the precipitation depth represented by valid samples over the given season. %, percent; precip., precipitation]

Year	Winter		Spring		Summer		Fall		Annual	
	Count	% precip.	Count	% precip.	Count	% precip.	Count	% precip.	Count	% precip.
2010	6	43	9	58	11	98	10	79	36	62
2011	5	38	11	83	11	85	12	99	39	86
2012	12	100	10	70	11	93	12	94	45	86
2013	10	82	7	42	11	96	8	51	36	57
2014	6	44	9	74	7	82	10	81	32	69
2015	11	90	12	68	11	98	13	100	47	85
2016	8	63	10	56	11	97	11	78	40	56
2017	6	54	11	87	11	95	12	100	40	92
2018	10	71	12	97	10	84	13	100	45	87
2019	9	66	11	86	11	90	12	100	43	93

Table 5. Central Analytical Laboratory method detection limits for precipitation analytes, 2010–19.

[Modified from Danielson (2020, table 8)]

Analyte	Method detection limit (milligrams per liter)								
	2010	2011	2012	2013	2014	2015	2016	2018	2019
Calcium ion	0.004	0.002	0.005	0.0010	0.001	0.002	0.002	0.004	0.001
Magnesium ion	0.001	0.001	0.002	0.0010	0.001	0.001	0.001	0.002	0.001
Sodium ion	0.001	0.001	0.002	0.0004	0.001	0.001	0.001	0.003	0.002
Potassium ion	0.001	0.001	0.003	0.0010	0.001	0.001	0.002	0.002	0.003
Chloride ion	0.003	0.005	0.009	0.0004	0.004	0.004	0.003	0.006	0.004
Sulfate ion	0.004	0.003	0.010	0.0004	0.002	0.004	0.006	0.008	0.007
Nitrate ion	0.005	0.004	0.010	0.0004	0.004	0.004	0.005	0.003	0.003
Ammonium ion	0.010	0.006	0.009	0.0060	0.008	0.008	0.009	0.004	0.002
Phosphate ion	0.008	0.008	0.005	0.0004	0.004	0.004	0.004	0.003	0.003

Table 6. Ammonia Monitoring Network sampling history in Loch Vale Watershed, 2011–19.

[For years with no invalid samples, the reason invalid is given as "–"]

Year	Number of valid samples	Number of invalid samples	Valid sample percentage	Reason invalid
2011	17	0	100	–
2012	23	1	96	Sampler broken
2013	25	0	100	–
2014	26	0	100	–
2015	26	0	100	–
2016	26	0	100	–
2017	25	1	96	Sampler not deployed
2018	25	0	100	–
2019	24	1	96	Overlong deployment
Total	**217**	**3**	**99**	–

Measures of Bias and Precision

As part of the QA plan, bias and precision in the AMoN data were measured at the CAL using travel blanks and triplicate samplers (Danielson, 2020). Travel blanks were Radiello passive samplers taken to the field but not deployed. Blanks were returned to the CAL and extracted and analyzed by standard methods using flow injection analysis (Lachat Quik Chem 8500 S2). Travel blanks from LVWS typically had mean annual NH_3 concentrations above detection limits by up to one order of magnitude, likely from contamination by ambient NH_3 in the air (table 7). The concentrations detected are on the order of tenths or hundredths of a microgram per cubic meter ($\mu g/m^3$) but, given that the average concentration of NH_3 observed in LVWS is 0.35 $\mu g/m^3$, some bias from contamination may be present in the data.

Contamination criteria for AMoN set by NADP specify an exceedance value of 0.2 $\mu g/m^3$ (Danielson, 2020). The mean blank value for LVWS was less than 0.2 $\mu g/m^3$ in all years except 2013, when the mean blank value was 0.29 $\mu g/m^3$ (table 7). From 2011 through 2014, the AMoN project found NH_3 exceedance in network-wide travel blanks. Travel blanks collected in LVWS in each of those years exceeded the 0.2 $\mu g/m^3$ NH_3 threshold (table 7). In 2015, CAL staff discovered NH_4^+ contamination present in paper wipes used in the laboratory and resolved the problem by switching wipe manufacturers (Gartman, 2016). No travel blanks collected in LVWS have exceeded the threshold since that time (table 7).

Precision in the AMoN data was monitored using triplicate samples, deployed at the same time under the same shelter between one and three times per year. To quantify the difference in NH_3 concentration between samples in a triplicate set, we calculated the relative standard deviation (RSD, also called the coefficient of variation) of each triplicate set. The RSD is the ratio of the standard deviation over the mean and describes the amount of variance in the data relative to the mean. Table 8 shows the NH_3 concentrations observed for each triplicate sample (arbitrarily notated as A, B, and C), along with the mean, standard deviation, and RSD as a percentage. The greatest variance in triplicates occurred in July 2013 (RSD=33.1 percent), whereas the least dispersion occurred in May 2019 (RSD=1.6 percent). There was no apparent trend in the RSD values over time, as the slope of a linear model was 0.003. All triplicates with an RSD of greater than 15 percent are retested at the CAL and noted as such in the published dataset (Danielson, 2020).

Surface Water Chemistry

Surface water samples are collected weekly from the Loch outlet and less frequently from other sites in LVWS and RMNP. Field measurements of conductance and temperature are taken at the time of sampling using a Thermo Scientific Orion Star A222 probe, which replaced the Thermo Orion 105Aplus probe used from the start of the study period until November 2015 (Thermo Fisher Scientific, Waltham, Mass., USA). All samples are processed at NREL, but laboratory analyses are performed elsewhere depending on the analyte. Table 9 details the location and MDL for each analyte over the study period from 2010 to 2019. Chlorophyll-*a* and silica (SiO_2) concentrations were measured at NREL between 2010 and 2016, as were dissolved organic carbon and total dissolved nitrogen. Most analytes were measured at RMRS, including acid neutralizing capacity (ANC), calcium (Ca^{2+}), chloride (Cl^-), conductance, fluoride (F^-), potassium (K^+), magnesium (Mg^{2+}), sodium (Na^+), pH, ortho-phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and, from 2017 to present, dissolved organic carbon and total dissolved nitrogen.

Natural Resource Ecology Laboratory

Protocols for laboratory analyses performed at NREL—as well as field sampling and measurement protocols—are described in the LVWS Methods Manual (Bowker and Baron, 2017). The field conductance and temperature probe were checked weekly using Orion calibration standards with conductance ranging from 10.00–100.0 microseimens per centimeter ($\mu S\ cm^{-1}$; Thermo Fisher Scientific, Waltham, Mass., USA). A

Table 7. Mean travel blank ammonia (NH_3) concentrations in Loch Vale Watershed, with standard deviations (SD) and yearly method detection limits (MDL), total number of blanks (n), and number with NH_3 concentrations above exceedance value, 2011–19.

[$\mu g/m^3$, micrograms per cubic meter; n, number; >, greater than]

Year	Mean blank (µg/m3)	SD (µg/m3)	MDL (µg/m3)	n	No. of samples >0.2 µg/m3
2011	0.158	0.121	0.047	17	6
2012	0.188	0.117	0.047	24	10
2013	0.292	0.222	0.047	5	3
2014	0.170	0.070	0.047	4	2
2015	0.087	0.039	0.047	7	0
2016	0.073	0.021	0.047	7	0
2017	0.106	0.026	0.047	7	0
2018	0.063	0.059	0.008	6	0
2019	0.086	0.048	0.016	7	0

Schimadzu TOC-V CPN Total Organic Carbon Analyzer was used to make dissolved organic carbon and total dissolved nitrogen measurements of filtered samples. Dissolved SiO_2 was analyzed with a Thermo Spectronic 20D+ spectrophotometer using the silicamolybdate method adapted from Clesceri and others (1998). Chlorophyll-*a* was measured using a Turner Designs 10AU Fluorometer following the nonacidification method adapted from Arar and Collins (1997).

Table 8. Ammonium concentrations in micrograms per cubic meter (µg/m^3) for triplicate Ammonia Monitoring Network samplers (arbitrarily notated as A, B, and C) with mean and relative standard deviation (RSD), in percent, for Loch Vale Watershed, 2011–19.

[Dates shown as month, day, and year (mm/dd/year). µg/m^3, micrograms per cubic meter]

Start of sampling period	End of sampling period	A (µg/m3)	B (µg/m3)	C (µg/m3)	Mean (µg/m3)	RSD
8/16/2011 15:16	8/30/2011 18:24	0.38	0.48	0.45	0.44	11.8
7/3/2012 15:05	7/17/2012 14:28	0.47	0.94	0.85	0.75	33.1
12/11/2013 19:57	12/17/2013 19:03	0.19	0.20	0.19	0.19	3.0
8/25/2015 18:16	9/8/2015 17:57	0.33	0.34	0.37	0.35	6.0
4/5/2016 15:38	4/19/2016 16:35	0.23	0.23	0.22	0.23	2.6
9/20/2016 16:46	10/4/2016 19:03	0.32	0.31	0.31	0.31	1.8
3/8/2017 19:30	3/21/2017 16:51	0.15	0.24	0.28	0.22	29.8
8/22/2017 16:21	9/5/2017 16:30	0.60	0.63	0.59	0.61	3.4
2/13/2018 19:12	2/21/2018 19:55	0.17	0.23	0.17	0.19	18.2
9/4/2018 18:01	9/18/2018 15:45	0.44	0.42	0.43	0.43	2.3
5/7/2019 16:52	5/14/2019 17:53	0.36	0.35	0.35	0.35	1.6
8/20/2019 16:15	9/3/2019 17:10	0.50	0.50	0.60	0.53	10.8
12/10/2019 19:05	12/23/2019 19:20	0.12	0.10	0.11	0.11	9.1

Table 9. Water chemistry analytes measured in Loch Vale Watershed over the study period, 2010–19, including the name of measuring laboratory and the method detection limit (MDL).

[RMRS, U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, Biogeochemistry Laboratory, Fort Collins, Colorado; –, not applicable; mg/L, milligrams per liter; µg/L, micrograms per liter; NREL, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado; High Sierra, High Sierra Water Laboratory, Tahoe City, California]

Analyte	Laboratory, years	MDL
Acid neutralizing capacity	RMRS, 2010–19	–
Calcium ion	RMRS, 2010–19	0.02 mg/L
Chlorophyll-*a*	NREL, 2016–19	0.03 µg/L
Chloride ion	RMRS, 2010–19	0.01 mg/L
Conductance	RMRS, 2010–19	–
Dissolved organic carbon	NREL, 2010–16	0.06 mg/L
Dissolved organic carbon	RMRS, 2017–19	0.06 mg/L
Fluoride ion	RMRS, 2010–19	0.01 mg/L
Potassium ion	RMRS, 2010–19	0.02 mg/L
Magnesium ion	RMRS, 2010–19	0.02 mg/L
Sodium ion	RMRS, 2010–19	0.02 mg/L
Ammonium ion	RMRS, 2010–19	0.01 mg/L (NH_4^+-N)
Nitrate ion	RMRS, 2010–19	0.01 mg/L (NO_3^-–N)
pH	RMRS, 2010–19	–
Orthophosphate	RMRS, 2010–19	0.04 mg/L (PO_4^{3-}–P)
Silica	NREL, 2010–19	0.40 mg/L
Sulfate ion	RMRS, 2010–19	0.01 mg/L (SO_4^{2-}–S)
Total dissolved nitrogen	NREL, 2010–16	0.05 mg/L
Total dissolved nitrogen	RMRS, 2017–19	0.05 mg/L
Total phosphorus	High Sierra, 2015–16	1.0 µg/L
Total phosphorus	Utah State, 2017–18	1.4 µg/L

U.S. Department of Agriculture Forest Service Rocky Mountain Research Station Biogeochemistry Laboratory

Samples were delivered to the RMRS between 24 and 48 hours after collection. Once at the RMRS, samples were added to a computer database; stored in a cold, dark refrigerator; and processed in accordance with EPA guidelines. Guidelines established in the Handbook of Methods for Acid Deposition Studies (U.S. Environmental Protection agency [EPA], 1987) and the Standard Methods for the Examination of Water and Wastewater (Clesceri and others, 1998) were followed for all analyses. Control charts and control samples were used daily to monitor internal QC. For every ten samples, a QA sample was run (laboratory blank, duplicate, or check standard). The laboratory manager, laboratory analyst, and data analyst check, verify, and archive all collected data.

The methods used at RMRS are described in the RMRS Quality Assurance Plan (Fegel, 2020) and in Fegel and others (2020). Conductance, ANC, and pH were measured using a Mettler Toledo InMotion Pro following EPA protocols 310.1 (ANC), 120.1 (conductance), and 150.1 (pH). Ions were measured on a Thermo Fisher Integrion Ion Chromatograph, with anions using EPA protocol 300.0 and cations using Standard Test Method D6919-03. The dissolved organic carbon and total dissolved nitrogen analytes were measured on a Shimadzu TOC-V Combustion Analyzer using EPA protocol 415.1 (dissolved organic carbon) and Standard Test Method D5176 (total dissolved nitrogen). All EPA protocols can be found at https://www.epa.gov/labs/laboratory-methods.

Total Phosphorus Measurement

Total phosphorus was measured at High Sierra Water Laboratory for June 2015 through September 2017 (HSWL; PO Box 843, Tahoe City, Calif., 96145) and from October 2017 through July 2018 at the Watershed Sciences Laboratory at Utah State University (USU), using a Lachat QuikChem 8500 Flow Injection Analyzer and the EPA 365.3 persulfate digestion method. Samples were collected from August 2018 through the end of the study period (December 2019) and measured at USU. However, because of issues arising from apparent contamination, data from August 2018 through December 2019 did not meet QA standards for accuracy or precision. As a result, those data have not been published or used in any research and are considered not usable.

Data Outliers

Outlier data differ notably from other values in a dataset. For this analysis, outliers were defined as values greater or less than three times the interquartile range (IQR). Because of high seasonal variability in stream discharge, IQR was calculated for each season. Four values of total dissolved nitrogen and one value of nitrogen as nitrate (NO_3-N) had concentrations outside of three times IQR (table 10).

Outliers may be produced by sample contamination or analytical error, but they might also be true but unusual values. The high total dissolved nitrogen and NO_3-N measurements made at Sky Pond on September 19, 2013, came from samples that were collected in different bottles (total dissolved nitrogen in an amber glass bottle, NO_3-N in a polyethylene Nalgene container) that had been cleaned by different methods, and the samples were filtered on different equipment and analyzed on different laboratory machines following different protocols. Although it is possible that both samples were contaminated individually in the field, or both laboratory analyses were faulty, it is equally likely that the high measurements represent true values three times higher than the median. Such a spike in total dissolved nitrogen and NO_3-N could result from natural hydrologic processes.

The outlier values for total dissolved nitrogen at the Loch outlet in early 2017 may represent analytical error. All three occurred during the baseflow period when inorganic N contributions were low (table 10). High total dissolved nitrogen could therefore only be achieved by a high organic N input. Dissolved organic nitrogen is not measured directly in LVWS; however, dissolved organic carbon is, and those values were not abnormally high in early 2017. This discrepancy indicates that approximately the same amount of dissolved organic matter was present at the Loch outlet as usual. This means that high total dissolved nitrogen could only be produced by a higher-than-normal N content in the dissolved organic matter, or by analytical error. A note was appended to the dataset in NWIS to indicate these outliers.

Table 10. Outlier values of total dissolved nitrogen (TDN) from the study period, 2010–19, compared with their percentage of the median TDN by season, the interquartile range (IQR) of TDN concentration in milligrams per liter (mg/L), also by season, and values of inorganic nitrogen contributed by nitrate nitrogen (NO_3-N) and ammonium nitrogen (NH_4-N).

[Dates shown as month, day, and year (m/dd/year). %, percent]

Site	Date	TDN (mg/L)	% of median (seasonal)	IQR (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)
Sky Pond outlet	9/19/2013	0.9	315	0.24–0.45	0.70	0.01
Loch outlet	1/24/2017	1.4	425.6	0.21–0.36	0.08	0.04
Loch outlet	3/28/2017	1.2	364.6	0.21–0.36	0.02	0.04
Loch outlet	4/11/2017	1.0	289.3	0.24–0.37	0.02	0.02

Ion and Conductance Balances

All LVWS surface water samples were checked for ion percent difference (IPD) and conductance percent difference (CPD; EPA, 1987, 2004; Stednick and Gilbert, 1998). Since all samples are electrically neutral and all major ions were measured, the sum of the measured equivalents of positive charge should approximately equal the sum of the equivalents of negative charge. The ion balance is expressed by the IPD, calculated with equation 1. All concentrations are expressed in microequivalents per liter (µeq/L).

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

where

$\sum cations$ is $[Ca^{2+}]+[Mg^{2+}]+[Na^{+}]+[K^{+}]+[NH_4^{+}]+[H^{+}]$

$\sum anions$ is $[SO_4^{2-}]+[Cl^{-}]+[F^{-}]+[NO_3^{-}]+[HCO_3^{-}]$, and

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

The IPD indicates analytical accuracy with the expectation that a balanced sample will have an IPD of zero. A negative IPD represents an excess of anions whereas a positive IPD represents an excess of cations. All samples that fail to meet the criteria in table 11 were flagged and rerun. If the IPD was still outside the acceptable range after being reanalyzed, each sample was checked by ion for possible contamination. The three samples from 2010 to 2019 that failed to meet the criteria are presented in table 12.

The CPD was calculated as the difference between the theoretical and measured conductance, multiplied by 100 and divided by the measured conductance, as shown in equation 2. The theoretical conductance was determined by the formula in equation 3. All concentrations were expressed in units of µeq/L.

$$CPD = \frac{Theoretical\ conductance - Measured\ conductance}{Measured\ conductance} \times 100 \qquad (2)$$

$$Theoretical\ conductance = \frac{\begin{pmatrix} [Ca^{2+}]59.47 + [Mg^{2+}]53.0 \\ + [Na^{+}]50.08 + [K^{+}]73.48 \\ + [NH_4^{+}]73.50 + [H^{+}]349.65 \\ + [SO_4^{2-}]80.0 + [Cl^{-}]76.31 \\ + [NO_3^{-}]71.42 + [HCO_3^{-}]44.5 \end{pmatrix}}{1000} \qquad (3)$$

All three samples with anion deficiencies may have resulted from anomalously low ANC measurements (table 12). Each of these three samples had the lowest recorded ANC values from their respective locations, and the measurements from Sky Pond outlet (October 4, 2011) and Andrew's Tarn inlet (August 20, 2013) had the only negative ANC values in the dataset. Samples with much lower-than-average ANC would be expected to have much lower pH. However, none of the samples had a significantly lower pH than expected. The ANC values for these three samples were probably erroneous and a note was appended to qualify each of these values in the dataset as possibly in error.

Table 11. Surface water sample reanalysis criteria for ion percent difference and conductance percent difference.

[Data from U.S. Environmental Protection Agency (1987). Values in italics are the average values for the study period for each sampling location. Ion strengths are in microequivalents per liter. Conductance is given in microseimens per centimeter. IPD and CPD are given in percent. IPD, ion percent difference; CPD, conductance percent difference; µeq/L, microequivalents per liter; µS/cm, microsiemens per centimeter; <, less than; ≥, greater than or equal to]

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

Table 12. Ion balance of the three samples from the study period, 2010–19, that did not meet Environmental Protection Agency criteria for ion percent difference (IPD).

[Avg., average, shown in italics; Σ, sum of; ANC, acid neutralizing capacity. Dates shown as month, day, and year (m/dd/year)]

Sampling location	**Date**	**Σ anions**	**Σ cations**	**Σ ions**	**IPD**	**ANC**
Sky Pond outlet	10/4/2011	35.9	116.2	152.0	−52.8	−21.7
Sky Pond outlet Avg.	*2010–19*	*102.8*	*119.4*	*240.2*	*−0.1*	*97.9*
Andrew's Tarn inlet	8/20/2013	3.3	27.3	30.6	−78.3	−6.4
Andrew's Tarn inlet Avg.	*2010–19*	*60.3*	*58.0*	*118.3*	*3.3*	*32.1*
Andrew's Tarn outlet	8/20/2013	20.3	43.2	63.5	−36.1	2.3
Andrew's Tarn outlet Avg.	*2010–19*	*56.5*	*55.2*	*111.2*	*0.7*	*30.0*

The two samples for which the CPD was greater than the acceptable limit are listed in table 13. In both cases, the CPD was within the acceptable limit if calculated using the field conductance measurement, rather than the laboratory measurement. The mean August conductance measurement over the sample period for the Loch outlet was 12.3 µS/cm, and no measurement in the record was as low as the 3.6 µS/cm recorded in the laboratory for the August 2, 2011, sample. The mean measurement for August at Sky Pond inlet was 12.1 µS/cm, and the laboratory value of 10.4 µS/cm was lower than average but not outside the range of variability. In both cases, we suspect an error in the laboratory measurement accounted for the CPD exceedance, and a note was added to the dataset suggesting the field measurement be used.

Median IPD and CPD were checked for consistently positive or negative bias. Over the 10-year study period, the median IPD was positive in 4 years and negative in 6 (fig. 2). The largest positive median IPD was 5.2 in 2011, whereas the largest negative median was −5.3 in 2015. The median CPD was positive in 5 years and negative in 5 years (fig. 3). The largest positive median CPD was 16.7, also in 2011, whereas the largest negative median was −7.6, also in 2015. Over the study period, there was no clear, consistently positive or negative bias in IPD or CPD.

Table 13. Conductance percent difference calculations that fell outside acceptable U.S. Environmental Protection Agency limits for samples collected over the study period, 2010–19.

[Both samples met EPA criteria for conductance difference when the field conductance measurements were substituted for the laboratory measurements. Dates shown as month, day, and year (m/dd/year). Lab, laboratory; CPD, conductance percent difference; µS/cm, microsiemens per centimeter]

Sample	Date	Conductance (µS/cm)			Lab CPD	Field CPD
		Field	Laboratory	Calculated		
Loch outlet	8/2/2011	9	3.6	7.1	96.8	−21.7
Sky Pond inlet	8/30/2012	13.8	10.4	15	44	8.5

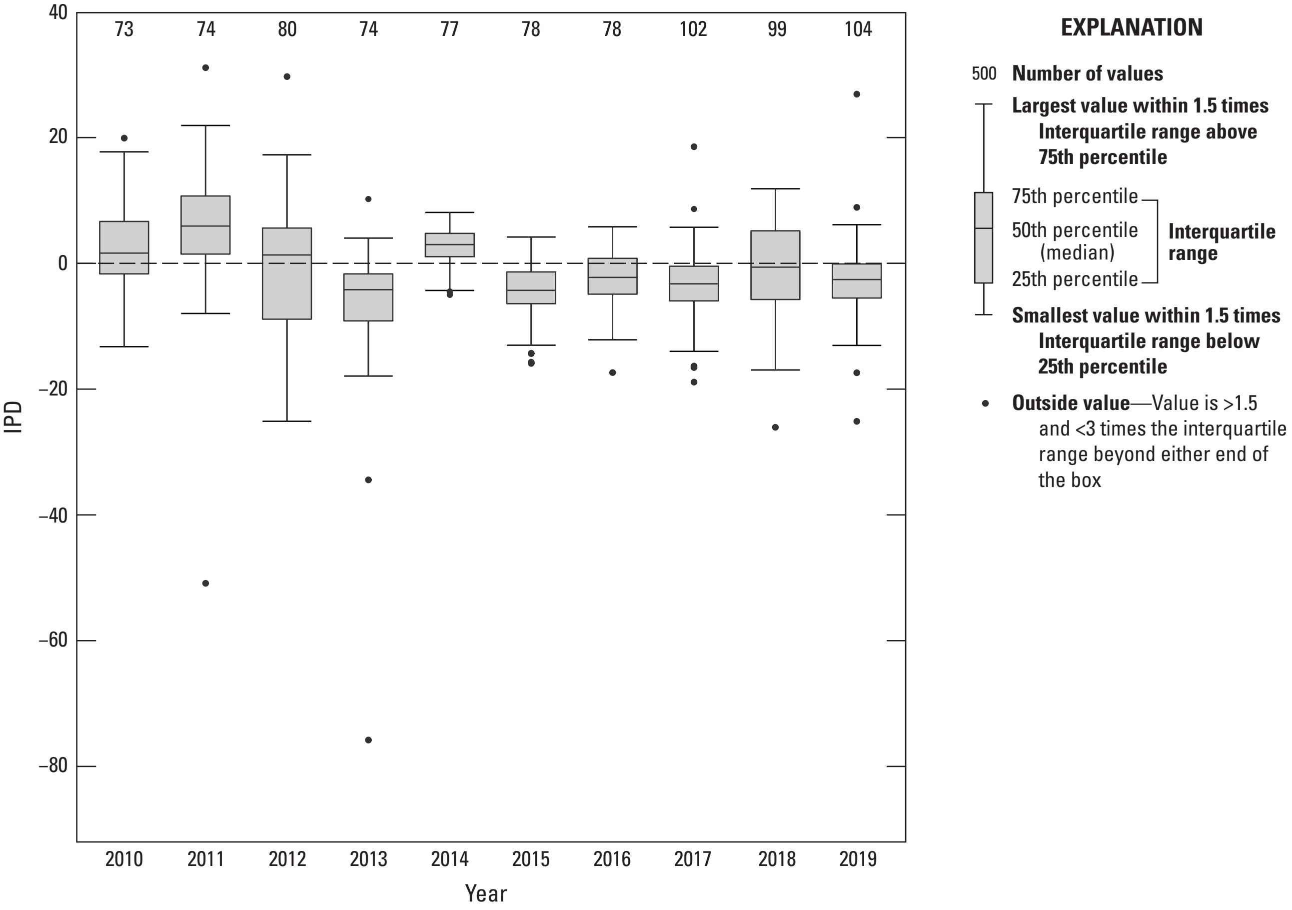

Figure 2. Ion percent difference (IPD) calculated from all samples collected in Loch Vale Watershed over the study period 2010-19, grouped by year. The numbers at the top of the figure indicate annual sample size. Dashed line appears at zero to easily show positivity and negativity.

Measures of Bias and Contamination

Of all field samples obtained from the LVWS, 10 percent were collected for QA purposes and were specified either as blanks or duplicates. Blank samples were collected to reveal potential contamination of samples that would bias measurements. Blanks were collected by bringing deionized water from NREL to the field and pouring it into a sample bottle set on site. This bottle set was then processed and analyzed in the laboratory according to standard procedures used for all other samples. Potential sources of bias and contamination of blanks included errors in bottle washing, sample processing and handling, laboratory measurement, data management, and contamination in the deionized water water filtration system. During the 2010–19 sample period, between 40 and 50 blank samples were measured for each analyte except total phosphorus and Chlorophyll-*a*, which were only included in regular sample collection for part of the sample period (see “Changes in Field and Laboratory Procedures: 2010–19” for details). There were 16 blank samples collected for total phosphorus analysis and 2 blank samples for chlorophyll-*a* analysis. The mean conductance of deionized water at NREL measured at the spigot was 0.38 µS/cm (standard deviation 11 µS/cm) over the study period.

The analytes with mean blank concentrations of note were dissolved organic carbon, SiO_2, and total phosphorus (table 14). Previous QA reports noted that the deionized water filtration system at NREL cannot produce completely pure water, resulting in detection of low levels of dissolved organic carbon and SiO_2 (Allstott and others, 1999; Botte and Baron, 2004; Richer and Baron, 2011). The mean dissolved organic carbon blank concentration over the study period was 0.16 mg/L, 0.1 mg/L higher than the MDL. The mean SiO_2 concentration was below the MDL. The mean total phosphorus blank concentration of 0.71 µg/L was high relative to the MDL of 0.14 µg/L achieved at the USU for the 2017–18 samples, but was below the MDL of the HSWL, which analyzed the 2015–16 samples.

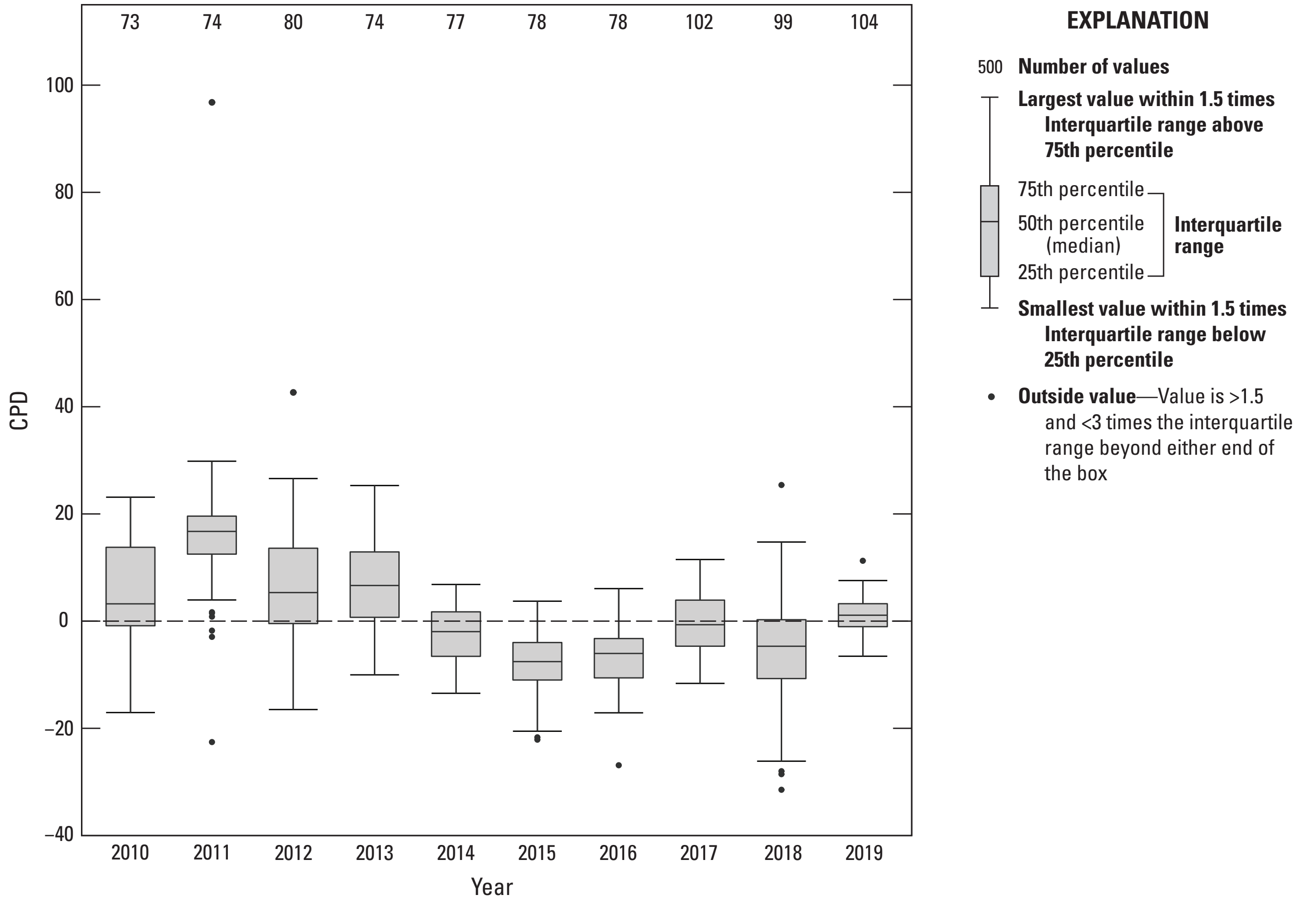

Figure 3. Conductance percent difference (CPD) calculated from all samples collected in Loch Vale Watershed over the study period 2010-19, grouped by year. The numbers at the top of the figure indicate annual sample size. Dashed line at zero to easily show positivity and negativity.

Table 14. Means and standard deviations (SD) for analyte concentrations in field blanks collected in Loch Vale Watershed from 2010 to 2019 with analytical method detection limits (MDL).

[n, number of samples; µg/L, micrograms per liter; mg/L, milligrams per liter; µS/L, microsiemens per centimeter; "–" indicates not relevant]

Analyte	Unit	Blankmean	BlankSD	n	MDL
Acid neutralizing capacity	µq/L	6.80	19.10	46	–
Calcium ion	mg/L	0.03	0.04	47	0.04
Chlorophyll-*a*	µg/L	0.03	0.02	2	0.03
Chloride ion	mg/L	0.03	0.08	46	0.02
Conductance	µS/cm	1.49	2.58	47	–
Dissolved organic carbon	mg/L	0.16	0.20	50	0.06
Fluoride ion	mg/L	0.02	0.04	47	0.01
Potassium ion	mg/L	0.03	0.07	47	0.02
Magnesium ion	mg/L	0.02	0.04	47	0.02
Sodium ion	mg/L	0.02	0.03	47	0.02
Ammonium ion	mg/L	0.02	0.02	47	0.01
Nitrate ion	mg/L	0.01	0.01	47	0.03
pH	–	5.56	0.40	47	–
Orthophosphate ion	mg/L	0.02	0.01	47	0.04
Silica	mg/L	0.21	0.27	41	0.40
Sulfate ion	mg/L	0.01	0.02	47	0.05
Total dissolved nitrogen	mg/L	0.04	0.03	50	0.05
Total phosphorus (2017–18)	µg/L	0.71	0.55	7	0.14
Total phosphorus (2015–16)	µg/L	0.65	0.47	9	1.00

Measures of Precision

Analytical precision was monitored in LVWS using duplicate samples. Pairs of samples were collected on field days, then processed and analyzed using identical standard procedures. Precision was measured by quantifying the differences between the paired samples. During the 2010–19 sample period, between 50 and 61 duplicate samples were collected and measured for each analyte except total phosphorus (26 duplicates) and chlorophyll-*a* (4 duplicates), which were not part of regular sample collection for the entire sample period (see "Changes in Field and Laboratory Procedures: 2010–19" for details).

Differences in duplicate pairs were quantified using three methods: absolute percent difference (APD), regression of mean against standard deviation, and hypothesis testing for the difference of medians using the nonparametric Wilcoxon signed-rank Test. The APD showed the difference between normal and duplicate samples on a proportional basis, the regression revealed the extent to which precision depends on concentration (EPA, 1987), and the hypothesis testing established whether statistically significant differences existed between paired samples. All results are presented in table 15.

The APD was calculated by dividing the absolute value of the difference (in paired samples) by the mean of the samples and expressed as a percentage. The median of all APDs (MAPD) was then calculated and compared between analytes. Over the study period, the largest MAPD occurred in total phosphorus, where the measured concentrations were low but the range of observed total phosphorus was an order of magnitude higher than the concentration values. The median difference between total phosphorus pairs was only 0.09 µg/L, but this amounted to an 11 percent MAPD. For NH_4^+, the difference in median concentrations was less than 0.01 mg/L but, because the typical concentrations measured were so low, the MAPD was 10 percent. Differences tend to be largest when analyte concentration ranges are low, because smaller absolute differences translate to a larger percentage of the median. The MAPD was below 5 percent in all other analyte duplicate pairs.

All measured analytes had weak ($R^2<0.5$) correlations between mean and standard deviation of the duplicate pairs. This suggests high precision over the range of concentrations measured. The greatest correlation ($R^2=0.44$) occurred with the chlorophyll-*a* data. Chlorophyll-*a* was not included in routine monitoring until 2018, and then was monitored only on a monthly, rather than weekly, basis. The higher correlation may be from small sample size (n = 4). Hypothesis testing found no significant difference between the means of duplicate pairs at α = 0.05. A Wilcoxon signed-rank test was used to avoid assumptions of normality in parametric tests, and the null hypothesis was that the difference between

Table 15. Comparison of duplicate mean values for all water-quality analytes and results of median absolute percent difference (MAPD), regression of mean over standard deviation (R^2 value) and hypothesis test that the means are not equal (p-value and Wilcoxon test statistic).

[n, number of samples; µg/L, micrograms per liter; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; –, no unit]

Analyte	Unit	Normal		Duplicate		N	MAPD	R2 value	p-value	p-value test statistic
		median	range	median	range					
Acid neutralizing capacity	µg/L	67.8	217	64.55	212	55	3	0	0.97	1,930
Calcium ion	mg/L	1.61	3.1	1.59	3	55	1	0	0.88	1,952
Chlorophyll-a	µg/L	1.69	7.1	1.7	5.2	4	4	0.44	0.99	5
Chloride ion	mg/L	0.15	0.3	0.15	0.3	54	3	0.01	0.86	1,826
Conductance	µS/cm	14.35	19.2	14.07	19.2	55	1	0.03	0.94	1,785
Dissolved organic carbon	mg/L	0.81	3.8	0.85	3.9	61	4	0	0.57	2,148
Fluoride ion	mg/L	0.1	0.5	0.1	0.5	55	4	0.01	0.98	1,916
Potassium ion	mg/L	0.19	0.3	0.2	0.3	55	0	0.05	0.94	1,938
Magnesium ion	mg/L	0.27	0.4	0.27	0.3	55	1	0.02	0.88	1,952
Sodium ion	mg/L	0.65	1	0.65	1	55	1	0	0.93	1,940
Ammonium ion	mg/L	0.03	0.1	0.03	0.1	55	10	0.12	0.94	1,786
Nitrate ion	mg/L	0.64	2.4	0.68	2.4	55	1	0.01	0.91	1,898
pH	–	6.59	1.8	6.6	1.5	55	0	0.03	0.89	1,773
Orthophosphate ion	mg/L	0.02	0	0.02	0	55	0	0	0.99	1,800
Silica	mg/L	2.15	3.5	2.21	3.6	50	3	0.03	0.92	2,026
Sulfate ion	mg/L	1.9	4.1	1.86	4.1	55	1	0.03	0.87	1,955
Total dissolved nitrogen	mg/L	0.33	0.8	0.33	0.8	61	0	0.02	0.87	2,283
Total phosphorus	µg/L	9.09	21.1	9	33.3	26	11	0	0.81	379

normal and duplicate sample means was zero. Because all analyte pairs were statistically similar with p-values much greater than 0.10, the duplicate data indicate no statistically significant differences between samples and duplicates for any analyte at $\alpha = 0.10$.

Measures of Accuracy

Analytical bias, or the quantification of accuracy, was measured using check standards. Standards were analyzed with each sample run and for each analyte measured. Samples were reanalyzed if drift greater than ± 5 percent is observed. The concentrations of standard used varied between analytes but represented the approximate median order of magnitude of the analyte, as well as one order above and below.

Most surface water analytes were measured by RMRS, and the QC procedures used by RMRS to maintain high accuracy are detailed in the quality assurance plan (Fegel, 2020). In addition, RMRS participated in the USGS Standard Reference Water test program. In this program, the participating laboratories measured analyte concentrations of reference samples prepared by USGS and then compared the results to the most probable value of the sample (Woodworth and Connor, 2003). Whether differences existed between the analyte values measured and the most probable values was determined used non-parametric methods (Hoaglin and others, 1983). The results of the comparisons are available on the USGS Office of Water Quality website (https://bqs.usgs.gov/srs_study/reports/index.php).

The analytical precision of five analytes was not measured at RMRS for at least a portion of the study period. For chlorophyll-*a*, dissolved organic carbon, total dissolved nitrogen, total phosphorus, and SiO_2, check standards were compared to analytical values to determine the APD between them. The MAPD value for each analyte and year is reported in table 16. The Wilcoxon signed-rank test was used to test the null hypothesis that the difference between the sets of paired check standards and analytical values was zero (table 17). In each case, the test resulted in failure to reject the null hypothesis.

Table 16. Median absolute percent difference between check standards and analytical measurements by year for each analyte measured at the Natural Resources Ecology Laboratory, as well as total phosphorus.

[“–” indicates not applicable]

Year	Chlorophyll-*a*	Dissolved organic carbon	Total dissolved nitrogen	Total phosphorus	Silica
2010	–	0.5	0.6	–	2.2
2011	–	5.4	3.4	–	2.7
2012	–	2.8	0.9	–	2.5
2013	–	0.9	1.5	–	2.7
2014	–	1.1	0.5	–	3.2
2015	–	0.9	1.4	0.6	3.7
2016	–	0.8	1.0	0.0	3.2
2017	5.0	–	–	3.1	2.5
2018	1.3	–	–	3.3	2.4
2019	0.3	–	–	–	1.3
Period	**2.6**	**1.0**	**1.1**	**2.8**	**2.7**

Table 17. Results of Wilcoxon signed-rank test of the null hypothesis that the difference between the set of check standards and paired analytical measurements was zero.

[n, number of samples]

Analyte	Test statistic	n	p Value
Chlorophyll-*a*	42	9	0.93
Dissolved organic carbon	993	47	0.40
Total dissolved nitrogen	1,008	47	0.46
Total phosphorus	180	19	0.99
Silica	6,790	109	0.19

Comparison Between Laboratories

Over the course of the study period, the laboratories used to measure three of the analytes were changed. Measurement of dissolved organic carbon and total dissolved nitrogen moved from NREL to RMRS in January 2017. Measurement of total phosphorus moved from HSWL to the USU in October 2017. To ensure consistency of measurements between laboratories, the data were compared qualitatively to assess for stepwise changes in measurements following laboratory change and were evaluated quantitatively by comparing analytical accuracy as determined using check standards.

No biases because of change in laboratory were apparent in the data for any of the three analytes, by either qualitative or quantitative measures. Time series plots of dissolved organic carbon and total dissolved nitrogen (fig. 4) and total phosphorus (fig. 5) are presented below. Note that the higher precision of data from the Utah State Water Sciences Laboratory is apparent in figure 5, but the variance in the data is roughly the same in measurements from the different laboratories. The small median annual percentage differences of dissolved organic carbon, total dissolved nitrogen, and total phosphorus measured in different laboratories (table 18) indicate that equivalently high accuracy was obtained at all laboratories used.

Continuous Dissolved Oxygen Data

Collection of dissolved oxygen (DO) data began in The Loch and Sky Pond in July 2017 and remains ongoing. In each lake, dissolved oxygen is measured in mg/L and percent saturation using a pair of miniDOT loggers (Precision Measurement Engineering, Vista, Calif., USA). Loggers are attached to buoys at the deepest point of each lake, one 0.5 m below the surface and the other 0.5 m above the lakebed. Once per year, the loggers are collected to download the data and perform QC checks. The loggers are then replaced in the field and continue to operate year-round.

The quality of DO data is checked using methods recommended by the manufacturer (Precision Measurement Engineering, 2021). Loggers are placed in a bucket of water that has been filled to several inches above the loggers. An aerator is also placed in the bucket and run for an hour until the water is oxygen saturated. Ice is then added to lower the water temperature to near freezing, and the logger records dissolved oxygen, temperature, and percent dissolved oxygen saturation for 24 hours. The percent saturation can then be compared to 100 to determine a percent difference. Loggers with a MAPD of five or more are returned to the manufacturer for recalibration. The MAPD calculated per lake over the study period ranged from 2.6 to 3.1 in The Loch and from 1.3 to 2.0 in Sky Pond (table 19).

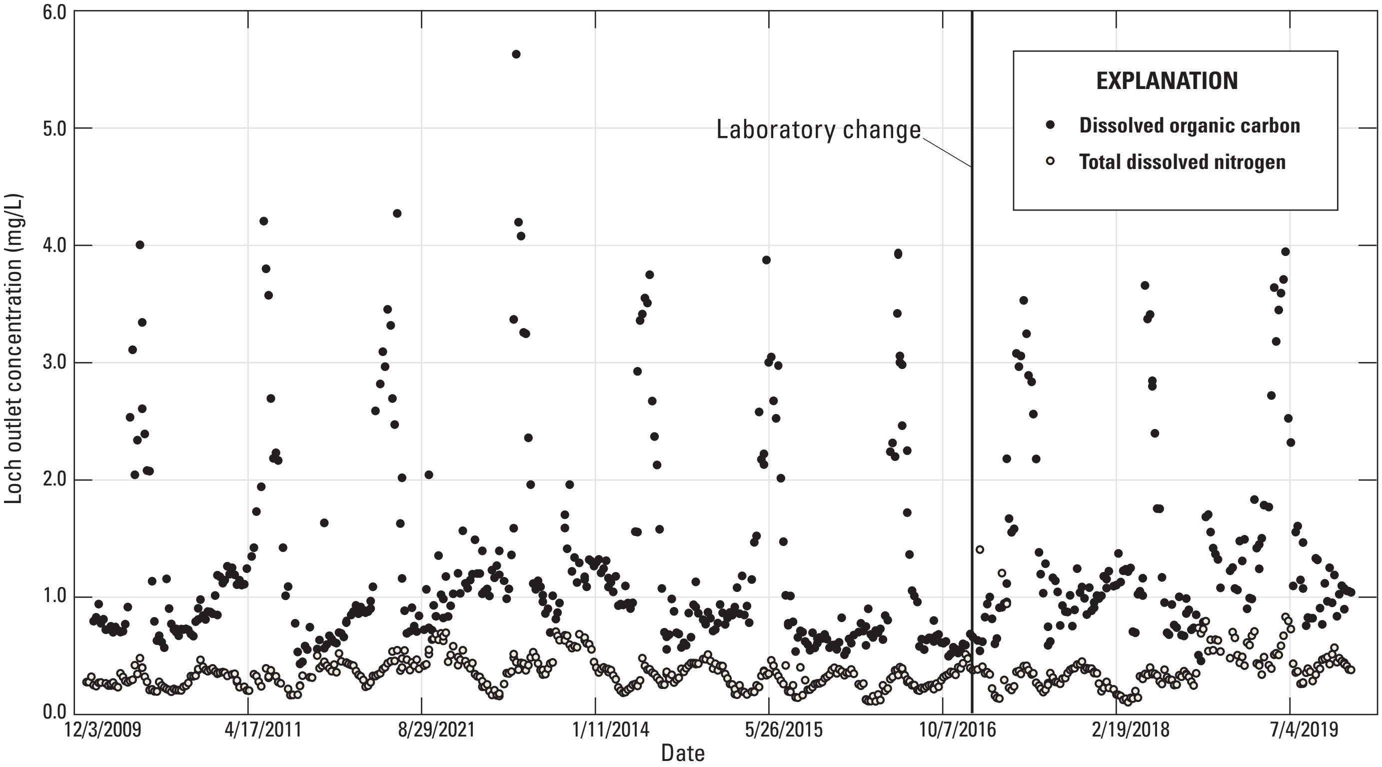

Figure 4. Time series of dissolved organic carbon and total dissolved nitrogen concentrations measured at the Loch outlet, 2016–19. The black line divides the samples analyzed at the Natural Resources Ecology Laboratory (2009–2016) from those analyzed at the Rocky Mountain Research Station Biogeochemistry Laboratory (2016–2019). (µg/L, micrograms per liter)

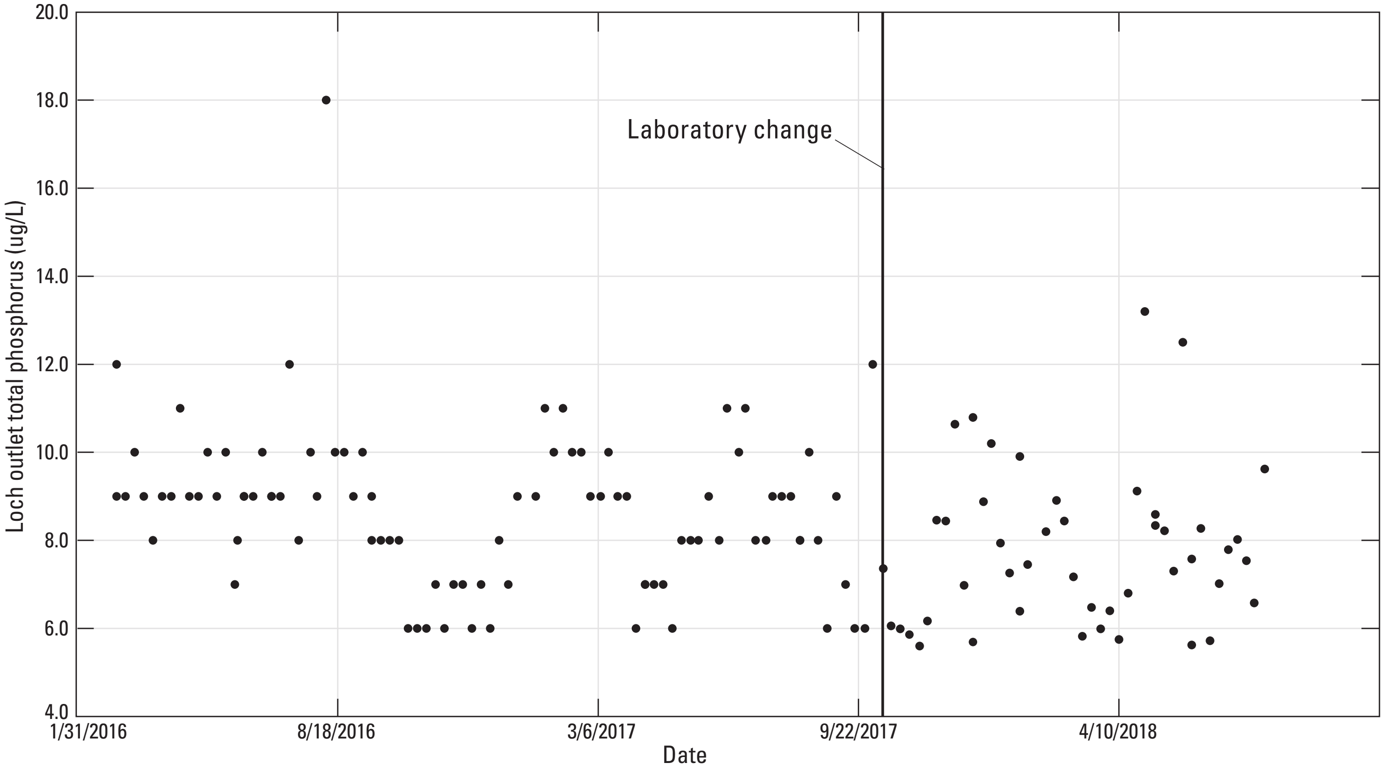

Figure 5. Time series of total phosphorus concentrations measured at the Loch outlet, 2016–18. The black line divides the samples analyzed at the High Sierra Water Laboratory (2016–17) from those analyzed at the Utah State University Water Sciences Laboratory (2017–18). (µg/L, micrograms per liter)

Table 18. Median absolute percentage differences between check standards and actual measured concentrations for the relevant analytes measured at multiple laboratories over the study period, 2010–19.

[mg/L, milligrams per liter; µg/L, micrograms per liter; "–", not applicable]

Laboratory	Dissolved organic carbon (mg/L)	Total dissolved nitrogen (mg/L)	Total phosphorus (µg/L)
Natural Resources Ecology Laboratory	1.9	1.6	–
Rocky Mountain Research Station Biogeochemistry Laboratory[1]	2.0	2.0	–
High Sierra Water Laboratory	–	–	2.9
Utah State University Water Sciences Laboratory	–	–	4.2

[1] Rocky Mountain Research Station Biogeochemistry Laboratory values reported in Fegel and others (2020).

Table 19. Median absolute percent difference between miniDOT Logger percent dissolved oxygen saturation and 100 percent saturation by lake over the study period.

[Dissolved oxygen sensors were first deployed in July 2017.]

Year	The Loch	Sky Pond
2018	3.1	1.3
2019	2.6	2.0

Changes in Field and Laboratory Procedures, 2010–19

The following list describes all procedural changes made to the LVWS program over the study period. Most of the changes consisted of replacing field instruments and infrastructure to mitigate against normal wear in the mountain environment. Laboratory changes were also made for dissolved organic carbon, total dissolved nitrogen, and total phosphorous to obtain the highest-quality data possible. New analyses were also added to the program: atmospheric ammonia monitoring beginning in 2011, in situ lake temperature and dissolved oxygen monitoring in 2017, and monthly lake chlorophyll-*a* measurements in 2018, all to better understand and quantify the effects of atmospheric deposition and (or) climate change on the LVWS environment.

- The bank of five 12-volt, deep-cycle batteries were replaced at the CO98/CO89 NADP site in January 2010, January 2011, September 2016, and September 2019.
- A third solar panel was added to the solar array in February 2010.
- The CO98 AMoN program began two-week NH_3 sampling at the LVWS main weather station in May 2011.
- The altar shield on the CO89 precipitation gauge was replaced in December 2011.
- The Thermo Orion 105Aplus field conductance and temperature probe was replaced by a Thermo Scientific Orion Star A222 in November 2015 (Thermo Fisher Scientific, Waltham, Mass., USA).
- Colocated precipitation collection at the CO89 site ended in 2014 when the CO89 ACM was removed. The colocated CO89 NOAH-IV precipitation gauge remains in place and continues to operate.
- As part of weekly surface water sampling in August 2015, total phosphorus measurements resumed after having been discontinued in January 2005 (Richer and Baron, 2011). Samples were analyzed at High Sierra Water Laboratory (PO Box 843, Tahoe City, Calif., 96145) from March 2015 to October 2017 and at the Watershed Sciences Laboratory at Utah State University (USU; 5210 Old Main Hill, Logan, Utah, 84322) from October 2017 through July 2018. Samples were collected for the remainder of the study period (August 2018 to December 2019) but were determined unusable because of apparent contamination.
- Continuous, year-round dissolved oxygen and temperature measurements began in The Loch and Sky Pond in July 2017 using miniDOT Loggers (Precision Measurement Engineering, Vista, Calif., USA).
- From January 2010 to January 2017, dissolved organic carbon and total dissolved nitrogen were analyzed at NREL using a Schimadzu TOC-V CPN Total Organic Carbon Analyzer. Subsequent samples were analyzed by RMRS using a Shimadzu TOC-V Combustion Analyzer (Shimadzu, Kyoto, Japan).
- Monthly chlorophyll-*a* analysis of samples collected at the Loch outlet was added to the regular monitoring program beginning in January 2018.

- The CAL moved operations from the Illinois State Water Survey at the University of Illinois in Urbana-Champaign to the Wisconsin State Laboratory of Hygiene at the University of Wisconsin-Madison in June 2018 (Danielson, 2020).
- A new Campbell TX321-G GOES transmitter was installed at CO98 in December 2019 to improve satellite communication between the CO98 NOAH-IV precipitation gauge and NADP.
- The Sunsaver MPP250 solar controller and 12-volt lithium-ion battery were replaced in December 2019, and the connections to the Li battery were replaced with new wire.

Summary

The overall quality of the Loch Vale Watershed data in the four datasets monitored by the program (precipitation/deposition, atmospheric ammonia [NH_3], Loch outlet discharge, and surface water chemistry) for 2010–19 was satisfactory. The precipitation record was 98 percent complete over the 10-year period; however, a substantial number of precipitation gauge data were lost during 2017–19, with some data lost in 38 out of 156 weeks during those 3 years. Valid precipitation samples were collected representing 77 percent of the study period. Passive collection of NH_3 was added to the monitoring program in May 2011; 99 percent of samples collected were valid. Less than 1 percent of water chemistry samples were either flagged in or removed from the data record. Chlorophyll-*a* and total phosphorus were added (or added back, in the case of total phosphorus) to the monitoring protocol. The Loch Vale Watershed program continues to produce high-quality ecological data for monitoring and research.

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