

Loch Vale Watershed Long-term Research and Monitoring Program

Methods Manual 2017



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Foreword

This manual is intended to serve as a guide for technicians, students, and other participants in the Loch Vale Watershed (LVWS) long-term ecological research and monitoring program in Rocky Mountain National Park, and others like it. Procedures are described for sample collection, analyses, quality assurance, and database management.

This is a living document, so we welcome suggestions and questions. This document was most recently revised in spring 2017, and is built from previous versions written by Jorin Botte and Eric Richer.

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Introduction

The National Park Service (NPS) initiated the LVWS monitoring program in 1983 with funding from the Aquatic Effects Research Program of the National Acid Precipitation Assessment Program. Initial research objectives were to understand natural variability and the processes that mitigate or accelerate the effects of atmospherically deposited pollution on soil and surface water chemistry, and to build a record in which long-term trends could be identified. The project is currently a cooperative effort between the NPS, U.S. Geological Survey (USGS), and Colorado State University (CSU).

Routine sampling of precipitation chemistry, surface water chemistry, hydrology, and meteorological conditions began in 1983. Since then, all samples and data have been analyzed according to accepted and published methods (e.g., Clesceri et al. 1998; U.S. Environmental Protection Agency 1987).

Collection and analyses methods for all data have been rigorously tested. Quality assurance methods and results are described in reports produced by LVWS personnel (Denning 1988, Edwards 1991, Allstott 1995, Allstott et al. 1999, Botte and Baron 2004, and Richer and Baron 2011).

Table of Contents

Foreword	1
Introduction	1
Table of Contents	2
FIELD PROCEDURES	3
General Introduction	3
Field Safety	4
Snow Stability	5
Field Communications	6
First Aid Kit	8
Basic Equipment for your Backpack	9
Precipitation Sampling	10
NOAH IV Raingage	14
Ambient Ammonia Sampling	18
Measuring Conductivity	21
Surface Water Sampling	24
Research Permits	29
LABORATORY PROCEDURES	30
General Introduction	30
Filtration for Major Ions	32
Filtration for DOC and DON	36
Measuring Silica	39
Measuring Chlorophyll <i>a</i>	43
Alpkem Procedures	45
LECO CN Analyzer Procedures	46
Acid Washing Procedures	50
SHIPPING SAMPLES	52
Surface Water Samples	52
Precipitation Samples	53
Total Phosphorus Samples	56
REFERENCES	57
APPENDICES	59
Appendix A: Sampling Locations and Trails	59
Appendix B: Sampling Schedule	64
Appendix C: Quality Assurance/Quality Control Samples	66
Appendix D: Lake Bathymetry	67
Appendix E: Recipes	68
Appendix F: Supplies	73
Appendix G: Radio Channels in Rocky Mountain National Park	75
Appendix H: Database Management	76
Appendix I: Historical Field and Laboratory Procedures	77
Appendix J: LVWS Watershed Staff	109

FIELD PROCEDURES

General Introduction

Weekly field procedures in LVWS include: 1) collection of precipitation for chemical analysis, 2) measurement of precipitation amount, and 3) sampling of surface waters for chemical analysis.

The National Atmospheric Deposition Program (NADP) monitoring site, CO98, was established within the LVWS in 1983. NADP is a national network of precipitation monitoring sites. The network is a cooperative effort between many different groups, including the State Agricultural Experiment Stations, USGS, U.S. Department of Agriculture, and other governmental and private entities. The objective of the network is to provide data on the amounts, trends, and geographic distributions of acids, nutrients, and base cations in precipitation. Samples from each station are collected weekly using clean handling procedures, and sent to the Central Analytical Laboratory (CAL) in Champaign, Illinois for chemical analysis.

Aerochem Metrics samplers collect precipitation samples for analysis of water chemistry. Concentrations of solutes in precipitation water can be multiplied with precipitation volume to estimate chemical deposition. Methods for operating precipitation collectors and raingages are found in the [NADP National Trends Network Site Operations Manual](#). An Alter-shielded Belfort raingage measured precipitation volume for CO98 from August 1983 to August 2010. NADP updated CO98 with an electronic NOAH IV raingage in June 2007. After recording three years of co-located data with the CO98 NOAH IV, the CO98 Belfort was removed from the Loch Vale NADP site on August 9, 2010. An additional, or co-located, NADP site was installed in October 2010 under the name CO89. CO89 consisted of an Aerochem Metrics precipitation collector and NOAH IV electronic raingage. After a five year co-location period, CO89 was dismantled and removed from the Loch Vale NADP site on September 30, 2014 (Wetherbee 2016).

A Parshall flume with stilling well was installed at the Loch Outlet in 1983. Prior to August 2006, stage was measured with a float within the stilling well. Stream levels were recorded with a Campbell Scientific CR500 stream recorder, and a Leupold and Stevens strip chart recorder served as a backup for the Campbell. Stage data were converted to discharge values ($m^3 s^{-1}$). Operation of the Loch Outlet stream gage was transferred to the USGS Water Resources Division (WRD) in August 2006. Discharge is currently monitored with a depth transducer and data logger, while stage is visually estimated by Loch Vale personnel each week during the open water season.

Surface water samples are analyzed for chemical concentrations. Five sites are currently sampled within the LVWS, as well as five others within Rocky Mountain National Park (ROMO). Sampling locations are shown in Appendix A. Sampling frequency ranges from

weekly (at the Loch Outlet) to annually (for Emerald, Haiyaha, Louise, and Husted lakes). A detailed sampling schedule is listed in Appendix B. As stream and lake waters in the LVWS are chemically dilute, sampling protocols need to be followed carefully to avoid contamination.

Weather was measured at a Remote Area Weather Station near the Loch Vale NADP site from 1983 to 1998. In 1991, the current Loch Vale weather station, operated and maintained by the USGS Colorado Water Science Center, was established approximately 30 meters from the location of the RAWS. Data was collected from both stations during a co-location period from 1991-1998. The RAWS was decommissioned on November 24, 1998, due to decreasing data quality, increasing maintenance costs, and lack of available replacement components. A detailed comparison of data from the two weather stations during this co-location period can be found in the LVWS Quality Assurance Report for 1995-1998 (Allstott et al. 1999).

Field Safety

LVWS is a remote basin that requires preparedness, advanced fitness, and survival skills. Never consider a trip to LVWS to be a simple day hike. Field days can be very long and stormy, even in the summer. High winds are common. Be prepared with appropriate gear to keep warm and dry during inclement weather. Gear should include, but is not limited to, a good waterproof and windproof shell, warm hat, two pairs of warm gloves, comfortable waterproof boots (suitable for long hikes), warm socks (plus an extra pair), light to medium weight long underwear, warm pants and sweater (fleece works well), headlamp or flashlight, knife, compass, map, emergency blanket, well-stocked food bag (bring more than you think you will eat), water (drink at least 2 quarts per day), and a well-stocked first aid kit (with the knowledge of how to use it).

Summertime hazards include lightning, hail, snowstorms, and hypothermia. Winter hazards include avalanches, blizzards, hypothermia, and frostbite. There is danger of serious injury (broken bones, cuts, concussions, etc.) in all seasons.

Ground squirrels in LVWS can be carriers of bubonic plague, so do not approach or feed them. Mountain lions have also been sighted in the area. If confronted by a lion, raise your hands high above your head and slowly back away. Fight back if attacked.

All group leaders should have a working two-way radio and the knowledge to use it, and be certified in wilderness first aid and CPR.

It is best to start the day with a clear plan of action. Know all your sampling points, routes between them, and how long you expect the work to take at each point. Reevaluate the plan, and your progress within the plan, frequently throughout the day. It is best to hike out while there is still light in the sky. Plan accordingly! Solo sampling is allowed during non-winter conditions, but is not safe during late fall, winter, and spring until the trails are passable

without snowshoes or skis. During these seasons you must not conduct field work alone. Let someone in Fort Collins know where you plan on going and when you are expected to return. Once back in communication areas, contact that person awaiting your return.

Never endanger yourself or anyone else for a sample. In the best conditions, a park-led rescue will take a minimum of 5 hours. If the weather is bad, a rescue can take over a day. Stay safe.

Snow Stability

Avalanche danger is a concern in LVWS. A good rule of thumb is that if a slope can be skied, it can also produce an avalanche. Standard routes to the most frequently visited sampling sites in LVWS involve relatively little avalanche danger. In spite of this, the trip leader needs to be constantly aware of present and changing snow conditions. When traveling to a non-standard sampling point during the winter, snow stability is your primary concern. If, after careful evaluation of snow stability, someone in the group is in doubt of the party's safety, TURN AROUND! The loss of a sample is inconsequential compared to injury or death.

Check the Colorado Avalanche Information Center (CAIC) website at:

<http://avalanche.state.co.us/> before traveling to the mountains, or call the CAIC hotline (970-498-5311). Know what to expect before leaving town. Weather, terrain, and snow conditions all influence avalanche danger. Be wary of slopes with angles greater than 25 degrees after new snowfall, especially when accompanied by winds greater than 15 mph.

When traveling in avalanche terrain, all parties must carry an avalanche beacon, probe, and shovel. Your partner or group is responsible for saving your life should you become buried in an avalanche, and vice-versa.

There is no substitute for proper avalanche awareness training. There are many avalanche awareness courses offered throughout the fall and winter. The CAIC class calendar (<http://avalanche.state.co.us/education/class-calendar>) is a good place to start in looking for courses, or check with the Colorado Mountain School (<https://coloradomountainschool.com>) in Estes Park. Awareness of all major factors contributing to avalanches is the first and best means of staying out of harm's way.

Field Communications

a. Introduction

As of 2017, Verizon Wireless cell phone service, especially text messaging, in Loch Vale is good, while other carriers are not as reliable. In an emergency, if you can get a call out to 911 or ROMO dispatch (970-586-1203), use your cell phone. If service is unavailable, radios are your link to emergency assistance. They also provide communication between separate groups in LVWS.

b. Equipment and supplies

- Bendix King portable radios with antennas
- Charged battery packs

c. Preparation

Make sure radios have charged batteries and are in good physical condition before going to the field. Batteries need to be on the charger for at least four hours for a complete charge. An optimum charge can only be attained if the batteries are drained of all charge each month. Do this by leaving power on overnight to the weather channel. Radio antennas, while flexible, can break if bent too far. To prevent this, unscrew the antenna from the radio and carry it separately in your pack.

d. Procedures

Do a radio check in the parking lot before starting up the trail to ensure your radios are functioning properly. Turn on radio by turning volume knob clockwise. Then adjust squelch by turning squelch knob clockwise until static is heard. Turn squelch down (counterclockwise) until static is no longer audible. Turn channel selector knob to channel 1. Listen to make sure there is no other radio traffic you would be interrupting. Once you are sure the channel is clear, push the transmit button and say "ROMO, Researcher Baron - Radio check." Release the button. They will answer "Researcher Baron - loud and clear." You then say, "Copy - Researcher Baron clear." If ROMO cannot hear you, there will be no reply to your call. Repeat your initial call two more times, spaced by 30 seconds between attempts. If no contact is made, say "No contact. Researcher Baron clear."

Channels 1 and 2 are the primary channels used by ROMO personnel on the east side of the park, and should reach radio repeaters. Channel 13 is recommended for communication among LVWS staff while in the field. Channel 12 is the NOAA weather channel, which can be useful for checking afternoon weather conditions. Keep your radio set on channel 1 or 2 while traveling as a group. That way you can assist, if requested, with an accident. If you

encounter an accident which requires outside assistance, do not hesitate to call for help. You may have to move to higher ground to increase the quality of transmission.

e. Be aware

Radio etiquette

You must use proper radio etiquette. Assume all of your transmissions are audible to park personnel. It is very important to keep communications with ROMO dispatch brief and to the point, since the rest of ROMO staff also use these frequencies. All frequencies programmed into radios (except the channel 13 work channel) are not intended to be used unless necessary.

If ROMO provides a volunteer to assist with sampling, this volunteer is generally responsible for all radio communication, but all LVWS staff traveling to the field should be familiar with radio operation and etiquette. When traveling with a Park Service volunteer, a back-country travel plan must be filed at the Resource Management Office at park headquarters. When filing this plan, include call signs for all parties in the group. Park Service volunteers will use a call sign of "VIP". LVWS staff should use a call sign of "Researcher".

In an emergency situation, a typical emergency radio call would resemble the following:

Us: "ROMO, Researcher Baron"

Them: "Researcher Baron"

Us: "I have a 28 year old male with possible femur fracture. Break."

Them: "Go ahead"

Us: "Patient is breathing and responsive, no external bleeding, vitals steady. Break."

Them: *ROMO dispatch will lead the conversation from this point.*

First Aid Kit

Item	Comments
Nitrile or latex gloves	Non latex gloves are best in order to prevent allergic reactions
Ziploc style freezer bags	Can be used for used dressings, bandages, miscellaneous garbage
Safety pins	Keep several sizes
Topper dressing sponges	Different sizes
Triangular bandages or cravats	
Large surgical dressings, sanitary napkins	Any dressing that can be used for absorbing large quantities of blood
Band-Aids	Keep different styles on hand
Butterfly closures	Good for deep incisions
Moleskin	Useful for blisters
Rolled bandages (2-4")	
Roll of adhesive tape	Athletic tape works well
SAM splint, wire ladder	
Tongue depressors	
Accident release form	Use if aid is declined by patient
Packetts of sugar, honey, energy gels	For diabetics
CPR mask with one way valve	
Traction application gear	Unless you have specialized training in applying traction with an improvised device, immobilize with a vacuum splint or suitable alternative and wait for assistance from ROMO personnel.
Trauma shears, hemostat	
Antiseptic wipes	
Emergency blanket	
Aspirin, Benadryl	For pain, allergic reactions

Basic Equipment for your Backpack

Item	Comments
Avalanche beacon, probe, and shovel	For winter only. Never carry one of these without the others. Know how to use them!
Multitool with pliers, knife, and Phillips and flat head screwdrivers	Leatherman type
Fieldbook, several pencils, pens, and Sharpies	
Rocky Mountain National Park topographic map	Trails Illustrated map #200 or USGS McHenry's Peak 7.5 minute topographic quadrangle
Compass	
ROMO sampling permit	
Sunglasses, ski goggles	Carry both in winter
Repair tape	
Hand and foot warmers	Carry year-round
Matches, lighter, flint	
Headlamp with spare batteries	
Extra socks	Can also be used as mittens
Extra gloves	
Sunscreen	
Lip balm	
Small nuts and bolts, replacement parts, spare powder basket	Ski, snowshoe, pole repair
Trash bags	

Precipitation Sampling

a. Introduction

The LVWS participates in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) precipitation chemistry monitoring network. An Aerochem Metrics bucket collector captures precipitation as rain or snow that is collected weekly for chemical analysis at the Central Analytical Laboratory (CAL) in Champaign, IL. The Aerochem Metrics collector lid covers a clean plastic bucket when there is no precipitation. The lid opens when precipitation completes an electric circuit through two plates on the sensor. The sensor is heated to melt frozen winter precipitation, and water evaporates when precipitation stops, breaking the circuit and closing the lid back over sample bucket. A sample bucket is collected for NADP site CO98 every Tuesday morning, throughout the year and including holidays. Detailed sampling and maintenance procedures are provided in the [NADP National Trends Network Site Operations Manual](#) online. There is a paper copy located in NREL A225. You must be familiar with these procedures before operating a collector. Training in NADP procedures is offered yearly, and should be taken by all regular operators of the LVWS NADP site. The following instructions are given as a brief synopsis of appropriate methods.

b. Equipment and supplies to be taken to the field

- Clean bucket and lid, in their closed plastic bags
- LVWS field book with pencil

c. Estimated time to complete procedure

Once on site, approximately 10 minutes are required to change the bucket and check the sensor. If there are problems that require troubleshooting or repair, or if the weather is bad, the time spent at the NADP site can increase substantially.

d. Preparation

Buckets and lids are shipped to and from the CAL in tall cardboard boxes. Within each box, there should be six buckets, six lids, six 1 L sample bottles in bags, and boxes for shipping sample bottles to CAL. Each box should also include a supply of Field Observer Report Forms (FORFs). Two to three of these boxes of clean and used supplies are stored in NREL A218. When six used buckets and lids have accumulated, a box of used buckets and lids should be shipped to CAL. CAL will automatically ship a replacement box of clean supplies when they receive a box of used buckets and lids.

e. Procedures

Carry a clean bucket and lid (still in their plastic bags) to the LVWS NADP site each Tuesday. Once on site, check the foam lid seal to ensure good contact with the sample bucket. There should be no gaps or openings. Check the temperature of the precipitation sensor by touching a finger to the sensor plate (not on the ribs suspended above the plate). It should be cool, but above freezing. Sprinkle a few drops of water or some snow onto the ribs above the sensor plate to open the wet side bucket. If the lid does not open, consult the [NADP National Trends Network Site Operations Manual](#) for troubleshooting procedures.

Peer into the wet side bucket from the downwind side (normally northeast). Note any contamination (soot, dust, dirt, insect parts, plant parts) in the field book. Using the plastic bag as a glove, seal the clean lid onto the sample bucket. Ensure the lid is firmly sealed on the bucket. Check the sensor heater again; it should now be warm. Remove the sealed wet side sample bucket from the collector table. Install the clean bucket using the bag as a glove. Blow remaining water off the sensor and away from wet side bucket, being careful not to blow directly on the nearby lid seal, or wait for the heater to evaporate remaining water on the sensor. Observe the lid seal as it covers the newly installed wet side bucket. If the seal is not complete, airborne particulates could contaminate the sample, or evaporation from the bucket could increase ion concentrations in the sample. Notify the NADP Site Liaison (217-244-2838) if the lid does not seal completely.

Place the sample bucket into the plastic bag from the clean lid or clean bucket. Record the bucket change time and date in the field book, and note the bucket weight written on the side of the bucket by CAL, as well as the lid weight. Record any other relevant information (i.e., contamination, malfunction, etc...) in the field notebook. Load the sample bucket into the bottom or onto the outside of your pack, being sure the bucket will not invert and spill any sample.

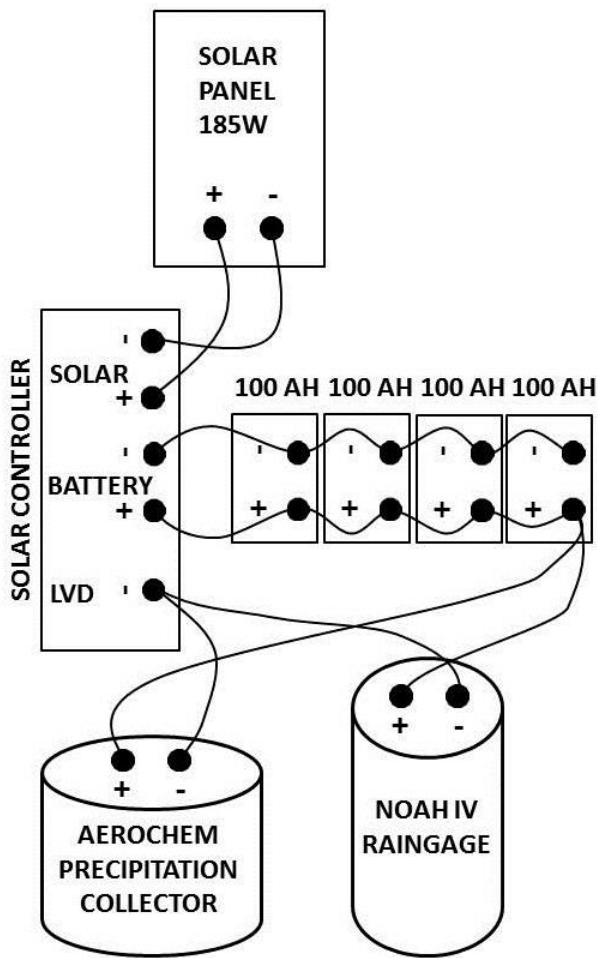
Clean the dry side bucket monthly with lab wipes and DI water. Clean the dry side bucket before replacing the wet side bucket. Begin by emptying the dry side bucket of any precipitation or debris. Do not touch the lip. With latex or nitrile gloves on, wet a Kimwipe with DI, wipe down the lip surface first, then progressively clean the inside of the bucket from top to bottom, finally wiping the entire inside bottom surface. Repeat if any visible debris remains in the bucket. The lid seal is changed as needed. Contact CAL for a new lid seal, and follow the installation instructions that come with the seal.

f. Be aware

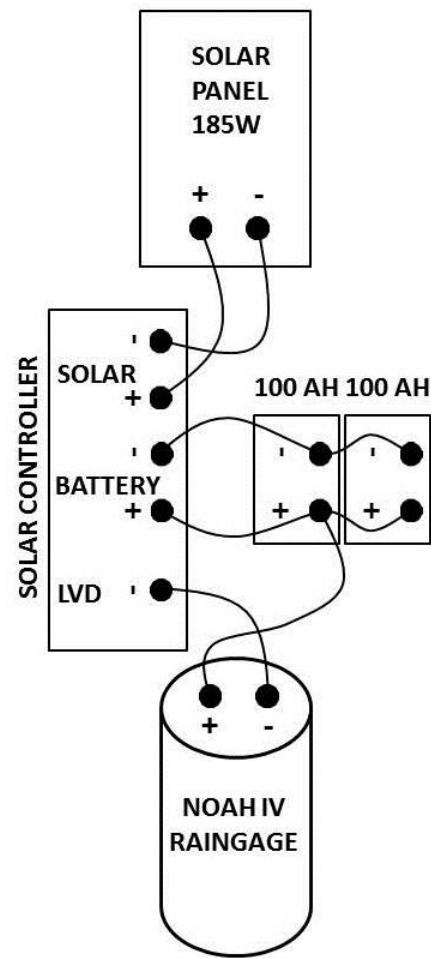
The Aerochem Metrics collectors can malfunction in many ways, but the most consistent problem is power loss during prolonged snow storms, especially during the short days of December and January. All Loch Vale NADP site equipment is powered by battery banks charged by solar panels. Be sure to remove snow from the solar panels and shovel snow

away that accumulates in front of the solar panels. Wiring for the solar power system is detailed in Figure 2. The solar power systems are designed for three to four days of autonomy. Power to the collector and raingages will automatically disconnect when the battery banks drop below 12 volts. In the summer, the solar panels, batteries, and wiring must be checked and repaired if needed. Beware of black widow spiders in the battery boxes, and wear gloves if you see them. Check connections to the Aerochem Metrics motor box and tighten any loose screws and nuts, especially those related to the movement of the roof and lid seal.

If you have concerns or problems with any NADP equipment, contact NADP immediately at (800) 952-7353.



CO98



CO89
backup raingage

Figure 2. Wiring diagrams for Loch Vale NADP site CO98, and the CO89 backup raingage. Both are 12 volt systems. The low voltage disconnect (LVD) system removes the load from the batteries when battery bank voltage drops below 12 volts.

NOAH IV Raingage

a. Introduction

An Alter-shielded NOAH IV electronic raingage was installed at the CO98 NADP site in June 2007. The ETI NOAH IV Total Precipitation Gage provides accurate and unattended measurements of rain and snow precipitation over a full range of temperatures and environmental conditions. An additional raingage was installed at the LVWS NADP site in October 2009 when the co-located CO89 NADP site was established. Though the co-located CO89 site was dismantled in September 2014, the raingage remains at the site as a backup. Site operators are required to download precipitation data from the CO89 backup raingage every Tuesday, while the main CO98 raingage transmits its data via satellite telemetry and does not require downloading. Raingages contain antifreeze year-round to maintain liquid water in the catch bucket. As the catch buckets fill with precipitation, the antifreeze/water mix becomes diluted and the catch buckets become full, requiring the catch buckets to be emptied periodically. Antifreeze is toxic to wildlife; raingage waste must be hauled out and disposed of properly.

b. Equipment and supplies

- Personal Digital Assistant (PDA) and downloading instructions are kept in NREL A225. Be sure to fully charge the PDA prior to leaving for the field.
- Antifreeze and funnel are kept in the storage box at the NADP site. Purchase the more environmentally friendly propylene glycol antifreeze for use in the raingages, not the highly toxic ethylene glycol type. Four gallons of new antifreeze should be enough for a year of changes, depending on how much precipitation is received throughout the year.

c. Estimated time to complete procedure

It takes around five minutes to download data from a NOAH IV. Emptying and refilling the antifreeze takes about 20 minutes, and is a two person job.

d. Preparation

Charge the PDA the day before going in the field. Be sure there is an adequate supply of antifreeze at the NADP site should you need to empty and refill the raingages. Make sure you have enough empty antifreeze containers to accommodate the volume of precipitation waste from the raingage. It will take 2 one gallon containers to empty each raingage collection bucket.

e. Procedures

Download data from CO89 NOAH IV backup precipitation gage

1. Stand next to CO89 raingage and turn on PDA. CO89 is closest to the bucket collector.
2. Tap once on **Bluetooth**, bottom left corner of start page.
3. Double tap on **CO89** icon. Wait for it to say connection is established.
4. Exit Bluetooth Manager (tap **X** in top right of page).
5. Tap once on **NADP Rain**, bottom right corner of start page.
6. Tap **Retrieve data from raingage**.
7. When page switches to **Connection type**, make sure it says **Bluetooth** in dropdown menu, then tap **Connect**.
8. Connection will be confirmed on bottom of page.
9. Tap **Download** on bottom right of page.
10. Download from: last Tuesday 8:00 AM; tap **Download**.
11. Wait for download to complete; should say 680-700 or so records were downloaded.
12. Tap **Data** on bottom right of page.
13. Set sample start to last Tuesday 8:00 AM; set sample end to current date and time (within 15 minutes).
14. Tap **View** on bottom center of page.
15. Write down daily precip totals in fieldbook.
16. Exit data view by tapping **X** on top right of page.
17. Tap **Time** on bottom right of page.
18. Tap **Check time**. There should be no difference in PDA and datalogger time. If there is a difference of more than one minute, set the time.
19. Tap **Raingage** on bottom right of page.
20. Tap **Refresh**; note voltage and bucket depth in fieldbook.
21. Tap **Collectors** on bottom right of page. As no collectors are connected to the CO89 backup raingage, ignore the information on this screen.
22. Tap **Disconnect** on bottom right of page, then **Disconnect** button, then **Exit** button.
23. Now back on main page of NADP Rain program, tap **Exit**.
24. Once the download is complete and you are back on the PDA welcome screen, tap the Bluetooth symbol  in the middle right of page.
25. Tap **Bluetooth**; will say **off**.
26. Exit Wireless Manager by tapping **X** on top right of screen.
27. Turn off PDA with power button on side.

If for some reason you have difficulty downloading the data, wait for any current functions to pause, then disconnect from the raingage and exit the NADP Rain program (steps 22 and 23 above). Once disconnected and back at the PDA home screen, begin again with step 1.

Transfer data files to NADP raingage data folder and email to NADP

1. Back in the office, connect the PDA to the computer.
2. Navigate to the folder where the data files are stored on the PDA.
3. Copy new files to: \LVWS_NADP\raingage\data downloads\site
There should be two files for the CO89 NOAH IV.

Example file names for CO89:

20161206T1919NPX3.txt

NPX320161206T1919.xml

20161206T1922 = Year (2016) Date (1206) Time (T1922)

4. Send both files to: nadp-precip@isws.illinois.edu

Subject: CO98/CO89 NOAH IV Files

Include information about site problems or maintenance performed.

Empty and refill raingages with antifreeze

The catch buckets in NOAH IV raingages can hold a maximum of 14 inches. However, to prevent overflow and enable easier handling, catch buckets should be emptied and refilled with fresh antifreeze when or before bucket depth reaches 10 inches. Bucket depth is noted in the fieldbook when downloading raingage data (steps 19-20 in the downloading procedure above). The following procedure is much easier as a two person job. Always note the exact start and stop times of stirring, adding, or changing antifreeze, and report these service times to NADP when emailing the raingage files each week.

1. Climb onto the raingage stand and work your way inside the wind shield. Remove the metal inlet ring and gently set it aside, being sure not to damage the top surface of the ring.
2. Gently remove the catch bucket by lifting straight up, using the two rectangular holes as grip points. Be extremely careful when lifting the bucket, especially when it has a lot of liquid in it. The load cell (the electronic weighing apparatus inside the gage) is very sensitive, and dropping even an empty bucket from a height of an inch or two will cause irreversible damage to the NOAH IV. Place the catch bucket on a surface such as a snowshoe or a rock, and do not allow snow or ice to freeze onto the bottom. Ice in the ring on the bottom of the catch bucket will prevent the bucket from sitting securely back on the load cell.

3. To empty the catch bucket, funnel the liquid into empty antifreeze containers. A catch bucket with 10 inches of liquid in it will fill approximately 2 antifreeze containers. You may need a thin stick to force small chunks of ice through the funnel.
4. Once empty, replace the catch bucket by very carefully lowering it back onto the load cell in the gage. Make sure the alignment guideposts on the load cell are inserted into the alignment ring on the bottom of the catch bucket. Align the notch on the catch bucket with the black alignment mark between the two LED emitters. The emitters must have an unobstructed view of the detectors through the opening in the catch bucket to effectively count particles of precipitation.
5. Place the black inlet ring back over the housing, and press down on the ring until it sits securely on the housing.
6. Pour one quart of fresh antifreeze into the catch bucket.
7. Back at NREL, funnel waste antifreeze into the 5 gallon metal containers underneath the lab bench in A256. Once a container is full, label the container with a hazardous waste sticker. Include your name as the responsible party, and label the contents "80% water, 20% propylene glycol." Inform the NREL lab manager that the container is full and in need of emptying.

f. Be aware

Containers of used antifreeze should be brought down from the station frequently, so as not to store waste in Loch Vale. Put a gallon jug of waste antifreeze in a plastic bag and bring it down in your backpack. Or, use the LVWS snow sled to get several jugs of waste antifreeze down at once.

If the raingage is not near the 10 inch fill limit, but you notice the liquid in the catch bucket is slushy or frozen, you can add some fresh antifreeze and stir to increase the proportion of antifreeze to water in the catch bucket. Again, be sure to note start and stop times while adding and stirring antifreeze.

Refer to the [NOAH IV Total Precipitation Gage Technical Manual](#) (a copy is in A225) for detailed maintenance procedures. Contact NADP immediately at (800) 952-7353 if there are any problems with the raingages.

Ambient Ammonia Sampling

a. Introduction

LVWS is part of the NADP Ammonia Monitoring Network (AMoN). Radiello passive diffusion-type ammonia (NH_3) samplers (www.radiello.com) are exposed for a 14-day sampling period. Every two weeks on a Tuesday, an exposed sampler will be retrieved from the site and a new sampler deployed. Approximately eight times a year, a travel blank sampler will be included in the box with the regular sampler as a quality assurance measure. This travel blank is treated just as the regular sampler, traveling to and from the site in its own sealed glass jar, except it is not exposed. Twice a year, the AMoN site operator will receive three samplers in place of the normal one, all included in the same glass jar. These triplicate samplers are deployed just as the regular singular sampler is, except instead of placing one sampler on one threaded post in the sampler shelter, the operator will place three samplers on three of the four threaded posts in the shelter. Additional information and detailed procedures are provided at the [NADP AMoN website](#). The following instructions provide a brief synopsis of appropriate methods.

b. Equipment and supplies to be taken to the field

- To-be-retrieved NH_3 sampler box containing:
 - Empty glass jar for placing exposed sampler in
 - Travel blank in its own sealed glass jar (if included)
 - Prepaid return shipping tag
 - Vinyl gloves
 - Sample field form
- To-be-deployed NH_3 sampler box containing:
 - NH_3 sampler(s) in its own sealed glass jar
 - Travel blank in its own sealed glass jar (if included)
 - Prepaid return shipping tag
 - Vinyl gloves
 - Sample field form
- LVWS field book with pencil

c. Estimated time to complete procedure

Once on site, approximately 5 minutes are required to change the NH_3 sampler(s).

d. Preparation

A box containing unexposed samplers (singular and/or triplicate and/or travel blank) will be shipped to you from CAL in advance of each change date. Upon arrival, open the box to

verify that everything arrived in good condition. Notify CAL immediately of any problems with the shipment (jars not tightly sealed, samplers broken, etc.), and also note any issues with the shipment in the **REMARKS** section of the field form. Once you verify the shipment is okay, close the box and store it in the NREL freezer to minimize NH₃ contamination.

e. Procedures

1. Once on site, inspect the sampler(s) and shelter for any contamination (e.g., bird droppings or dirt) or other conditions that might affect sample integrity. If necessary, clean the sample shelter with DI water and a Kimwipe.
2. Retrieve the exposed sampler(s): Put on clean vinyl gloves, included in the box with the sampler(s). Hold your breath and unscrew the sampler from the holder, taking care to handle it only by the white threaded section. Do not breathe into the shelter! Place the sampler(s) into the empty glass jar it was shipped in. Tightly seal the jar, and enclose the jar in the plastic bag, leaving the citric acid impregnated filter paper in the plastic bag. This filter paper acts as an ammonia scavenger. Place the bagged sampler jar into the shipping box for return shipment to CAL. Record the date and time the sampler(s) was retrieved in the field notebook.
3. Install the new sampler(s): While still wearing vinyl gloves, remove the jar from the plastic bag. Stand under the sampler shelter, hold your breath, and remove the new sampler from the jar. Taking care to handle the sampler only by the white threaded section, screw the sampler securely onto the mounting bolt inside the shelter. Again, do not breathe into the shelter! Reseal the now empty glass jar and place the jar back in its plastic bag with the citric acid impregnated filter paper. Record the date and time the sampler was installed in the field notebook. Repeat installation procedure for any remaining samplers.
4. Sampler storage: Bring the two boxes back to NREL. Store the box with the empty jar from the newly installed sampler with its travel blank, if included, in the NREL freezer.
5. Complete the field form: Record the NADP site ID (CO98), your name and initials, and the sample on and off dates and times. Report site conditions applying to the sampling period. Record the field blank storage location. Note any unusual site conditions in the **REMARKS** section. Each sampler is labeled with a unique code on the bottom of the sampler.
6. Pack and ship exposed sampler(s): Ensure the plastic bag with the sampler(s) in its glass jar and the citric acid filter paper is sealed, and place it in the box. Include the top (white) copy of the field form. Keep the bottom (blue) copy for your records. Seal the

box with tape, affix the prepaid shipping label, and place the box in the NREL mail pickup location next to the elevator on the second floor.

f. Be aware

Be very careful not to contaminate the sampler with your breath or by careless handling. Store all samplers in the NREL freezer while they await deployment to the field or shipment to CAL. Be sure to wear the vinyl gloves provided by NADP whenever handling a NH₃ sampler. Never breathe into the ammonia sampler shelter!

If the sampler falls onto the ground or another surface but remains intact, simply pick it up and deploy or pack the sampler as you would normally. Make a note on the field form. If in doubt, contact the CAL for guidance:

AMoN Site Liaison
Telephone: (800) 952-7353
Email: amon@isws.illinois.edu

Measuring Conductivity

a. Introduction

The conductivity of a solution is its ability to conduct an electrical current, and is the reciprocal of its electrical resistance. It is an indicator of the ionic strength of a solution. As with all other analyses we perform, conductivity measurements are susceptible to contamination. Conductivity of tap water can be 50 times greater than that of surface waters in LVWS. Make sure that everything that may contact sample waters has been thoroughly rinsed with DI before attempting any measurement.

In the field, measure the conductivity and temperature of all stream and lake waters with the portable conductivity meter prior to water sample collection.

b. Equipment and supplies

- Field notebook
- Thermo Scientific Orion Star A222 portable conductivity meter
- Deionized (DI) water
- Fisher Scientific conductivity standard $10 \mu\text{S cm}^{-1}$ (part # 2236-16, Ricca Chemical)
- Fisher Scientific conductivity standard $100 \mu\text{S cm}^{-1}$ (part # 2237-16, Ricca Chemical)
- Kimwipes

c. Estimated time to complete procedures

Allow 5 minutes for measurement of conductivity and temperature in the field.

d. Preparation

Check the battery level on the conductivity meter before taking it to the field. Extra batteries are kept in the meter field case. The calibration of the conductivity meter should be checked against standard solutions in the laboratory weekly, and calibrated as necessary. Calibration procedures are detailed in the conductivity meter instruction manual, in A225. The nominal cell constant for the conductivity probe is 0.475 cm^{-1} . Check the amount and date of the standard solutions prior to calibration. It is best to fill a small bottle (250 ml HDPE narrow neck bottles work well) about half full of conductivity standard, and dip the conductivity probe into this bottle. Every two months, discard the standard solution in this bottle, rinse with fresh standard solution, and refill.

e. Procedures

Checking the meter for accuracy in the laboratory

1. Rinse conductivity probe with DI water under faucet.
2. Turn meter on. Fill a small acid washed beaker with ~80 ml of DI, agitate probe in the DI, and record temperature and conductivity values in lab notebook. The conductivity of DI water should be no greater than $0.5 \mu\text{S cm}^{-1}$. If it is higher, something may be wrong with the laboratory DI system. Contact the lab manager and report the high conductivity value.
3. Lightly tap the conductivity probe on the edge of the waste beaker to get drops of DI out of the probe, then dry the probe with a Kimwipe.
4. Insert the conductivity probe into the $10 \mu\text{S cm}^{-1}$ standard, agitate the probe, then record temperature and conductivity values in the lab notebook.
5. Rinse the probe with DI, tap it lightly, and dry it with a Kimwipe.
6. Insert the conductivity probe into the $100 \mu\text{S cm}^{-1}$ standard, agitate the probe, then record temperature and conductivity values in the lab notebook.
7. Rinse the probe with DI, tap it lightly, dry it with a Kimwipe, and put the meter away in the lab drawer.
8. If the values noted are not within $1 \mu\text{S cm}^{-1}$ of the expected standard value, calibrate the conductivity meter.

Measuring conductivity and temperature of surface waters in the field

1. At each sampling location, measure conductivity and temperature prior to collecting water samples.
2. Turn the meter on and submerge the probe in the lake or stream. Do not let the probe rest on the bottom. Agitate the probe until "Ready" is displayed and the meter records the values. Sometimes it may be necessary to take several readings in order to allow the submerged probe's temperature equilibrate to the water temperature.
3. Record the location, date, time, conductivity, and temperature in the field book.
4. Turn the meter off between each sample, and put it away in the field case.

f. Be aware

The conductivity meter is a sensitive and expensive instrument. Turn the meter off between each sample, and transport it in its storage case. Do not travel from site to site with the probe on and outside its storage container.

Surface Water Sampling

a. Introduction

Surface water samples are collected from the Loch Outlet every Tuesday; from other flowing streams, lake inlets, and lake outlets in Loch Vale monthly during summer; and from other lakes in Rocky Mountain National Park annually (see sampling schedule in Appendix B). Stream samples are analyzed in the laboratory for pH, conductivity, acid neutralizing capacity, major ions, silica, dissolved organic carbon, total nitrogen, and total phosphorus. Samples from the Loch Outlet are used in conjunction with precipitation chemistry to calculate chemical budgets and for long-term trend analysis. Samples taken elsewhere in the watershed are used for analyzing processes and trends. Water samples for chlorophyll *a* are collected monthly year-round from the Loch, and monthly during the open water season from Sky Pond. Chlorophyll *a* provides a measure of primary productivity.

Stream and lake waters in LVWS are chemically dilute. Follow sample protocols carefully to avoid contamination.

Three types of samples are collected: normal, duplicate, and blank. Duplicates and blanks are quality control samples, and should be collected on a regular schedule (see Appendix B), so that a minimum of ten percent of all LVWS samples are analyzed to assess sample quality. Repeatability and accuracy of analysis is tested with duplicate sample results. Bias is assessed by analyzing blank samples. Instructions for conducting QA/QC sampling are in Appendix C.

b. Equipment and supplies

- Field notebook and pencil
- Conductivity/temperature meter
- Chemistry bottle set consisting of 5 bottles for each sample site:
 - 500 ml translucent HDPE acid washed bottle (FU: filtered and untreated, analyzed for major ions)
 - 250 ml brown HDPE acid washed bottle (RU: raw unfiltered, analyzed for pH and ANC)
 - 60 ml translucent HDPE acid washed bottle (SiO₂: analyzed for silica)
 - 60 ml translucent HDPE acid washed bottle (TP: analyzed for total phosphorus)
 - 480 ml baked borosilicate bottle (DOC/TDN: analyzed for dissolved organic carbon and total dissolved nitrogen)
- Biology sample kit for monthly chlorophyll *a* sampling:
 - Peristaltic hand pump with 5.5 m long flexible tubing marked in 0.5 m increments

- Filter flask, vacuum tubing, filter holder, 47 mm GF/F filters, PetriSlide containers, graduated cylinder, vacuum hand pump, cooler with ice packs
 - 1 L brown HDPE bottle (not acid washed) for each sampling site
- c. Estimated time to complete procedure

Once on site, it will take ~15 minutes to collect all samples. For monthly chlorophyll *a* sampling, expect ~30 minutes to filter each sample.

d. Preparation

All supplies needed for surface water sampling are located in the cabinet below the lab bench, or in the program manager's office. Instructions for ordering new supplies are in Appendix G. Orders are frequently filled within a few days, but can also take weeks, so plan ahead. Check with a supervisor prior to making a purchase to ensure you have the correct account number.

Assemble a bottle set for each site. Retrieve the necessary bottles from the storage cabinet. All HDPE bottles, except those used for chlorophyll *a*, are acid washed and stored filled with DI to minimize sample bottle contamination. Prior to inclusion in a bottle set, the conductivity of the water inside each HDPE bottle must be tested, again except for those used for chlorophyll *a*. If the conductivity is $<2 \mu\text{S cm}^{-1}$, the bottle may be included in a set. If the conductivity is $>2 \mu\text{S cm}^{-1}$, the bottle must be removed from rotation and acid washed again prior to use.

Once all bottles have been tested for conductivity, wrap a piece of labeling tape completely around the bottle so that the tape overlaps, and label each bottle with sampling date, sampling location, analysis that will be conducted on that sample, and sample type (NORM, DUPE, or BLANK). For example, the 500 ml HDPE bottle for the Loch Outlet would have this label:

LOCH.O 161220
NORM FU

Place all bottles for each sampling location in a large plastic bag, and label the bag with sampling location, sample type, and date.

e. Procedures

Regular weekly sampling

1. Begin sampling at a given site by recording site name, weather conditions, time of sampling, and names of technicians in the field notebook.

2. For the Loch Outlet, record the stage to nearest fraction of a foot from the staff gage inside the flume at the time of sampling.
3. Take conductivity and temperature measurements and record the values in the field notebook.
4. Rinse all bottles three times with sample before filling. To rinse, dip bottle several inches under the water surface with the bottle mouth upstream, fill to one third of capacity, replace cap, shake vigorously, uncap, and pour water from bottle over threads of cap, and from cap over threads of bottle. Make sure you pour rinse water downstream, or away from eventual sample point.
5. When finished triple rinsing, fill all bottles except TP to top and tightly replace cap. Fill TP bottle slightly below shoulder, to allow for expansion upon freezing.
6. Upon your return to NREL immediately place TP sample in box in NREL freezer. All other samples should be placed in the LVWS cabinet in the NREL walk-in cooler.

Monthly chlorophyll a sampling

1. Be sure to collect a full chemistry bottle set when taking chlorophyll *a* samples. This is necessary to correlate chlorophyll *a* levels with water chemistry results. For example, take the Loch outlet set of samples immediately following monthly sampling of Loch.LS and Loch.LH chlorophyll *a*, and take the Sky outlet set of samples immediately following summer monthly chlorophyll *a* sampling at Sky.O.
2. During the months when the Loch is frozen over, chlorophyll *a* samples should be taken from the deepest part of the Loch. (See Appendix D for lake bathymetry.) Drill through the ice with an auger, and record the thickness of the ice in the field book.
3. Using the peristaltic pump and flexible tubing, drop the weighted end of the tubing into the hole until it is 0.5 m below the bottom of the ice. This is the surface, or epilimnion, sample. Turn the pump handle 40 revolutions to flush out the hose, then triple rinse and fill the 1 L brown HDPE bottle for Loch.LS chlorophyll *a*.
4. Now drop the weighted end of the tubing into the hole until it is 0.5 m above the lake bottom. If you are over the deepest spot of the Loch, you should be able to lower the opening of the tubing to around 4.5 m deep. This is the bottom, or hypolimnion, sample. Turn the pump handle 40 revolutions to flush out the hose, then triple rinse and fill the 1 L brown HDPE bottle for Loch.LH chlorophyll *a*.
5. During open water season, the monthly Loch chlorophyll *a* sample should be taken along the shore, before the lake water enters the meadow on its way to the lake outlet. As the lake is not nearly as deep along the shore, only take the surface sample.

6. Set up a filter station in the shade at the Loch Outlet. The plywood roof on the flume is a good place to do this.
 7. Place a GF/F filter in the filter holder, and assemble the filter tower, tubing, and vacuum hand pump.
 8. Rinse the filter three times with a small amount of sample. Be conservative with the rinses, as it often takes at least 750 ml of sample to get enough color on the filter, especially in the beginning of the season.
 9. Shake the sample bottle and measure out ~500 ml of sample with the graduated cylinder. Record the volume to the nearest ml in the fieldbook.
 10. Pour the sample into the filter tower, put on the cover, and begin pumping the hand vacuum pump. Do not exceed 9 in Hg of vacuum.
 11. Once the sample has filtered through, shake the bottle again and measure out the remaining sample. Record the volume in the fieldbook. Apply vacuum and filter the remaining sample.
 12. Once filtration is complete, remove the filter, fold it in half carefully with forceps (colored side facing inward), and place the filter into a PetriSlide container labeled with site and date of chlorophyll sample collection.
 13. Immediately put the filter container into a cooler with ice packs.
 14. Repeat this procedure for the other 1 L sample bottle obtained from the Loch.
 15. For monthly open water season chlorophyll *a* sampling at Sky Pond, take one sample at the Sky Pond Outlet water surface. The filtration procedure for this sample is the same as above.
- f. Be aware

Make sure no person or animal is disturbing the stream immediately upstream of the sampling site. There should be no sediment in the sample. If necessary, wait until the water has cleared before sampling.

Streams flow at very low levels under the snow in the wintertime. If you have to dig snow or chop ice in order to sample, choose a spot with sufficient flow. After opening up a sampling location, wait 5-10 minutes for the water to clear of snow, ice, and sediment before sampling.

Algae in the water column are very sensitive to changes in light, temperature, and consumption by zooplankton. When weather permits, filter the chlorophyll *a* sample before

leaving the watershed. In the winter, it is permissible to filter at the Beaver Meadows entrance station, or back at the NREL laboratory if it can be done within 4 hours of taking the chlorophyll *a* sample, to avoid extreme weather. Chlorophyll *a* samples should be extracted and analyzed in the laboratory within 30 days.

Research Permits

Our presence in Rocky Mountain National Park is a privilege granted yearly by park staff, and as such, we apply yearly for research permits. We must also file an Investigator's Annual Report after each year of research, or the privilege to work in the park will be revoked.

We renew our Scientific Research and Collecting Permits every few years, depending on the expiration date. The project title for our primary research permit is "Long-term Ecological Research and Monitoring in the Loch Vale Watershed." Research permits are applied for and renewed through the NPS Research Permit and Reporting System. Application and renewal instructions are found at: <https://irma.nps.gov/rprs/>. Login information can be obtained from Jill Baron. Once logged in, existing and previous research permits can be viewed and renewed, and annual reports can be submitted under existing permits.

No one may collect samples within the park without a research permit. Be sure to keep copies of all applicable permits in the field vehicle, and in the crew leader's pack while on the trail. When renewing permits, update the list of field crew members, removing those who no longer work in Loch Vale, and adding those who will be on the field crew the following season.

LABORATORY PROCEDURES

General Introduction

The NREL laboratories are shared among a number of different projects. It is important to follow general laboratory practices of safety and cleanliness. All lab users must complete safety training with a lab manager. If you have any questions or concerns, do not hesitate to ask the lab manager. Make sure all LVWS personnel (including volunteers) are properly trained for the tasks they are asked to perform.

The following procedures are used both in preparation for field sampling and for processing samples in the lab. Refrigerate all water samples except those collected for total P (these get frozen) immediately upon return from the field. Process samples by noon the day following collection. Samples are filtered, preserved (as directed), and refrigerated or frozen at NREL before delivery to the appropriate analytical laboratory.

A note on cleanliness: Since LVWS waters are extremely dilute, assume any surface you touch is sufficiently contaminated to affect the outcome of analysis. Be careful of what you, sample bottles, and lids come in contact with during lab work. Rinse hands frequently with DI water. Latex gloves are available in the lab. The gloves themselves are not completely clean, and they become slippery when wet. To minimize the potential for sample contamination, the LVWS lab bench at NREL is used exclusively for processing LVWS water samples. Clean the bench top with DI water and lab wipes before starting lab work, and continually wipe away any water that accumulates on the bench. Leave the area clean for the next user.

Procedures for processing and storage of surface water samples are summarized in Tables 1 and 2.

Table 1. Summary of laboratory procedures for processing LVWS weekly and synoptic surface water samples.

Bottle Set for Surface Water	Treatment	Label	Analysis	Destination
500 ml HDPE acid washed bottle	Filtered with peristaltic pump into 60 ml translucent HDPE acid washed bottle	FU (Filtered Untreated)	Major ion concentrations	RMRS lab
Baked 480 ml amber borosilicate bottle	Filtered with baked glass filter tower into baked 120 ml amber borosilicate bottle	DOC/TDN	Dissolved organic carbon and total nitrogen concentration	RMRS lab
250 ml brown HDPE acid washed bottle	None	RU (Raw Untreated)	ANC, pH, and specific conductivity	RMRS lab
60 ml translucent HDPE acid washed bottle	None	SiO ₂	SiO ₂ concentration	NREL refrigerator
60 ml translucent HDPE acid washed bottle	None	TOTAL P	Total phosphorus concentration	NREL freezer → High Sierra Water Lab

Table 2. Summary of laboratory procedures for processing LVWS monthly surface water samples.

Bottle Set for Surface Water	Treatment	Label	Analysis	Destination
500 ml HDPE acid washed bottle (same bottle used to collect weekly FU sample)	Filtered with peristaltic pump into 250 ml brown HDPE acid washed bottle	ARCHIVE - FU	As needed	NREL freezer → FORT freezer
1 L brown HDPE bottle (not acid washed)	Filtered on field filter tower through a 47 mm GF/F filter	CHL A	Chlorophyll <i>a</i>	GF/F filter → NREL freezer

Filtration for Major Ions

a. Introduction

Solutes present in surface waters are primarily derived from precipitation inputs and geochemical weathering. Because samples must be delivered to laboratories for chemical analysis, it is important that the original chemical composition remains unchanged before and during transport. Particulates in a sample can affect chemical results as well as clog the tubing of sensitive instrumentation. Biological activity in the sample can alter chemical composition. Therefore, unless the sample is a measure of a total element (such as total P) we filter to remove particulate materials, spores, and bacteria from sample water to minimize their effects on chemical analysis.

Samples used to determine the concentration of major ions are filtered with the peristaltic pump and labeled FU (Filtered Untreated).

An ARCHIVE sample is collected monthly from the Loch Outlet, from the surface and hypolimnion of Sky Pond once a year in mid-August, and from Sky Pond's south inlet and outlet once a year in early September (see sampling schedule in Appendix B). These archive samples are obtained from the same 500 ml HDPE sample bottle that is used to collect the regular FU sample. These samples are filtered with the peristaltic pump into brown 250 ml HDPE bottles, labeled as "ARCHIVE - FU", and stored in the NREL freezer. Archive samples are transferred from the NREL freezer to the LVWS freezers in the USGS Fort Collins Science Center (FORT) laboratory as needed.

b. Equipment and supplies

- 500 ml HDPE sample bottle(s)
- Peristaltic pump with filter holder
- Millipore Isopore 0.4 μm membrane filters (catalog# HTTP04700)
- Clean forceps
- Deionized (DI) water
- Waste beaker
- Conductivity tested 60 ml HDPE bottle(s) labeled with site name, date, sample type, & FU
- Conductivity tested 250 ml brown HDPE bottle(s) labeled with site name, date, sample type, & ARCHIVE - FU (as needed)

c. Estimated time to complete procedure

Allow approximately 15 minutes per sample, although filtering times may vary greatly depending on the amount of particulate matter in the sample.

d. Preparation

The pump apparatus should be acid washed once a month. This can be done on the lab bench. To acid wash the pump, fill a one liter bottle with 10% HCl from the acid bath, run the acid through the pump as you would a regular sample (only without the filter membrane and without the rubber o-ring installed), allow the acid to sit in the tubing for about 1 hour, then copiously rinse with at least 12 liters of DI water. Conductivity of the rinse water should be $<2 \mu\text{S cm}^{-1}$, even after sitting in the pump for several hours. pH paper can be used to check that the pH of the DI rinse water did not change as it passed through the peristaltic pump (i.e., that all acid has been removed from the pump).

Make sure there are enough filters on hand to process all samples. Filters may take several weeks to be delivered from suppliers, so keep plenty on hand.

Plastic bottles must be acid washed before use (see acid washing section). Bottles are stored filled with DI water. Check the conductivity before using any bottle. A bottle with a conductivity $>2 \mu\text{S cm}^{-1}$ should be taken out of rotation, and washed again.

e. Procedures for filtering samples

Rinse peristaltic pump

1. Get a piece of clean tubing from the Tupperware box in the LVWS clean drawer, under the peristaltic pump. Handle tubing only on the end marked with ink. Rinse inside and out with DI water.
2. Place non-inked end of tube in 1-liter bottle of DI water.
3. Attach inked end of tube to the stopcock on peristaltic pump.
4. Place waste beaker under filter holder.
5. Retrieve rubber o-ring from DI soaking bottle, rinse it under DI faucet, and place it in filter holder.
6. Turn pump on forward to a setting of 3. Rinse pump tubing with 1 liter of DI before working with sample. Never run pump in reverse.
7. Turn pump off.

Load filter

1. Being careful not to touch any of its inner surfaces, remove bottom half of filter holder. Place on clean surface (e.g., a Kimwipe or inside of filter box lid).
2. Flame forceps with Bunsen burner and douse with DI water to cool.
3. Using forceps, remove rubber o-ring from filter holder and set it on a clean surface (e.g., a Kimwipe or inside of filter box lid).
4. Use forceps to remove paper over filter and carefully remove one filter (Isopore 0.4 µm) from box. Inside the filter box, the order is paper, filter, paper, paper, filter, paper, etc. Place the filter on filter holder. If filter is not centered on the holder, carefully adjust its position by pulling on edge with forceps. Be careful handling filters, as any contact between the filter and forceps in any area except its extreme outer edge will result in contamination or damage to the filter. Do not use any filter you think may be punctured or contaminated.
5. Replace the rubber o-ring on top of filter and carefully secure the o-ring in holder by pushing into filter holder with forceps.
6. Screw filter holder slowly back into the filter head and rinse the assembly with more DI water.

Filter sample

1. Take tube out of DI water bottle and remove from stopcock, walk away from bench, and spin tube to remove all DI water.
2. Place tube into sample bottle and attach to stopcock. Turn pump on to a forward setting of 3 to purge all DI water and allow tubing and filter to be rinsed with sample. Watch bubbles from the sample as they move through the pump tubing, to be sure you are collecting filtered sample and not DI rinse water. Samples that have been refrigerated overnight will be colder than the DI rinse water. When you feel colder water coming from the filter head, you know that sample water is passing through the pump. Filtering pressure must be less than 15 psi so that the filter does not rupture. This corresponds to a setting of 3 on pump motor control.
3. Rinse bottles three times with filtrate before filling (a few ml per rinse is sufficient). Fill FU bottles to the top to minimize head space above the sample. Fill archive bottles slightly below the shoulder, as sample will expand when frozen. If sample contains enough matter to clog the filter before the FU bottle is filled, it may be necessary to stop,

change the filter, and resume filtering. Remember to rinse the new filter with sample before beginning to fill bottle again.

4. Remove the used filter, rinse tubing with DI, and rinse pump with one liter of DI between samples, as described above. Use a new filter for each sample. Follow filter rinsing procedure as previously directed.
 5. After all samples have been filtered, remove used filter and give the unit a final rinse with one liter of DI water to purge all sample water. Be sure there is no water left in the filter tubing.
 6. Rinse inked tube with DI water, spin to dry, and place back into box in clean drawer.
 7. Remove rubber o-ring, rinse under DI, and place back in soaking bottle with fresh DI. Acid wash the soaking bottle periodically.
 8. Store the 60 ml FU sample bottles in the walk-in cooler before delivery to the analytical laboratory. Store archive samples in the NREL freezer, and transfer to the FORT freezers periodically.
- f. Be aware

It is a good idea to have a number of spare cut, acid washed pieces of silicone replacement tubing. Disassemble the pump tubing head to replace the old piece of tubing with a new piece of tubing. Wrap the outlet side of silicone tubing with strapping tape to prevent ballooning under filtration pressure. Pump assembly is easier if the pump rotor is rotating slowly (do this by hand with screwdriver) while the tubing is held in place and the plastic pump head halves are gradually pushed together. New tubing for pump is located in lab bench drawers. Any other pump related supplies can be bought from VWR.

Filtration for DOC and DON

a. Introduction

Dissolved organic carbon (DOC) is created in natural systems by leaching of soil organic matter, or from decomposition of algal biomass. DOC is operationally defined as organic carbon that passes through a 0.45 µm filter. Therefore, we filter water samples prior to analyzing DOC. Proper washing and baking is essential to remove all surface contaminants, most importantly carbon, and will also prolong the useful life of the filtration apparatus. Total dissolved nitrogen (TDN) is a measure of the total organic and inorganic nitrogen in a sample, after passing through the same 0.45 µm filter. Samples are analyzed for DOC and TDN using a Shimadzu auto analyzer at the USFS Rocky Mountain Research Station lab.

b. Equipment and supplies

- Water sample(s) in 480 ml amber borosilicate bottle(s)
- Whatman GF/F filters, baked at 500 °C for 5 hours (catalog# 1825-047)
- Forceps
- Baked filter tower (ground fitted glass 1000 ml flask, ground glass 47 mm fritted glass filter support, ground glass 47 mm funnel, clamp)
- Vacuum line
- Baked 120 ml amber borosilicate bottle(s), labeled with site name, date, sample type, & DOC/TDN

c. Estimated time to complete procedure

Allow approximately 15 minutes per sample, although filtering times may vary greatly depending on the amount of particulate matter in the sample.

d. Preparation

All glassware and glass fiber filters (GF/F) must be baked in the muffle furnace in NREL A121 before use. Rinse equipment in DI water and cover all openings with aluminum foil. Place in muffle furnace for five hours at 500 °C (one hour to reach temperature, and four hours at full temperature). Temperature in the furnace must not exceed 500 °C. If it does, the glass will deform. Allow oven to cool overnight (to < 150 °C) before opening furnace and removing glassware, otherwise it may crack from sudden cooling. Bake glassware on either Friday or Monday so it is ready for use by Wednesday morning.

e. Procedures for filtering samples

Rinse filter tower

1. Assemble filter tower by placing filter support on flask, center funnel on filter support, then clamp together.
2. Fill funnel with DI water. Plug in vacuum line and turn on full vacuum until all DI water has been pulled into flask.
3. Remove vacuum line, remove funnel and filter support as a unit and place upside down on a Kimwipe, then swirl DI water in flask sufficiently to rinse entire inside of flask.
4. Dump rinse water into waste beaker.
5. Reassemble and repeat 2 more times, using a full liter of DI water.

Filter sample

1. Place rinsed filter support on rinsed flask.
2. Flame forceps with Bunsen burner and douse with DI water to cool.
3. Using forceps, place a single GF/F filter over fritted glass on filter support. Center filter as well as possible with forceps, but be careful not to tear the filter. Place funnel on filter support, and clamp support and funnel together. Do not connect to vacuum line yet.
4. Add ~20 ml of sample to funnel. Pick up entire tower as a unit, swirl to rinse sides of funnel, put down the tower, and then connect vacuum line to port on filter support.
5. Turn on vacuum slightly, enough to cause sample to begin dripping through filter, but not enough to cause bubbles to form at the edge of the filter. Disconnect vacuum line just as sample water completely leaves funnel. Do not allow vacuum to pull on dry filter. Otherwise, trapped particles may fracture and be washed into the sample.
6. Remove clamped funnel and filter support as a unit and place upside down on a Kimwipe. Shake and swirl filtrate around in flask sufficiently to rinse entire inside of flask with sample filtrate, and then pour into waste vessel.
7. Repeat rinsing procedure two more times.
8. Pour remaining sample into funnel, attach vacuum line, and filter sample into flask under gentle vacuum. If there is a substantial amount of suspended material in the

sample, filtering will be very slow. If the sample appears to contain substantial suspended material, only pour half of the sample into the filter tower so that the filter can be changed midway through sample.

9. Once the sample has been filtered, rinse a 120 ml amber borosilicate bottle three times with sample, and then fill to shoulder.
10. Repeat all steps for each sample. Be sure to rinse the filter tower with one liter of DI between samples, and use a new filter for each sample.
11. Store the 120 ml DOC/TDN sample bottles in the walk-in cooler until delivery to the analytical laboratory.
12. After processing samples, rinse filter tower again with one liter of DI water. Disassemble tower, cover all openings with aluminum foil, and bake as previously described.

Measuring Silica

a. Introduction

If necessary, make new standards and keep in refrigerator. Make standards of 0.0, 0.1, 0.5, 1.0, 2.0, and 5.0 mg/L, using formula $C_1V_1=C_2V_2$, where C_1 is the initial concentration, V_1 is the initial volume, C_2 is the desired concentration, and V_2 is the desired volume. Use MilliQ water instead of DI water to make the standards, as the DI stream can have appreciable levels of silica that will skew your standard curve. Refer to the SPECTRONIC 20⁺ and SPECTRONIC 20D+ User Guide (copy on LVWS PC) for troubleshooting and additional operating procedures.

b. Equipment and supplies

- SPECTRONIC 20D⁺ spectrophotometer
- Vortex Genie 2 stirrer
- Timer or clock
- Wide mouth/flat bottom optically matched cuvettes
- 10 ml automatic pipette and clean pipette tips
- 10 mg/L SiO₂ solution for standards (Fisher Scientific catalog# 674032)
- Silica high range reagent set (VWR catalog# 97009-930)
 - Acid reagent powder packs
 - Citric acid reagent powder packs
 - Molybdate reagent powder packs
- Samples for analysis

c. Estimated time to complete procedure

As it takes a while to get everything set up and running for silica analysis, it is best to allow a minimum of three hours for this procedure. Shorter time spans will be too consumed with set up and takedown to allow many samples to be run.

d. Preparation

Zero the absorbance

1. Turn on the spectrophotometer, turning the power knob on the left side of the instrument clockwise. Allow the spectrophotometer to warm up for at least 15 minutes.
2. After the warm up period, set the analysis wavelength to 420 nm by rotating the wavelength control knob.
3. Set the filter lever to 340-599 nm.

4. Set the display mode to TRANSMITTANCE by pressing the MODE key until the appropriate LED is lit.
5. Adjust the display to 0% transmittance using the knob on the front left side of the instrument. Make sure that the sample compartment is empty and the cover is closed.
6. Set the display mode to ABSORBANCE by pressing the MODE key until the appropriate LED is lit.
7. Fill a clean cuvette with DI and wipe the cuvette with a Kimwipe to remove liquid droplets, dust, and fingerprints.
8. Place the DI filled cuvette in the sample compartment and align the guide mark on the cell with the guide mark at the front of the sample compartment. Press the cell firmly into the sample compartment and close the lid.
9. Adjust the display to 0.0 absorbance (0.0 absorbance = 100% transmittance) with the transmittance/absorbance control knob on the right side of the instrument.
10. Remove the cuvette from the sample compartment.

Match cuvettes

1. Allow samples and standards to reach room temperature.
2. Fill each cuvette with ~10 ml of DI water.
3. Wipe each cuvette with a Kimwipe, as any scratches or marks will affect results. After wiping a cuvette, insert it into the sample compartment and note the absorbance in the lab notebook. All matching cuvettes should have absorbance values ≤ 0.002 .
4. Set cuvettes that do not match aside. Keep all that do match.

e. Procedures

Create a standard curve

1. Check that the pipette is dispensing the correct volume of sample (10.00 ml). Put a small weighing dish on the balance in the lab, zero the balance, then pipette 10 ml of DI into the weighing dish. Adjust the pipetting volume until the balance consistently reads 10.00 g.
2. Pipette 10 ml of each standard (0.0, 0.1, 0.5, 1.0, 2.0, and 5.0 mg/L) into 6 cuvettes.

3. Add 1 molybdate reagent powder pack to each cuvette. Use the Vortex Genie to speed dissolving of the reagent powder.
4. Note time before beginning this step. Add 1 acid reagent powder pack to each cuvette and use Vortex Genie to dissolve reagent powder.
5. After 10 minutes have elapsed since adding the acid reagent powder pack to the first cuvette, again note time, and add 1 citric acid reagent powder pack to each cuvette and use Vortex Genie to dissolve the reagent powder.
6. No sooner than 2 minutes after adding the citric acid powder pack to the first cuvette, but no later than 5 minutes, wipe the outside of the cuvette with a Kimwipe and place into the spectrophotometer.
7. Record the absorbance reading in the lab notebook.
8. Repeat this procedure for the rest of the cuvettes containing the six standards.
9. Use Excel to create a linear regression to find the equation that describes the relationship between the standard concentrations and their absorbances.
10. If the R^2 of this regression is ≥ 0.99 , enter the absorbances for the 6 standards into the regression equation as the x variable. The resulting concentration values should be within $+/- 5\%$ of the expected standard concentration values. If they are not, consider making new standards.

Run samples

1. Pipette standards and samples into 12 clean and dry cuvettes. Keep a written log of what sample or standard goes into each cuvette in the silica lab notebook.
2. Each group of 12 cuvettes should contain a standard, a MilliQ blank, 9 samples, and a lab duplicate of one of the samples.
3. Use the procedure detailed above to obtain absorbances for each of the 12 samples and standards in each run.
4. After a run is finished, thoroughly rinse all of the cuvettes with MilliQ water, put in a metal test tube rack, and place in the 60 degree C drying oven. Once dry, let the cuvettes cool to room temperature before reusing.
5. Use the standard curve equation to convert absorbance to concentration.
6. Run no more than 3 sets of 12 samples before creating a new standard curve.

f. Be aware

Liquid waste from this procedure must be disposed of as hazardous waste. Carefully pour the liquid into an empty, rinsed 4 L glass jug, and affix a hazardous waste label. On this label, write “?????????????????.” Place the glass jug in the appropriate hazardous waste collection location in the lab. Notify the lab manager to dispose of this waste.

Measuring Chlorophyll *a*

a. Introduction

The level of chlorophyll *a* in the water column is an important measure of the productivity of a water body. Monitoring of the chlorophyll *a* level in the Loch is performed monthly year-round.

b. Equipment and supplies

- Turner Trilogy fluorometer
- 90% acetone (under a fume hood, dilute HPLC grade acetone with MilliQ water)
- Samples for analysis

c. Estimated time to complete procedure

It will take longer for the fluorometer to warm up than it will to analyze the few samples each month. This procedure should be able to be completed in about an hour.

d. Preparation

The GF/F filters containing the chlorophyll samples should be extracted in 90% acetone for 24 hours prior to analyzing them on the fluorometer. With each set of samples, include a blank consisting of an unused GF/F filter extracted in the same 90% acetone used for the samples. Always work with acetone under a fume hood. The level of acetone must be sufficient to completely submerge the filter, in order to extract all the chlorophyll. After extraction, samples may need to be centrifuged or filtered before analyzing on the fluorometer if there are visible filter particles floating in the acetone. If you have an even number of samples, they can be centrifuged at 2400 rpm for 5 minutes. If not, samples can be filtered through a 25 mm GF/F syringe filter. If there are no visible particles in the acetone after extraction, the acetone can be gently poured off into a cuvette without disturbing the filter.

Make sure the fluorometer warms up for at least 30 minutes before analyzing samples. Samples must be at room temperature, so remove them from the refrigerator an hour before analysis, gently shake them to mix the extraction, and allow them to warm in a dark place. Limit light in the lab while performing the analyses. Pull the blinds down, avoid direct light, and turn off the overhead lights in the lab.

e. Procedures

1. When you turn on the fluorometer, select the CHL-NA module. This is the non-acidification method.

2. Select the most recent calibration before running any samples. The fluorometer must be calibrated at least once a year.
3. A blank consisting of an unused GF/F filter extracted in the same 90% acetone used for the samples should be analyzed prior to analyzing samples. This blank should also be read every 10 samples.
4. At the beginning and end of each run, read the secondary solid standard and record the RFU reading.
5. Rinse the cuvette with a small amount of sample before pouring the sample out for a proper reading.
6. Be sure to wipe the cuvette very well with a Kimwipe and ensure there are no smudges or lint on the glass.
7. If you can see particles in the cuvette, centrifuge or filter the sample again.

f. Be aware

Acetone is regulated as a hazardous waste. Dispose of acetone waste by carefully pouring it into an empty, rinsed 4 L glass jug. Place a hazardous waste label on the jug, and write "acetone 90%, water 10%" on the label. Place the glass jug in the appropriate hazardous waste accumulation location in the lab. Notify the lab manager to dispose of this waste.

Alpkem Procedures

The Alpkem is an instrument that colorimetrically analyzes aqueous solutions for concentrations of different compounds. NREL's AlpKem can be configured to analyze ammonium (NH_4^+), nitrate (NO_3^-), and orthophosphate (PO_4^{3-}) concentrations. Technicians must have proper training from a laboratory manager before attempting to use this instrument. Due to the difficulty in setting up, calibrating, and operating the instrument effectively, the LVWS program contracts with the NREL EcoCore lab to analyze samples on the Alpkem.

Contact the EcoCore lab manager to set up a time for sample analysis on the Alpkem. On the day of analysis, work with the Alpkem technician to get your samples ready for analysis. Pull samples out of the refrigerator and allow them to reach room temperature. Create a spreadsheet that lists the samples in numerical order, with each sample having a unique number from 101-190, 201-290, and 301-390. These numbers will correspond to the position numbers in each of the three sample racks placed into the machine. The left rack contains positions 101-190, the middle rack 201-290, and the right rack 301-390. Pour your numbered samples into the provided 2 ml sample cups and place into the correct position in each of the three racks. The Alpkem technician will take it from there. Once complete, your results will be emailed to you, with a list of the sample vial position numbers and their corresponding concentration values.

LECO CN Analyzer Procedures

a. Introduction

The LECO TruSpec CN carbon and nitrogen analyzer is a non-dispersive, infrared, microcomputer based instrument, designed to measure the carbon and nitrogen content in a wide variety of organic compounds. For LVWS purposes, the LECO is used for the analysis of percent (%) carbon (C) and nitrogen (N) on finely ground soil and plant samples.

b. Equipment and supplies

- LECO TruSpec CN analyzer
- Plant/soil samples (ground and stored in well-labeled scintillation vials)
- Ball mill soil/tissue grinder (Room A127A inside Room A121)
- Microbalance
- Foil for analyzer cups
- Blanks and standards (mixed meadow grass [plant] or sidhigh [soil])

c. Preparation

1. Separate plant or soil samples by site and date.
2. Grind oven dried samples to a fine powder using the ball mill grinder for soil or Wiley mill for plants in downstairs lab.
3. Place each ground sample in a well-labeled scintillation vial and store according to date, site, and treatment.

d. Procedures

1. **Check gases:** Compressed air should read 40 psi. Helium and oxygen should read 35 psi on the left gage. Consult a lab manager if the pressure on the oxygen or helium tanks is less than 300-400 psi on the regulator closest to the tank.
2. **Check furnace temperature:** the temperature should be close to 950°C.
3. **Check to see if crucible is in the furnace** (same procedure used to change crucible):
 - Carefully lift off sampler carousel and gently set aside
 - Loosen the 3 main screws on the loading head - *very carefully* remove the loading head and set it on its side on top of the machine
 - Screw the lance extractor tool into the lance tube, *carefully* remove the tube and place in the tray next to the machine. THE LANCE TUBE IS EXTREMELY HOT!

- Replace crucible with tongs if necessary. Don't forget to reset the counter if you replace the crucible.
- Replace the lance tube, using a Kimwipe to clean any grit from the o-ring.
- Replace the loading head by *very carefully* lining up the connecting pins and stems.
NOTE: you should hear compressed gas if seated properly. This is normal and will stop once the loading head is tightened.
- Carefully push down on the loading head, and then tighten the bottom right hand screw first until you feel resistance. Tighten the other two screws until you feel resistance, and then fully tighten each screw by rotating among the screws.

4. Balance:

Turn on the balance. Use the $\frac{42\text{ g}}{205\text{ g}}$ button to switch display to 0.0000 g. Press the **CAL** button to calibrate the balance.

5. Counters:

- Select **Configuration** from the menu bar to access the counter window, then click on **Counters**. The *Warn* column indicates the maximum number of samples that should be run before that item needs replacement or maintenance. The *Count* column will increase by 1 each time you run a blank, standard, or sample. Make sure that the *Count* column will not exceed the *Warn* value during your run.
- NOTE: *It is especially important that the crucible count is not exceeded. Overfilling the crucible can result in expensive damage to the machine and considerable downtime. Please consult the lab manager if you are uncertain if the crucible needs to be replaced.*
- **Resetting the counters (if necessary)** - After changing the crucible or performing other maintenance, reset the *Count* to zero. To access this window, select **Maintenance**, then click **Login**, select the item that maintenance has been performed on, then click **OK**. Click **Yes** if maintenance was performed. Click **No** if maintenance was not performed. Return to the Counter window to ensure the proper item was reset.

6. Leak checks:

- Before running any samples it is in your best interest to check for leaks. Select **Diagnostics** from the main menu, then click **Leak Check**.
- Select **Whole O₂**, click *Start*, wait until *Passed* or *Failed* appears in the Results column. If *Passed* appears, be sure the value is less than 2.0 mbars.
- Select **Whole He**, click *Start*, wait until *Passed* or *Failed* appears in the Results column. If *Passed* appears, be sure the value is less than 2.0 mbars.
- Contact a lab manager if either of the leak checks fails.

7. Calibration:

- **Initial blanks** - First, make sure the next available (i.e., empty) cell on the spreadsheet has been selected. Select **Samples** from the main menu, then click

Login. From the *Sample* window, use the drop down arrow next to *Sample Name* to select **Blank**. The *Mass* must be 1.0000 (which is the default). Select **4** repetitions. Using the drop down arrow at the end of the *Method* line, select the appropriate *Method*.

Material	Method	Standard/ Check	Weight Range (g)	Carbon Range (%)	Nitrogen Range (%)
<i>Plant</i>	PLANT 10ML LOOP	mixed grass	0.1000 - 0.1100	10.8 - 100	0.62 - 8.5
<i>Soil</i>	SOIL 10ML LOOP	sidhigh	0.2000 - 0.2100	0.62 - 5.3	0.065 - 0.55

Note: The organic soils collected for the ongoing fertilization experiment in Loch Vale are high in both carbon and nitrogen, and are therefore analyzed with the PLANT 10ML LOOP method.

Enter your name or supervisor's name on the *Operator* line. The other *Attributes* should be left blank in most cases. Click **OK** to add the blanks to the sample list.

Click **Cancel** if necessary to close the *Sample* window. Four blanks should have been added to the sample table. To help keep track of your samples, change the numbers in the *Location* column to match the numbers on the sample carousel.

- **Initial standards** – Select **Samples** from the main menu, and click **Login Drift Samples**. Select the appropriate method using the drop down arrow, and the associated calibration standard will appear in the *Drift Standards* box, along with the weight range (your standards must be within this range; see table above). Select **4** repetitions. The standards appear after the blanks on the spreadsheet. *Note: The weights in the Mass column for the standards will appear with a ~ symbol. This is just to remind you of the approximate weight you should use. The actual weights will replace the reminder weights as you enter them using the Print button on the balance.*
- To start the analysis, click the **Analyze** button or press **F5** to start analyzing the blanks and standards. To halt the machine after the blanks (in order to run the blank calibration), first left click on the row containing the first standard, then right-click, select **Pause** from the **Samples** menu, and choose **Manually** from the drop down list. A red stop sign should appear next to the first standard. This will stop the analysis temporarily after the last blank sample.
- **Blank calibration** – If the carbon values vary by less than 0.04 and the nitrogen values vary by less than 0.02, you may proceed with the calibration. If not, continue running blanks until the values stabilize. After the blanks have finished running (and the machine is paused), choose the blanks you wish to use for the blank calibration by highlighting the appropriate group of blanks (left click and drag, or left click and use control to select individual blanks). Select **Configuration** from the main menu, then click **Blank**. From the *General Blank* window, *Include* both nitrogen and carbon if necessary, using the *Include/Exclude* button. Click **Ok**. After the blank calibration, restart the analyses by clicking the **Analyze** button or **F5**.
- **Standard calibration** – Select the appropriate standards you want to use in calibration. Select **Configuration** from the main menu, click **Drift**, then from the

next menu click **Drift** again. *Include* both nitrogen and carbon if necessary, using the *Include/Exclude* button. Click **OK**.

8. Running samples:

- Run one blank and one standard immediately after calibration to ensure the values are correct. If the values are out of range, run a few more blanks and/or standards, checking to see if they stabilize in the correct range. Contact the lab manager if the values are still questionable, and enter a **Pause** at the beginning and end of the calibration check.

Standard	Carbon ($\pm 5\%$)	Nitrogen ($\pm 5\%$)
mixed grass	43.78 (41.59 – 45.97)	2.53 (2.40 – 2.65)
sidhigh	2.589 (2.460 – 2.718)	0.269 (0.255 – 0.282)

- Enter the sample name in the **Name** column. Weigh the appropriate amount of sample for the method and press the **Print** button on the balance. The sample weight should appear next to the name you just entered.
- Run a blank and/or standard every 10 samples to ensure the machine is running properly.
- At the end of your run, **DO NOT** shut off the machine and **DO NOT** close the software. Change the crucible if necessary, select and download your data, and fill out the log book.

9. Exporting data:

Select the samples you want to download by clicking and dragging in the row column. Go to **Samples** on the main menu bar and click on **Text Export Data**. Enter a filename and the appropriate drive, then click **Save**.

10. Printing data:

Select the rows containing the samples you want to print. Select **Samples** on the main menu bar, click **Print**, then click **OK**.

Acid Washing Procedures

a. Introduction

All plastic bottles and tubing used for collection, processing, and storing of water samples must be cleaned in 10% HCl acid prior to use. This cleaning removes any contaminants adhering to the walls of bottles that can affect sample quality.

b. Equipment and supplies

Acid baths are located in NREL A254

- Plastic bottles and caps, various sizes
- 10% (by volume) HCl acid bath (see recipe in Appendix E)
- DI water
- Plastic dishpans
- Lab coat, goggles, rubber gloves, and closed toe shoes
- Sodium bicarbonate to neutralize acid spills

c. Estimated time to complete procedure

Time to complete this task will vary with the number and size of bottles to be cleaned.

d. Preparation

1. Make sure you are aware of safety procedures for dealing with strong acids. All persons using the acid baths must have lab safety training.
2. Bottles to be washed should have no visible dirt or oil. Do not use any soap, detergent, or other cleaning agents on LVWS water sample bottles.
3. Completely remove any tape or labels on bottles before placing in the acid bath. The acid will alter the labels, causing them to fragment and dirtying the acid bath, as well as making them much harder to remove from the bottle.

e. Procedures

1. Fill each bottle 1/3 full of DI water, loosely screw on cap, and shake vigorously. Remove cap and pour out DI water, while rinsing cap under DI faucet. Repeat 2 more times, for a total of 3 DI rinses for each bottle and cap.
2. Submerge bottles and caps in acid bath. Make sure bottles are completely full of acid, not air bubbles. Caps should be submerged so that acid fills the cap as the cap floats.

(Do not put the green Teflon lined caps in the acid bath. They are rinsed and soaked in DI water only.)

3. Bottles must be completely immersed in the acid bath for at least three hours prior to removal. Wear all protective gear available when submerging bottles, being careful not to splash or drip acid outside the acid bath. Sodium bicarbonate and water can be used to neutralize and clean up any acid spills.
 4. After pouring acid back into bath, place bottles and caps into a plastic dishpan. Again, be careful not to spill or drip acid.
 5. Rinse all outside surfaces briefly with DI water. Fill each bottle 1/3 full of DI water, loosely screw on cap, and shake vigorously. Remove cap and pour out DI water, while rinsing cap under DI faucet. Repeat 6 more times, for a total of 7 DI rinses for each bottle and cap.
 6. After seventh rinse, fill bottle with DI water and cap bottle.
 7. Store washed bottles under the lab bench in NREL A235.
 8. Check conductivity of water in the bottles before use (see page 34 for instructions on how to measure conductivity). Rewash any bottle with a conductivity value $>2 \mu\text{S cm}^{-1}$.
- f. Be aware

Protective clothing, gloves, and eyewear must be worn when working with strong acid solutions.

Bottles may soak longer than three hours, but should not remain in the acid bath for longer than three days.

Used bottles are returned to us each year from the RMRS analytical laboratory. After performing QA/QC checks on the data, these bottles may be washed and reused the next year.

The acid bath is effective for about six months depending on how heavily it is used. Replace the acid bath if there is substantial particulate material in it or if the acidity has decreased. Acid must be neutralized before disposal. Consult a lab manager for assistance neutralizing the acid, after which it can be poured down the drain.

SHIPPING SAMPLES

Surface Water Samples

a. Introduction

Deliver surface water samples weekly to the USFS Rocky Mountain Research Station water chemistry analytical laboratory for chemical analysis. When Wednesday's lab work is complete, walk the RU, FU, and DOC/TDN samples over to the USFS building and place them in the appropriate refrigerator. Contact the RMRS chemist (Tim Fegel; tfegel@fs.fed.us) for assistance if necessary.

b. Equipment and supplies

- Small plastic cooler or grocery bag

c. Estimated time to complete procedure

Allow 20 minutes for delivering samples to the RMRS laboratory.

d. Preparation

Samples must be filtered and stored in the walk-in cooler until ready for transport.

e. Procedures

1. Make sure all sample bottles are sealed tightly.
2. Place samples into cooler or bag, assuring that they will not get broken on the way.
3. Deliver samples to the USFS RMRS laboratory. You will need a USFS keycard to enter any buildings, so if you are not in direct contact with the RMRS chemist about sample delivery, go to the front desk so the receptionist can contact the chemist.

Precipitation Samples

a. Introduction

A 1-liter sample bottle is sent to the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP) for chemical analysis of the collector bucket precipitation sample. Following is a brief synopsis of procedures. Detailed instructions are given in the [NADP National Trends Network Site Operations Manual](#). The person responsible for shipping the precipitation sample should be certified as an NADP site operator.

Precipitation samples are weighed in the bucket. Subtract lid and bucket weight (written on each bucket and lid) from the total weight of lid, bucket, and sample to find the sample volume. Decant the sample from the bucket into a clean NADP 1 L HDPE Nalgene bottle and send to the NADP Central Analytical Laboratory (CAL) in Champaign, Illinois, for complete chemical analysis.

b. Equipment and supplies

- 1 L bottle for precipitation sample
- Precipitation sample in white plastic bucket with snap on lid
- Card board box for 1 L sample bottle
- Field Observer Report Form (FORF)

c. Estimated time to complete the procedure

Allow 30 minutes to process sample, fill out FORF, and ship the package.

d. Preparation

The sample, bucket, and lid must be weighed on the balance in NREL A121. All precipitation samples of any volume whatsoever must be transferred to the 1 L sample bottle. Only when the bucket is completely dry can a dry week envelope be mailed rather than a sample bottle. See the NADP field procedures for further details.

e. Procedures

1. Enter all necessary information in the Field Observer Report Form. Remove the pink copy, which is added to the NADP Field Forms notebook in NREL A225.
2. Place the white copy of the FORF in the sample box with the 1 L sample bottle. Seal the box with packing tape found in the NREL shipping center. Print a Traveler label using

the CSU iShip software (instructions below), and affix this label to the outside of the box with packing tape. Place the box in the outgoing mail by the NESB elevator.

3. Place used bucket and lid back into plastic bag, leave bag open, and let dry under the lab bench. When the bucket is dry, place it into a large supply box in A218 with other used buckets and lids. Once six used buckets and lids have accumulated, the box of used supplies should be shipped to CAL. They will automatically replace the used supplies with another box of fresh supplies.
4. To ship a box of used supplies back to CAL, fill out the supplies on hand form affixed to the inside lid of the supply box. Then seal with packing tape, print a Traveler label with the CSU iShip software (instructions below) and affix with shipping tape. Place the box in the outgoing mail near the NESB elevator.

f. iShip instructions

1. Navigate to the iShip website:
https://wsnet2.colostate.edu/cwis194/cr/shiprec_auth.aspx
2. Login with your CSU eID.
3. On the iShip homepage, click **Ship It**.
4. Verify your contact information in the **SENDER** area.
5. The NADP address should be entered in your address book. If it is, enter the nickname you gave the address in the **Nickname** box. The correctly formatted address should appear in the **RECIPIENT** area. If it is not in your address book, click **Add** to add a new address to your address book. The NADP CAL shipping address is:

NADP CENTRAL ANALYTICAL LABORATORY
2204 GRIFFITH DR
CHAMPAIGN, IL 61820-7463
(217) 244-2838

6. In the **PACKAGE INFORMATION** area, enter the weight of your package. For a 1 L sample bottle full of sample, estimate 2 lbs. For a box of used buckets and lids, estimate 15 lbs. For both, packaging is **Other Packaging**, and type is **Rectangular**. For the 1 L sample bottle box, length x width x height is 10 x 4 x 4 inches. For the box of used buckets and lids, it is 32 x 16 x 16 inches. Enter nothing in the **Package Reference 1 and 2 boxes**.
7. In the **SHIPMENT REFERENCE INFORMATION** area, enter the current account number for the LVWS project (as of February 2017 this is 5300466). Enter your name in

the **Shipper Name** box. Enter **water sample or used supplies** in the **Description of Goods** box.

8. Accept the defaults in all other areas, unless you need to change the shipping date.
9. Click **Get Rates** at the bottom of the form.
10. The default shipping method on iShip is UPS Ground. Make sure this is the highlighted box in the **RATES, SERVICES, & DELIVERY TIMES** area. It will have a green exclamation point next to the highlighted price.
11. Verify everything is correct in the **YOUR SHIPMENT SUMMARY** and **SHIPMENT CHARGES** areas.
12. Click **Get Label** at the bottom of the page. Ensure your browser allows pop-ups for the iShip webpage.
13. The pop-up window that appears will be your shipping label. Print this label, cut off the label below the dotted line, and affix the label with barcode to the outside of your box.

Total Phosphorus Samples

Total phosphorus samples are shipped to Collin Strasenburgh at the High Sierra Water Lab in Tahoe City, California, for analysis. As these samples are frozen upon return from the field, you can wait until there are 50 or so samples in the freezer before packaging and shipping them. These samples should be packed securely in a Styrofoam or plastic cooler with plenty of ice packs so they will stay frozen. Seal the cooler with shipping tape.

These samples should be shipped FedEx Priority Overnight, as UPS delivery is not as reliable for this location. FedEx is not approved for shipping through the CSU iShip software. To ship FedEx from CSU, navigate to <https://secure.jotformpro.com/form/41406982781966> and fill out the **Manual FedEx Shipment Request** form. Though this form is relatively straightforward, there are a few items to watch out for:

1. Do not bill the recipient's FedEx account number.
2. Send the package to:
Collin Strasenburgh
High Sierra Water Lab
3090 North Lake Blvd Unit 3
Tahoe City, CA 96145
3. Do not include dry ice, just regular refreezeable ice packs.
4. There is no reference number on the package.
5. Describe goods as "lake water samples for analysis".
6. Value of items is zero; do not insure for value.
7. Send package **No Signature Required**, and by **FedEx Priority Overnight**.
8. Describe the reason this package cannot be shipped via UPS using iShip as "The receiving company says that UPS is very unreliable in their area, and these are time and temperature sensitive water samples."

Once this form is submitted, a barcoded sheet will appear. Print this barcoded sheet, attach to the package with shipping tape, and carry the package to the Shipping and Receiving desk to allow them to make sure it is ready to ship.

High Sierra Water Lab will analyze the samples and email the results after analyses are complete.

REFERENCES

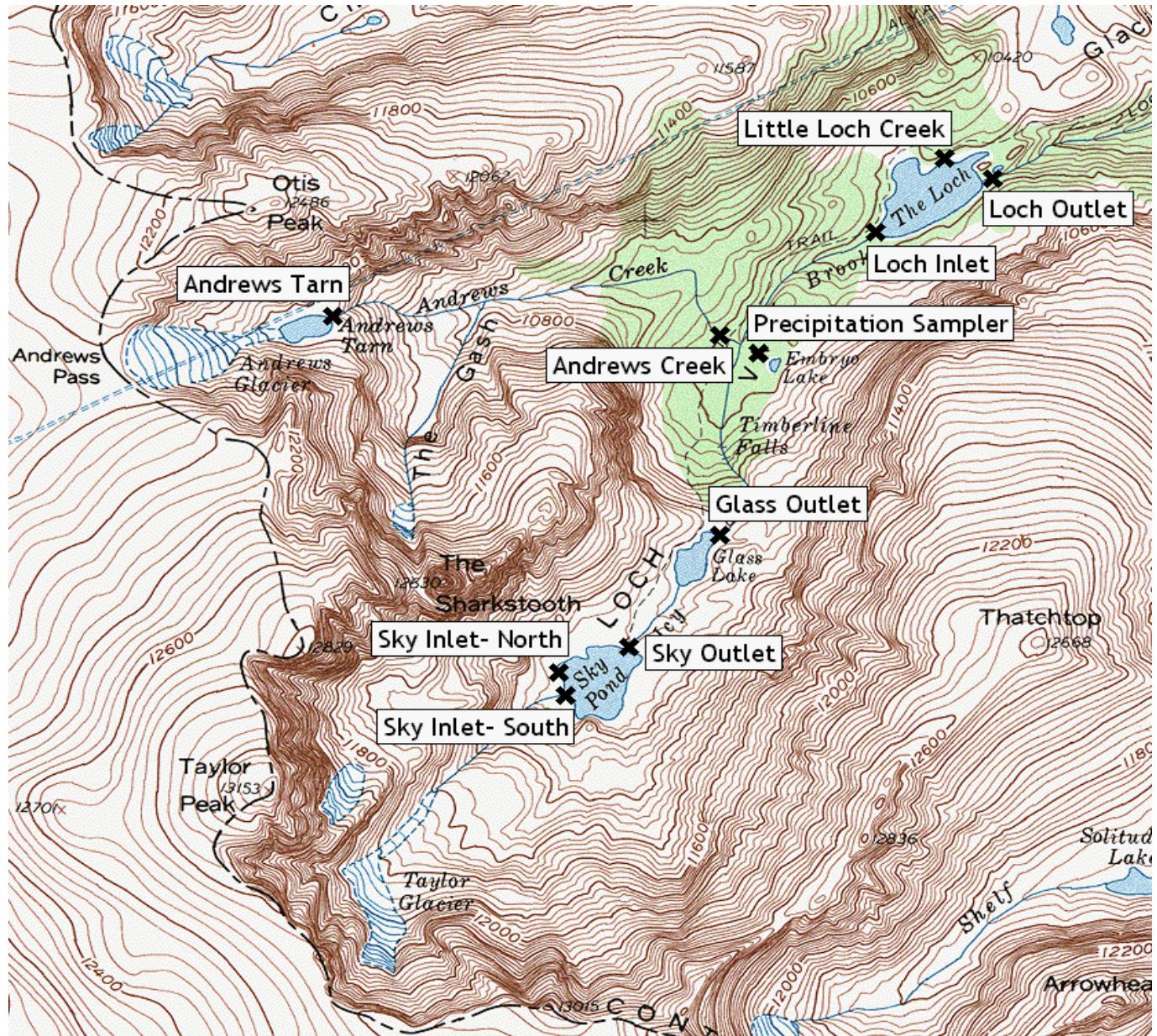
- Allstott, E.J., M.A. Bashkin, and J. Baron. 1999. Loch Vale watershed project quality assurance report: 1995-1998. U.S. Geological Survey, Open File Report 99-111, 23 p.
- Botte, J.A. and J. Baron. 2003. Loch Vale watershed project methods manual, 2003. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, 80 p.
- Botte, J.A. and J. Baron. 2004. Quality assurance report – Loch Vale watershed: 1999-2002. U.S. Geological Survey, Biological Resources Discipline, Open File Report 2004-1306, 17 p.
- Clesceri, L.S., A.E. Greenberg, and A.D. Eaton, eds. 1998. Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, Washington, D.C., 1,325 p.
- Denning, A.S. 1987. Quality assurance report: 1982-1987, Loch Vale watershed project. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, 19 p.
- Edwards, R.L. 1991. Quality assurance report, Loch Vale Watershed Study, 1989-1990. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, 22 p.
- ETI Instrument Systems. 2006. [NOAH IV Total Precipitation Gage Technical Manual](#). Fort Collins, Colorado. 23 p.
- National Atmospheric Deposition Program. 2015. [NADP National Trends Network Site Operations Manual](#), version 2.3. Champaign, Illinois, 19 p.
- Newkirk, B.K. 1995. Loch Vale watershed methods manual, 1995. Natural Resource Ecology Laboratory. Colorado State University, Fort Collins, Colorado, 124 p.
- Richer, E.E. and J.S. Baron. 2011. Loch Vale Watershed Long-term Ecological Research and Monitoring Program: Quality Assurance Report, 2003-09. U.S. Geological Survey, Open-File Report 2011-1137, 22 p.
- Thermo Fisher Scientific. 2007. Spectronic 20+ and Spectronic 20D+ User Guide. Thermo Fisher Scientific Inc., Madison, WI 53711.
- U.S. Environmental Protection Agency. 1987. Handbook of methods for acid deposition studies: Laboratory analysis for surface water chemistry. U.S. Environmental Protection Agency, Acid Deposition and Atmospheric Research Division, Office of Research and Development, Washington, D.C., EPA600/4-87/026, 376 p.

Wetherbee, G.A. 2016. Evaluation of National Atmospheric Deposition Program measurements for colocated sites CO89 and CO98 at Rocky Mountain National Park, water years 2010–14. USGS Scientific Investigations Report SIR 2016-5051.

APPENDICES

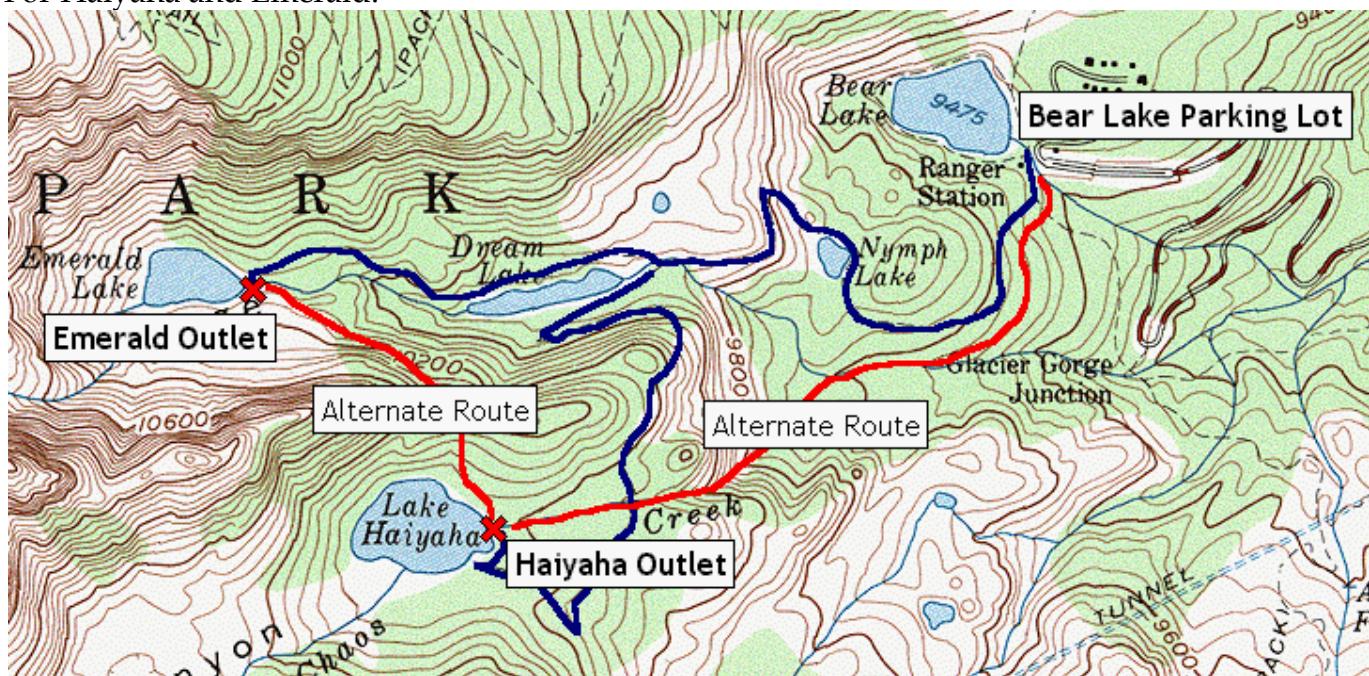
Appendix A: Sampling Locations and Trails

For LVWS:



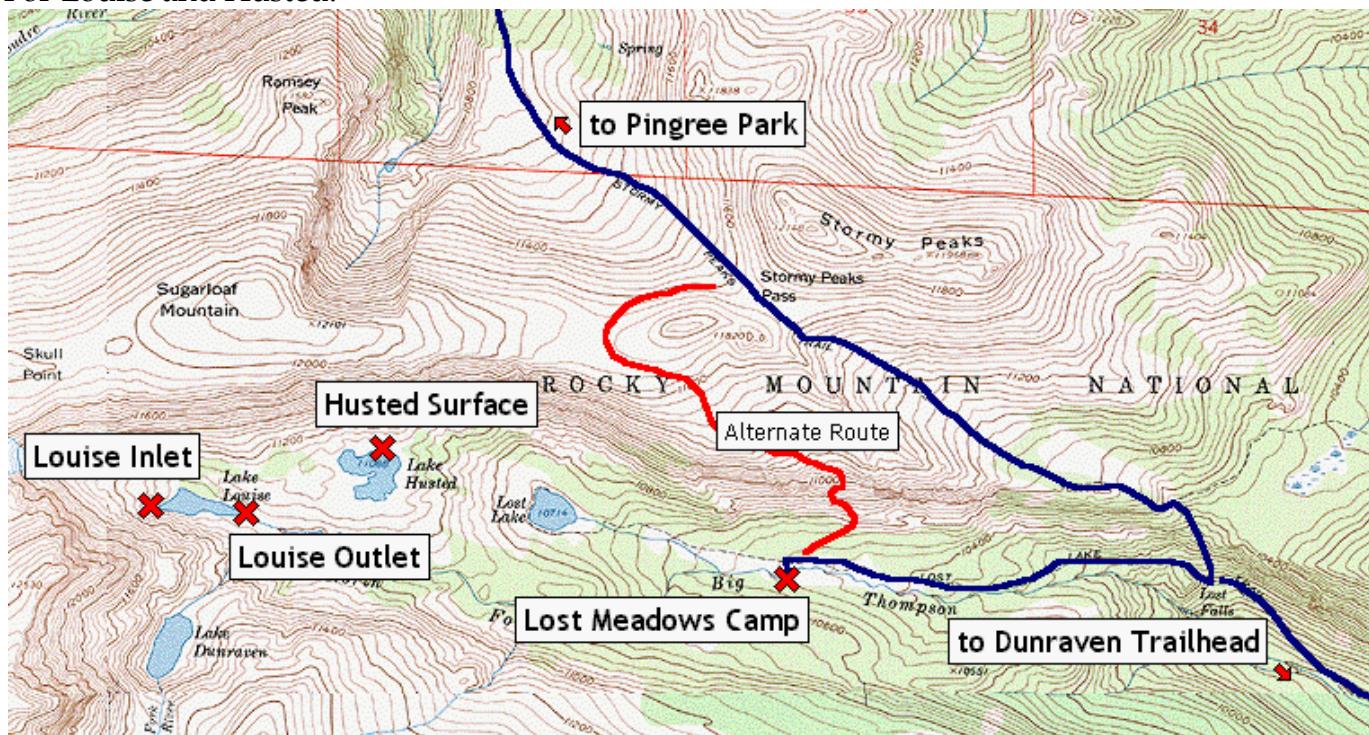
Nearly all sample points are on or near the trail. Consult with supervisor for exact locations.

For Haiyaha and Emerald:

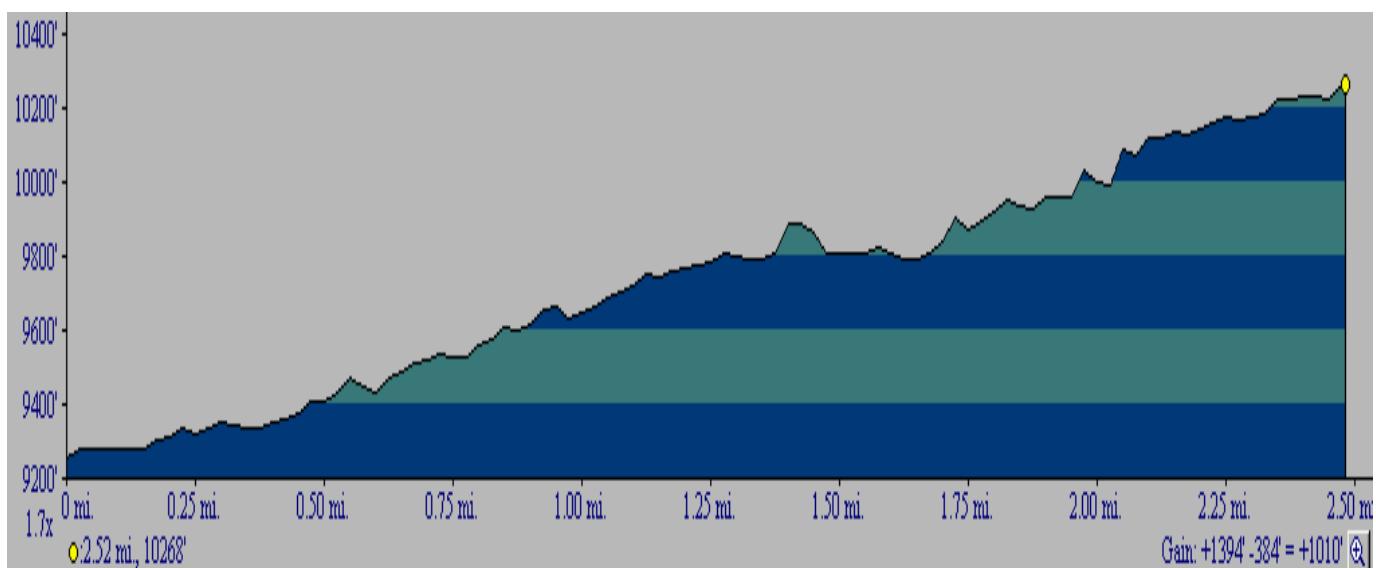
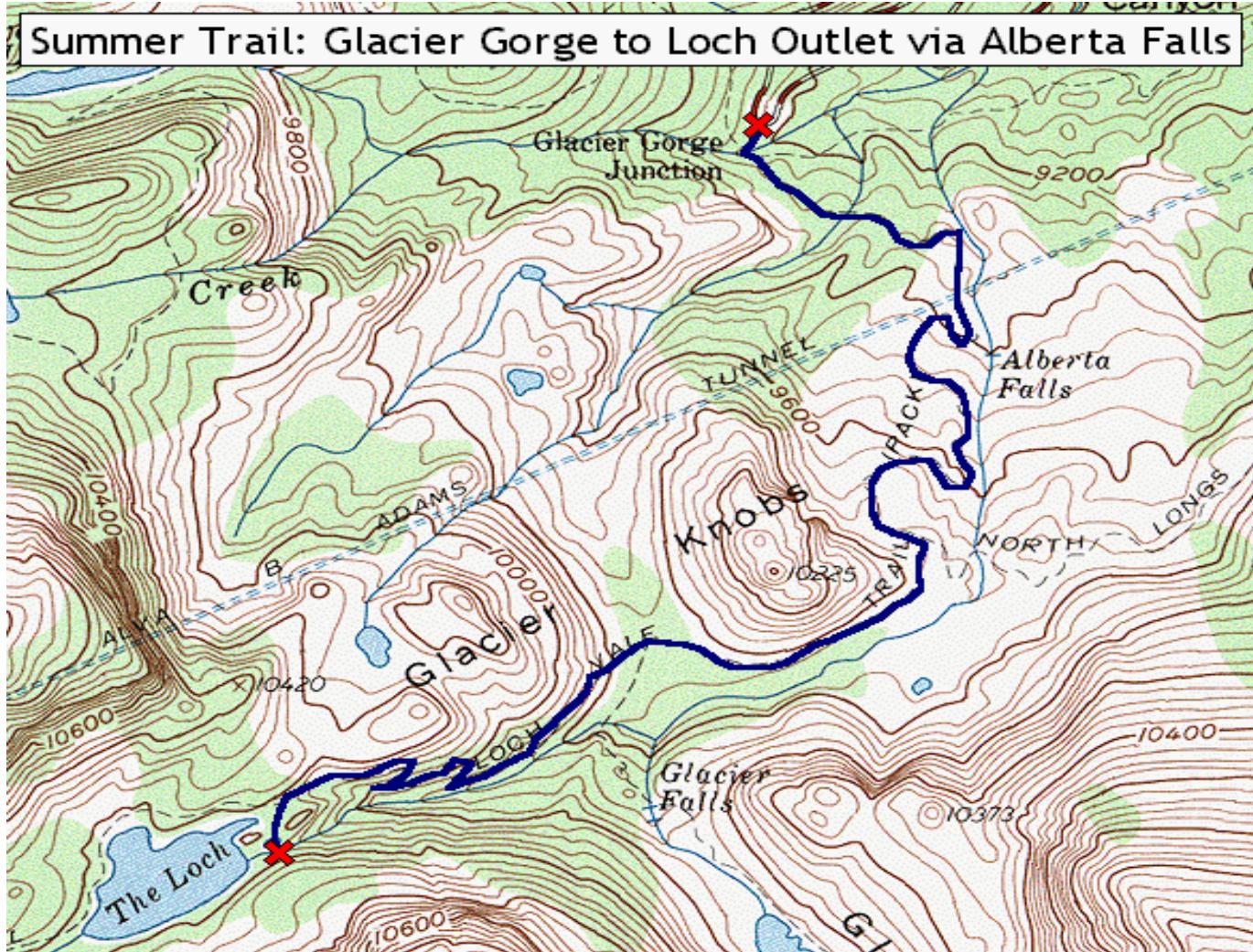


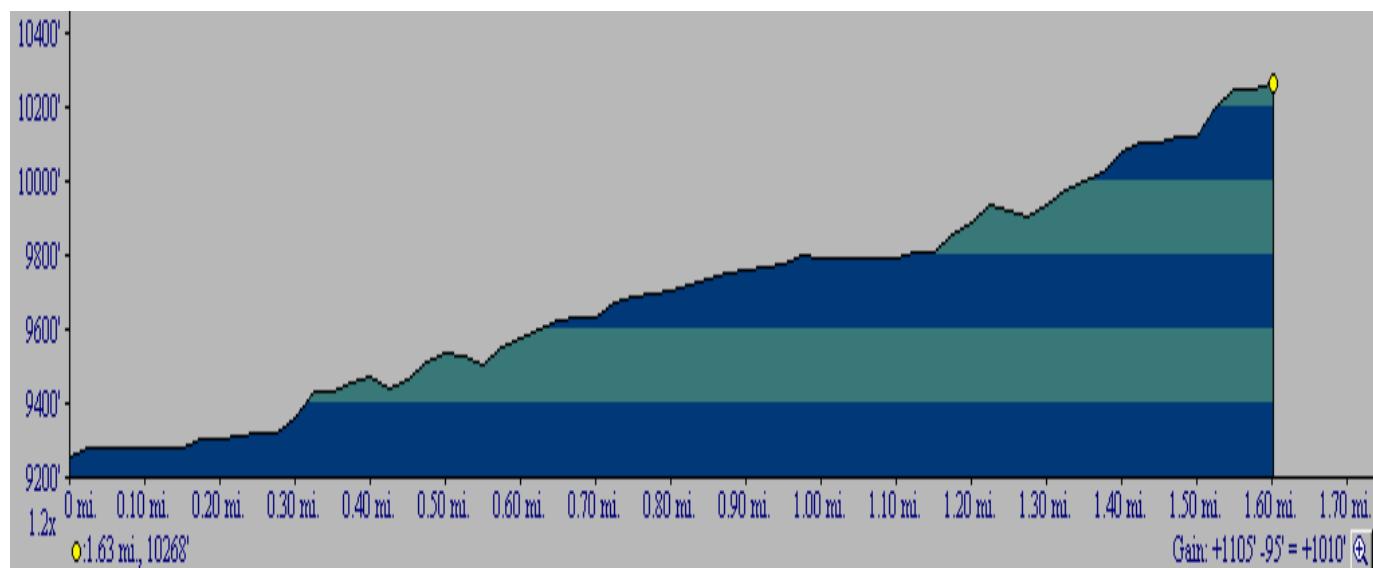
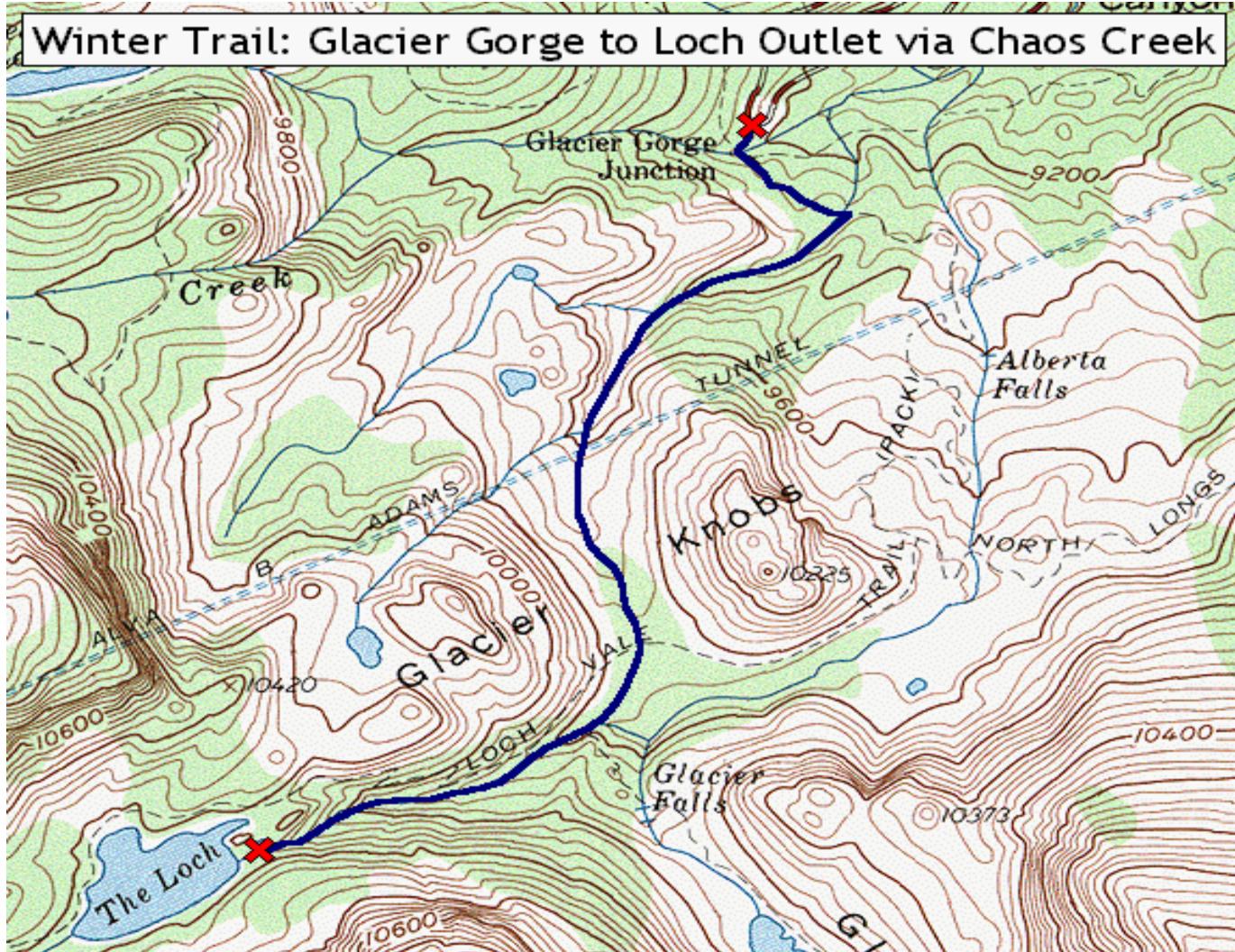
Alternate routes are off trail, and are very rugged. Travel with caution.

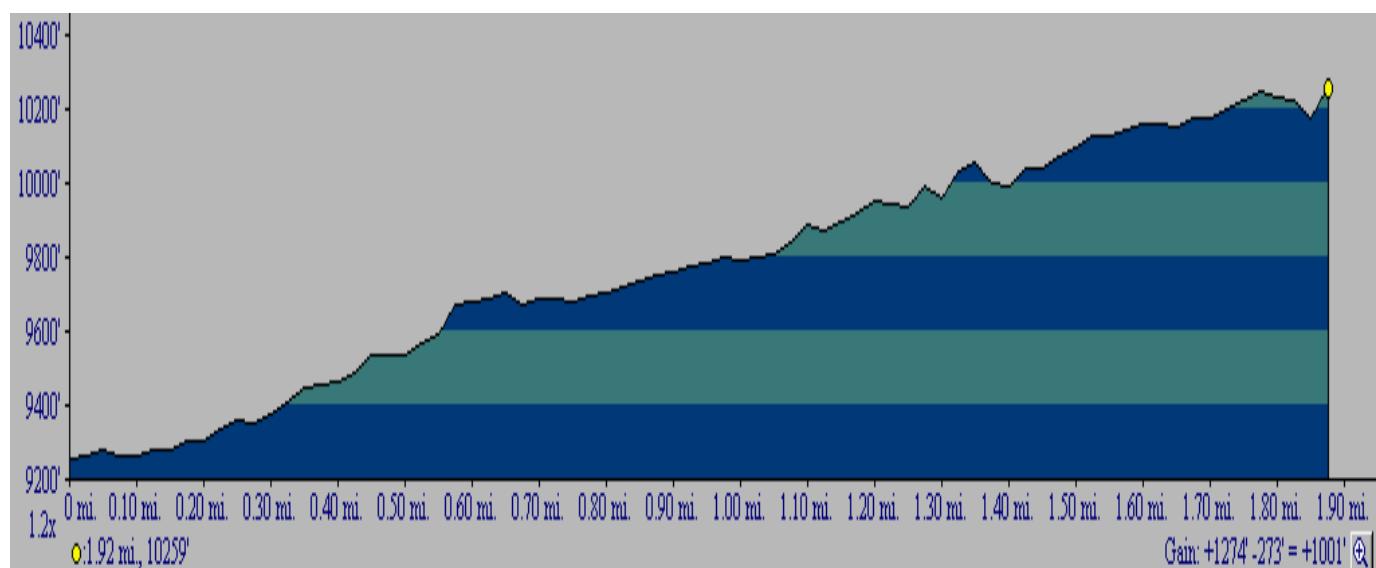
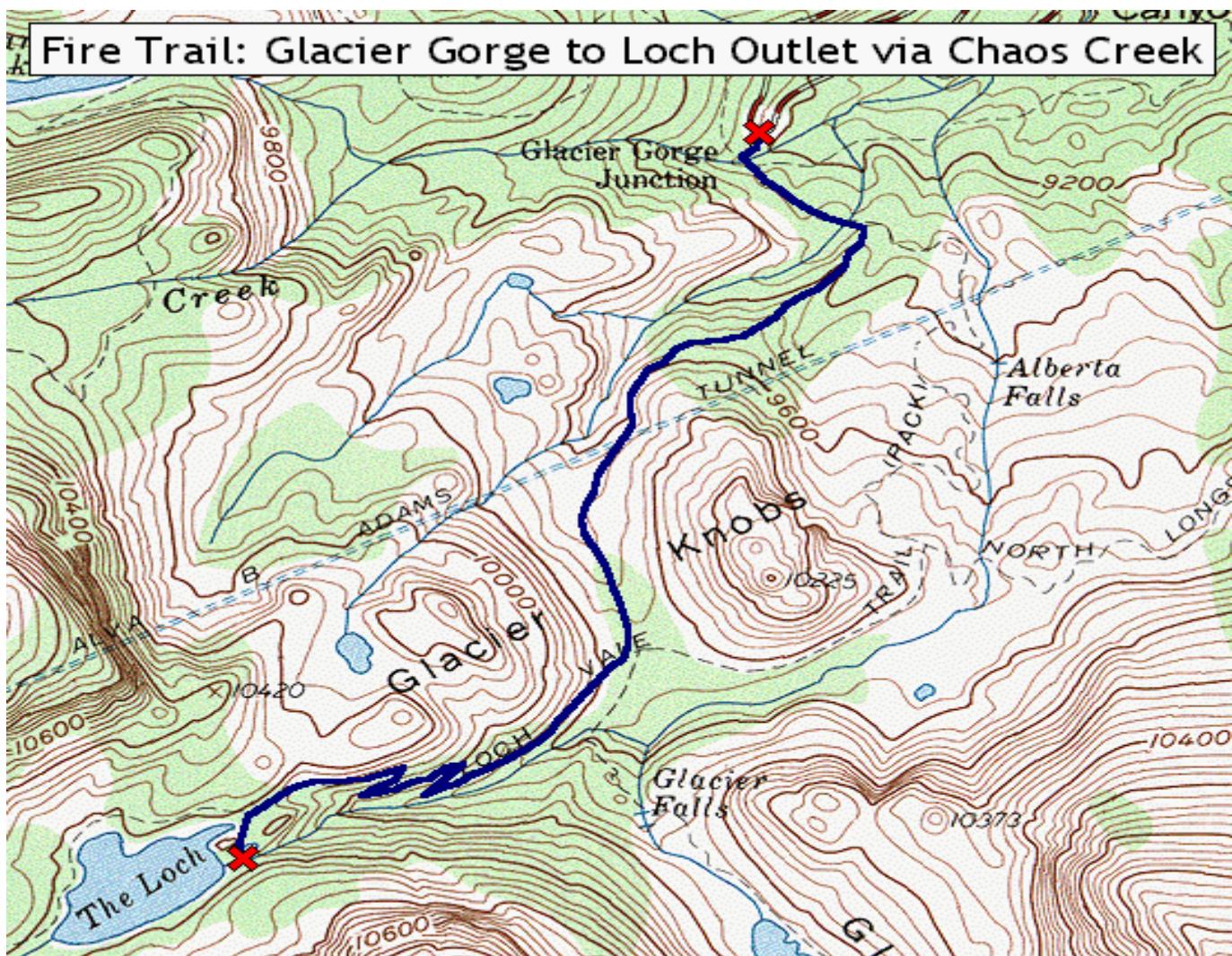
For Louise and Husted:



Alternate route involves a very steep descent into the Lost Meadow Basin. Travel with caution.







Appendix B: Sampling Schedule

Table B1. LVWS surface water sampling schedule for active sites.

Name	Sampling Frequency	Analyses
Andrews Creek	1/month, summer	RU, FU, DOC/TDN, SiO ₂ , TP
Emerald Outlet	1/year, fall	RU, FU, DOC/TDN, SiO ₂ , TP
Haiyaha Outlet	1/year, fall	RU, FU, DOC/TDN, SiO ₂ , TP
Husted Surface	1/year, fall	RU, FU, DOC/TDN, SiO ₂ , TP
Loch Outlet	1/week, year round	RU, FU, DOC/TDN, SiO ₂ , TP, Archive*
Loch Surface	1/month, year round	Chlorophyll <i>a</i>
Loch Hypolimnion	1/month, winter	Chlorophyll <i>a</i>
Loch Inlet	1/month, summer	RU, FU, DOC/TDN, SiO ₂ , TP
Louise Inlet	1/year, fall	RU, FU, DOC/TDN, SiO ₂ , TP
Louise Outlet	1/year, fall	RU, FU, DOC/TDN, SiO ₂ , TP
Sky Outlet	1/month, summer	RU, FU, DOC/TDN, SiO ₂ , TP, Chlorophyll <i>a</i> , Archive*
Sky Inlet South	1/month, summer	RU, FU, DOC/TDN, SiO ₂ , TP, Archive*
Sky Hypolimnion	1/year, summer	RU, FU, DOC/TDN, SiO ₂ , TP, Archive*
Sky Surface	1/year, summer	RU, FU, DOC/TDN, SiO ₂ , TP, Archive*

*Archive samples are collected once a month from the Loch Outlet. Archive samples are collected in mid-August (peak chlorophyll) for Sky Pond surface and hypolimnion, and in early September (base flow) for Sky Inlet South and Sky Outlet. Archive samples are filtered with the peristaltic pump into brown 250 ml HDPE bottles and stored in the NREL freezer. The frozen archive samples are transferred from the NREL freezer to the LVWS chest freezer at the USGS Fort Collins Science Center (FORT) laboratory once a year, or as needed.

Synoptic sampling occurs once a month during the summer, starting in June and ending in September. Synoptic sampling entails collecting surface water samples at Sky Inlet South, Sky Outlet, Andrews Creek, and Loch Inlet, in addition to the regular weekly sampling at the Loch Outlet. This is normally done on the same day, starting at the top of the watershed and proceeding downstream.

A sampling schedule should be prepared by the program manager at the beginning of each calendar year. Ten percent of the total number of samples collected must be quality assurance samples (DI field blanks or field duplicate samples). 80-90 samples (normal, blank, and duplicate) are collected yearly. To obtain 10% quality assurance, a blank or duplicate sample should be collected from the Loch Outlet every other month, alternating between field blanks and field duplicates. Quality assurance samples should be taken at other synoptic and outside watershed sites as well. Details of taking and processing archive samples are found in Appendix C.

Table B2. Historical LVWS sampling sites that are no longer actively sampled, or no longer sampled at the same frequency.

Name	Sampling Frequency	Analyses
Andrews Tarn	1/year, summer	RU, FU, DOC
Andrews Tarn Inlet	1/year, summer	RU, FU, DOC
Emerald Inlet	Variable, summer	RU, FU, DOC
Emerald Hypolimnion	Variable, summer	RU, FU, DOC
Emerald Metalimnion	Variable, summer	RU, FU, DOC
Emerald Surface	Variable, summer	RU, FU, DOC
Glass Inlet	Variable, summer	RU, FU, DOC
Glass Hypolimnion	Variable, summer	RU, FU, DOC
Glass Metalimnion	Variable, summer	RU, FU, DOC
Glass Surface	Variable, summer	RU, FU, DOC
Glass Outlet	1/month, summer	RU, FU, DOC, DOP, DON
Haiyaha Hypolimnion	Variable, summer	RU, FU, DOC
Haiyaha Metalimnion	Variable, summer	RU, FU, DOC
Haiyaha Surface	Variable, summer	RU, FU, DOC
Husted Inlet	Variable, summer	RU, FU, DOC
Husted Hypolimnion	Variable, summer	RU, FU, DOC
Husted Metalimnion	Variable, summer	RU, FU, DOC
Husted Surface	Variable, summer	RU, FU, DOC
Husted Outlet	Variable, summer	RU, FU, DOC
Little Loch Creek	1/month, summer	RU, FU, DOC, DOP, DON
Loch Hypolimnion	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto
Loch Metalimnion	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto
Loch Surface	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto
Louise Hypolimnion	Variable, summer	RU, FU, DOC
Louise Metalimnion	Variable, summer	RU, FU, DOC
Louise Surface	Variable, summer	RU, FU, DOC
Sky Inlet North	1/month, summer	RU, FU, DOC, DOP, DON
Sky Hypolimnion	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto
Sky Metalimnion	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto
Sky Surface	Bi-monthly, winter	RU, FU, DOC, DOP, DON, Phyto

Appendix C: Quality Assurance/Quality Control Samples

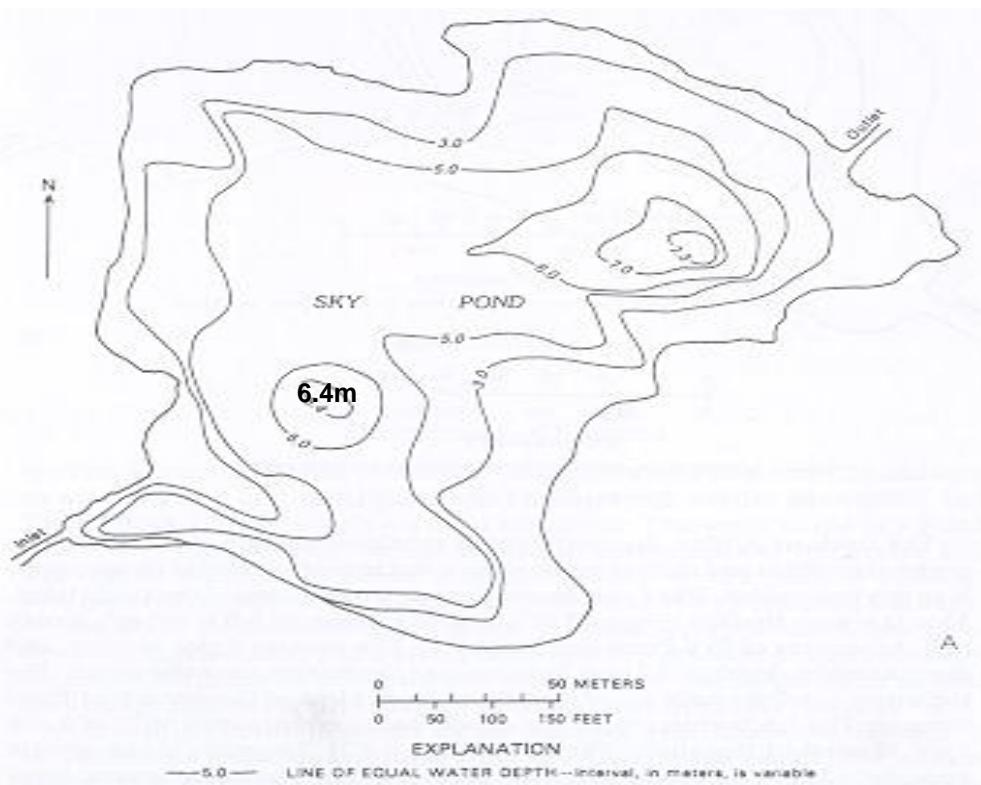
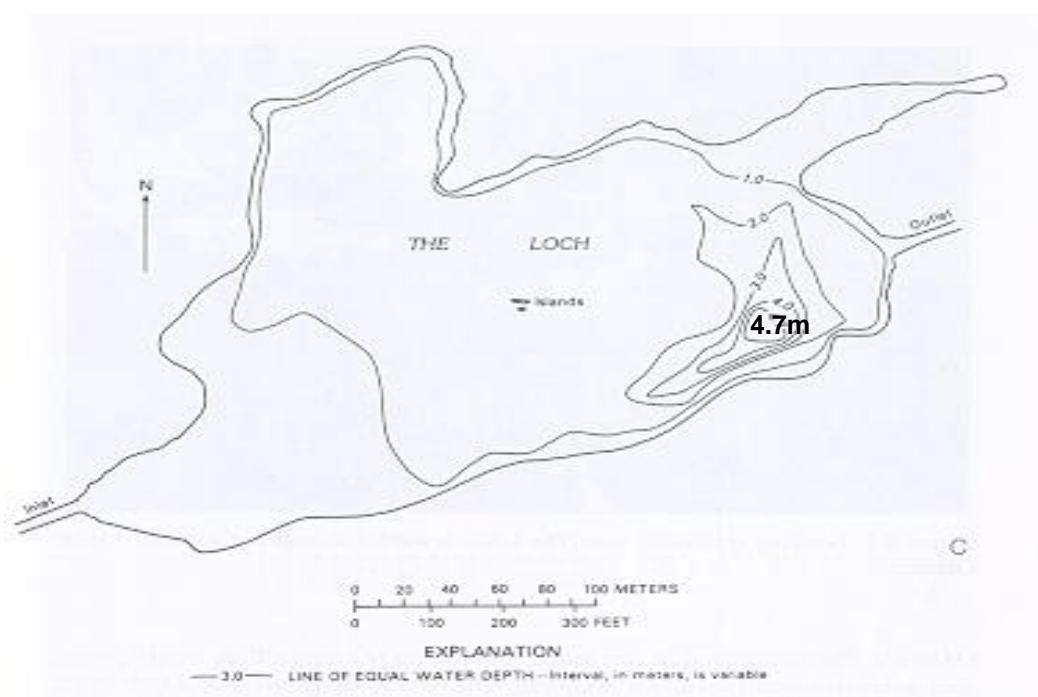
Field blank samples

1. When taking a blank sample, a normal sample is taken at the same time. Prepare two bottle sets for the sampling site in the lab. Label one bottle set "NORM" and the other "BLANK."
2. On the day of sampling, fill two 1 L acid washed plastic bottles with conductivity tested DI water from the lab. Conductivity of this water must be $<2 \mu\text{S cm}^{-1}$. Notify the lab manager if the conductivity is $>2 \mu\text{S cm}^{-1}$, and postpone the blank sample.
3. After taking the normal Loch Outlet sample, triple rinse and fill each bottle in the field blank bottle set from the DI water bottles using the same methods as described in the Surface Water Sampling section of this manual, except pouring DI into the field blank sample bottles instead of filling them from the stream.
4. Process the field blank sample just as you would a normal sample. Make sure the correct sample type label is transferred to bottles that receive the filtered samples.

Field duplicate samples

1. A duplicate sample is just that - a duplicate of a normal sample from the particular sampling site. A normal sample is taken at the same time. Prepare two bottle sets for the sampling site in the lab. Label one bottle set "NORM" and the other "DUPE."
2. Take two sets of samples according to the methods detailed in the Surface Water Sampling section of this manual. Fill both sets of bottles from the same sampling location, one right after the other.
3. Process the field duplicate sample just as you would a normal sample. Make sure the correct sample type label is transferred to bottles that receive the filtered samples.

Appendix D: Lake Bathymetry



Appendix E: Recipes

Current recipes

Acid Baths: To make a new acid bath, add one part concentrated 37% HCl to nine parts DI water under a fume hood. Make sure you use safe procedures for working with strong acids. Always add acid to water, NOT water to acid. This is most easily done by measuring 3600 ml of DI water in a graduated cylinder, pouring this into a mixing bucket under a fume hood, then measuring 400 ml of 37% HCl in another graduated cylinder, and carefully pouring this acid into the mixing bucket with the DI water, again under a fume hood. The mixture can then be poured into the acid bath container. Depending on the size of the container available for the acid bath, this procedure may have to be done several times to make a sufficient amount of acid bath.

Lugol's Fixative Solution: Dissolve 10 g I₂ (pure iodine; *caution:* toxic) and 20 g KI in 200 ml distilled water and 20 ml concentrated glacial acetic acid. Store in amber borosilicate bottle. Transport to field in 20 ml plastic vial.

Historical recipes, no longer used

NADP Quality Control Check Sample (QC): pH = 4.9 ± 0.15; conductivity = 14 ± 2 µS cm⁻¹. To make this quality control check sample, get 0.5 liters of DI water stirring in a 1 L volumetric flask on a stir plate. Slowly add 4.00 g NaCl and 0.78 ml HNO₃. Bring volume up to 1 liter. Dilute 1 ml of this solution to 1 liter. Freeze remainder of original liter for later use. This standard does not need to be refrigerated, but it should be stored in a dark cupboard and shaken before use.

NADP Specific Conductance Standard (SCS): pH = 5.62 ± 0.20; conductivity = 74 ± 1 µS cm⁻¹. To make this conductivity standard, first dry ~100 g of KCl crystals at 105°C for >5 hours. Then dissolve 93.2 g of the dried KCl in a 1 L volumetric flask to create a 1.25 M KCl stock solution. Dilute 0.40 ml of this stock solution to 1 L to make the 5.0 × 10⁻⁴ M KCL SCS.

Alpkem Reagents:

Prepare all recipes in their written order.

When filtering is necessary, use 8.0 µm membrane filters located in NREL A256.

For NH₄ Channel

Manifold Startup Solution

Add 0.5 ml BRIJ or other surfactant to 1 L DI

NH₄ Buffer

12 g NaOH

29 g Na Citrate
50 g disodium EDTA
Bring up to 1000 ml with DI water
Filter through 8.0 μ m polycarbonate membrane
Add ~6 drops Dowfax to actual dispensing container

Salicylate

0.6 g Na Nitroferricyanide
300 g Na Salicylate
Bring up to 1000 ml with DI water
Filter through 8.0 μ m polycarbonate membrane
Store in refrigerator in dark glass bottle

Hypochlorite

24 ml bleach
Bring up to 400 ml with DI water
Be sure to use fresh bleach (opened within the week)

For NO₃ Channel

NO₃ Color Reagent
100 ml H₃PO₄
40 g sulfanilamide
2 g N-1-Naphthylethylenediamine
Add to 800 ml DI water
Bring up to 1000 ml with DI water
Filter through 8.0 μ m polycarbonate membrane
Store in refrigerator in dark glass bottle

NO₃ Buffer

638 g NH₄Cl
0.75 g disodium EDTA
Bring up to 7.5 liters with DI water
Filtered inline from dispensing bottle

NH₄/NO₃ Standards

Use the formula C₁V₁=C₂V₂ to make ammonium/nitrate working standards from a 1000 mg/L stock solution

For Orthophosphate Analysis

Stock Sulfuric Acid 5N
140 ml concentrated H₂SO₄

Slowly added to ~800 ml of DI water in a cool water bath
Bring up to 1000 ml with DI water

Stock Antimony Potassium Tartrate Solution

3 g Antimony Potassium Tartrate
Dissolve into ~500 ml DI water
Bring up to 1000 ml with DI water
Store at 4°C in a dark glass bottle

Stock Ammonium Molybdate Solution

40g Ammonium Molybdate
Dissolve in ~800 ml DI water
Bring up to 1000 ml with DI water
Store at 4°C in polyethylene bottle

Stock Ascorbic Acid Solution

1.8 g Ascorbic Acid
Dissolve into ~70 ml DI water
Bring up to 100 ml with DI water
Stable for 1 week at 4°C

PO₄ Color Reagent

100 ml Stock Sulfuric Acid (5N)
10 ml Stock Antimony Potassium Tartrate Solution
30 ml Stock Ammonium Molybdate Solution
60 ml Stock Ascorbic Acid Solution
Add reagents in order
Filter through 8.0 µm polycarbonate membrane
Prepare daily

Stock 1000 mg/L P (1 L)

4.393 g Potassium DI-hydrogen Phosphate (KH₂PO₄)
Dissolve into ~900 ml DI water
Bring up to 1000 ml with DI water

Intermediate Calibrant 100 mg/L P (100 ml)

Using a volumetric pipette, add 10 ml Stock to ~80 ml DI
Bring up to 100 ml with DI water

Working Calibrants (100 ml)

Use C₁V₁=C₂V₂ to measure out desired range of standards
Bring up to 100 ml with DI water

For TP analysis:

Potassium Persulfate (Oxidizing Solution).

Dissolve 5g K₂S₂O₈ into ~90 ml DI water using stir bar and low heat
Bring up to 100 ml with DI water

Stock Sulfuric Acid 5N

140 ml concentrated H₂SO₄
Slowly added to ~800 ml of DI water in a cool water bath
Bring up to 1000 ml with DI water

Stock Antimony Potassium Tartrate Solution

3 g Antimony Potassium Tartrate
Dissolve into ~500 ml DI water
Bring up to 1000 ml with DI water
Store at 4°C in a dark glass bottle

Stock Ammonium Molybdate Solution

40 g Ammonium Molybdate
Dissolve in ~800 ml DI water
Bring up to 1000 ml with DI water
Store at 4°C in polyethylene bottle

Stock Ascorbic Acid Solution

1.8 g Ascorbic Acid
Dissolve into ~70 ml DI water
Bring up to 100 ml with DI water
Stable for 1 week at 4°C

PO₄ Color Reagent

100 ml Stock Sulfuric Acid (5N)
10 ml Stock Antimony Potassium Tartrate Solution
30 ml Stock Ammonium Molybdate Solution
60 ml Stock Ascorbic Acid Solution
Add reagents in order
Filter through 8.0 µm polycarbonate membrane
Prepare daily

Stock 1000 mg/L P (1 L)

4.393 g Potassium DI-hydrogen Phosphate (KH₂PO₄)
Dissolve into ~900 ml DI water
Bring up to 1000 ml with DI water

Intermediate Calibrant 100 mg/L P (100 ml)

Using a volumetric pipette, add 10 ml Stock to ~80 ml DI

Bring up to 100 ml with DI water

Working Calibrants (100-ml)

Use $C_1V_1=C_2V_2$ to measure out desired range of standards

Bring up to 100-ml with DI water

Appendix F: Supplies

Order new supplies from the VWR or Fisher Scientific catalogs via the CSU Kuali Financial System website. Purchases made through Kuali do not require a purchase request form. However, all Kuali purchases must have a justification, and use a valid account number. To make a purchase via Kuali, go to the CSU Administrative Applications and Resources webpage (<https://cap.is.colostate.edu/>), and click on **Kuali Financial System**. Choose your campus and login with your CSU eID. Under **Purchasing/Accounts Payable**, choose **Shop Catalogs**. Add the needed items to your cart, proceed to checkout, and submit the cart to Kuali. Enter the justification for the purchase at the top of the form, and use the current LVWS purchasing account number in the accounting area. Enter "6201" as the object type for general supplies. A separate Kuali purchase should be completed for each vendor (i.e., one order for VWR, and another for Fisher Scientific). See the NREL business office for further training on how to use Kuali.

For all other purchases, you must fill out a purchase request form on the Warner College of Natural Resources website. Log in to the WCNR intranet with your CSU eID (<https://taurus.cnr.colostate.edu/logon/webauth.cfm>), and select **Business Office**. Click on **Purchasing**, and start a new purchase request. Fill out the form completely and submit. Once submitted, you will receive an email that the request is pending, then another email when the request is approved. At that point you are able to make the purchase. Turn in all receipts to the NREL business office. See the NREL business office for questions about purchasing.

Supplies can also be obtained from the CSU Chemistry Stockroom (<http://sites.chem.colostate.edu/stockroom/>) in the Chemistry building on campus. Purchases from the Chemistry Stockroom do not require a purchase request form, but do require a stockroom purchase card. The LVWS program manager has a stockroom purchase card, and is able to make purchases for other LVWS personnel.

Any purchase over \$500 requires approval from the Principal Investigator. All purchases require a justification statement. Some frequently ordered supplies are listed on the next page.

VWR

- 60 ml translucent round HDPE bottles (414004-155, case of 72)
- 250 ml brown square HDPE bottles (16186-270, case of 72)
- 125 ml amber borosilicate glass round bottles with green Teflon lined caps (16153-135, case of 24)
- GF/F glass fiber filters (28497-958, pack of 100)
- 60 ml square wide mouth glass bottles, for sample grinding (16188-720, case of 48)
- Silica high range reagent set for 10 ml sample size (97009-930, pack of 100 each)

Fisher Scientific

- Millipore Isopore 0.4 μm 47 mm membrane filters (HTTP04700, pack of 100)
- 10 $\mu\text{S cm}^{-1}$ conductivity standard (223616, 500 ml bottle)
- 100 $\mu\text{S cm}^{-1}$ conductivity standard (223716, 500 ml bottle)
- Silica standard solution 10 mg/L (674032, one liter bottle)
- Millipore PetriSlide containers (PD1504700, pack of 100)

Appendix G: Radio Channels in Rocky Mountain National Park

List of channels available on LVWS Bendix/King Radios.

Channel	Area	Action	Use
E1 PROSP	East side	Radio to Prospect Mt. Repeater	East Side Command System
E2 TWIN	East side	Radio to Twin Sisters repeater	East Side Command System
E3 ALPINE	East Side	Radio to AVC repeater	East Side Command System
E4 MEADOW	East Side	Radio to Meadow Mt. repeater	East Side Command System
W5 Red	West side	Radio to Red Mt. repeater	West Side Command System
W6 SHADOW	West side	Radio to Shadow Mt. repeater	West Side Command System
W7 HAGUES	West side	Radio to Hague Peak Repeater	West Side Command System
M8 DIRECT	East & West	Radio to Radio Direct	Facility Management 1-5 Miles
M9 MTWIN	East Side	Radio to Twin Sisters Repeater	Facility Management Long Distance Communications
R10 DIRECT	East & West	Radio to Radio Direct	Resource 1-5 Miles
R11 TWIN	East Side	Radio to Twin Sisters Repeater	Resource Long Distance Communications
NOAA	East & West	Weather Channel	Weather Channel
V13 WORK	East & West	Radio to Radio Direct	ROMO Work Channel Volunteers Only 1-5 Miles
CH14 MRA	East & West	Radio to Radio Direct	Mountain Rescues
CH15 A/G	East & West	Radio to Aircraft Direct	Aviation Ops in ROMO ONLY
G16 DIRECT	East & West	Radio to Radio Direct	Admin and LE use

Transmit only as necessary on all channels except for #13 (Work). Channel 13 is open to work related conversation. Although you may talk freely on this channel, please keep conversation brief and concise.

Emergency radio transmissions should go out to channel 1 first. Protocols are described in the Radio Protocol section. If you cannot get a response on channel 1, try channel 2, and then either channel 9 or 10.

Appendix H: Database Management

1. All LVWS databases should be updated annually. Ensure that all new data have passed QA/QC procedures prior to adding data to the LVWS master databases. See LVWS quality assurance reports for QA/QC methodology (Denning 1988, Edwards 1991, Allstott 1995, Allstott et al. 1999, Botte and Baron 2004, Richer and Baron 2011).
2. For new surface water chemistry data: arrange quality assured data from the RMRS laboratory so that the fields are consistent with the LVWS surface water chemistry master database. Ensure that all data fields are in the correct order and in the correct units, and that all site names are consistent with those in the master database. Copy and paste the new data into the master database. Be sure all values that are below published detection limits are stored appropriately in each column (i.e., if the detection limit is 0.02 mg/L, all values less than 0.02 should be stored as "<0.02"). Values of zero should not be entered into the database. All missing data should be left blank. Sample times, along with field temperature and conductivity readings, should be obtained from the field books and entered into the database as well. Update the surface water chemistry database on the NREL N drive (N:\Research\Baron\LVWS_master\data), as well as on the LVWS website. Once complete, format the data according to USGS National Water Information System (NWIS) standards, and email it to Alisa Mast at the USGS Lakewood office (mamast@usgs.gov).
3. New precipitation data should be obtained from the National Atmospheric Deposition Program website, and added to the LVWS temperature and precipitation master database (N:\Research\Baron\LVWS_master\data). Update this information on the LVWS website as well.
4. New temperature data should be obtained from the Water, Energy, and Biogeochemical Budgets program, and added to the LVWS temperature and precipitation master database (N:\Research\Baron\LVWS_master\data). Update this information on the LVWS website as well.
5. Be sure to plot all new data to ensure units and formatting are correct, and note all data that are preliminary and subject to change.

Appendix I: Historical Field and Laboratory Procedures

These procedures are no longer used to collect and analyze samples from the LVWS, but are provided as a reference for past methods.

Belfort Raingage (*Discontinued in August 2010*)

a. Introduction

An Alter-shielded Belfort raingage was used in LVWS to measure precipitation amount from August 1983 to August 2010. The Belfort recorded cumulative precipitation depth, as well as frequency and length of precipitation events. The Belfort was initially installed in 1983, and removed on August 16, 2010. The CO98 Belfort and CO98 NOAH IV provide a continuous precipitation record for the Loch Vale NADP site.

Detailed sampling and maintenance procedures for the gages are provided in the NADP/NTN Site Operation Manual (Dosset and Bowersox 1999) and in the Belfort Equipment Manual. Both manuals can be found in NREL A225.

b. Equipment and Supplies

- Raingage charts, cylinders, cylinder clips, rubber bands, dashpot oil, D-cell batteries, and pencils are kept in the NREL lab and/or inside shell of Belfort.
- Antifreeze and transmission fluid are kept in the storage box at the NADP site. Raingage ink is kept inside the Belfort.

c. Estimated time to complete procedures

It takes five to ten minutes to change charts, an additional 20-30 minutes if the Belfort catch bucket is full. To prevent overflow, consider bucket full when the chart reads 7 inches.

d. Preparation

Include a new chart with Tuesday's sample set. Make sure all required supplies are present in the gage shell each Tuesday. If some are missing, make sure they are replaced by the following Tuesday.

e. Procedures

To change charts, open the sliding access door. Move the pen up and down to mark the end of the week's record. Move pen away from chart with the pen shift bar. Remove drum and chart by lifting drum up off the clock gears. Write the time/date off in appropriate places

on chart. Install new chart on drum. Fold edge at end of week and slip it under the beginning portion of the chart. Mark the station ID (CO98), date, and time on chart. Return drum and new chart to clock, making sure gears are properly meshed. Rotate the drum so pen rests on the current day and time. Refill the pen nib with ink if needed, usually a small drop is sufficient. The pen can usually go 2-4 weeks between refills. Do not over fill the pen. ONLY FILL THE PRECIPITATION PEN, WHICH IS THE BOTTOM PEN. The top two pens are no longer used after installation of the NOAH IV electronic raingages. Mark the beginning of the week's record by moving pen up and down against the chart paper.

f. Be aware

The catch bucket in the Belfort should be emptied when chart reads 7 inches; otherwise, the bucket will likely overflow during a major storm event. The gage works best in the range of 2-6 inches. When emptying bucket, funnel waste into empty antifreeze containers (most other containers will leak). Containers of used antifreeze should be brought down from the station immediately (in a plastic bag to protect pack against leakage). Add two inches of fresh antifreeze to the empty bucket and just enough transmission fluid to cover surface area of antifreeze (~0.5 cups). Return bucket to scale.

The mechanical linkages of the Belfort are sensitive to water, oil, dirt, dust, and abuse of any kind. Be careful to keep the internal area clean. Do not allow the catch bucket to overflow with precipitation (see section on changing antifreeze above).

Calibration of the Alter-shielded Belfort must be checked once a year. Complete procedures are given in the Belfort manual. Advanced Technology Systems, Inc. provided a better set of instructions in 1999. These procedures are included as loose-leafs in the Belfort manual. Procedures are quite tricky, so if adjustment is required the process should be thoroughly understood before attempting.

The antifreeze mixture brought down from the weather station should be carried in antifreeze jugs and Nalgene containers, not milk jugs. Milk jugs are not durable enough to withstand the abuse they will receive on the trip down the trail. Back at NREL, funnel waste antifreeze into the five-gallon metal jugs labeled "Un-Regulated, Contents: 18% Ethylene Glycol, 2% Transmission Fluid, 80% Water." Include start and stop dates on the label for each jug. These jugs are found in NESB A101A, ask the Laboratory Manager for keys to A101A. Dispose of waste through the CSU Hazardous Waste Office (x1-6745).

Replace D-cell batteries in the clock at least twice a year (mandatory each November and March).

Measurement of Hydrologic Discharge (*Transferred to USGS-WRD in 2006*)

a. Introduction

Operation of the Loch Outlet stream gage was transferred to the USGS-WRD in August 2006. LVWS personnel are no longer responsible for measurement of hydrologic discharge within the LVWS.

Icy Brook carries most surface water out of LVWS. A Parshall Flume with a four-foot throat was installed in Icy Brook approximately 100 meters downstream from the Loch during the fall of 1983. The flume is rated so that a given water level in the flume can be directly related to a discharge volume/rate. A Campbell Scientific CR500 stream recorder recorded stage height in a stilling well, and a Leupold and Stevens chart recorder served as a backup for the Campbell. Water level data from both gages were converted to instantaneous flow and cumulative flow (m^3s^{-1}). When the USGS-WRD assumed responsibility for operation of the flume at the Loch Outlet, a depth transducer was installed to measure water levels and a stage-discharge was developed for the flume.

The stilling wells can only function when sufficient flow is present. Generally, this is from late April to late October. Winter flow is a small proportion of the annual total, and was estimated prior to installation of the depth transducer in 2006. Although stage has been recorded during the winter since 2006, these measurements may be affected by ice formation within the flume.

b. Equipment and Supplies

- Flume field notebook and pencil
- Campbell Scientific CR500 stream recorder
- Eight D-cell batteries for CR500
- EnviroSystems encoder w/ pulley wheel, pulley tape, float, and counter weight
- Laptop computer (with PC208 program), RS232 cable, and a SC32A converter
- A 9 to 25 pin serial cable
- Data storage module (SM192)
- One D cell battery for Stevens gage
- Stevens gage w/ pulley line, float, and counter weight
- Strip chart paper, Stevens gage pen, and cylinder (kept in lab over winter)
- Cylinder paper spring and rubber bands (kept in lab over winter)

c. Estimated time to complete procedures

Initial set-up of the gages requires about an hour at the site, not including time to dig snow from around the flume. For weekly service, allow 20-30 minutes to download data, change

chart, record the current stage height, and make minor adjustments. Closing down the flume for the winter requires only slightly more time than the weekly service.

d. Preparation

For initial set-up, make sure the CR500 is in operating order (do test runs in office). Also ensure the Stevens gage is in good shape with no visible corrosion. WD-40 and graphite dust work well to care for and prevent corrosion.

The area around the flume throat and stilling well must be dug out of the snowdrift. This is usually accomplished over several weeks beginning in early April. There should be no obstructions (i.e., snow) in the flume.

e. Procedures

Initial Set-up for CR500

- 1) The CR500 should be set up in mid to late April. Open the CR500 stilling well lid (it's the big PVC tube). Remove ice from the stilling well (by gently chopping with an ice axe or spud bar and by melting with water heated with a backpacking stove) when the outlet stage height is just greater than 0.1 foot. Be VERY careful not to crack or move the PVC barrel. The link from it to the flume is a point of instability.
- 2) Fasten the EnviroSystems shaft encoder to platform inside stilling well. Place float and weight in the stilling well, with the metal pulley tape passing over the external pulley of the shaft encoder. The float goes on the left and weight on right as you look towards the creek. Make sure the spikes on pulley mate with holes in pulley tape.
- 3) Attach screw cap connection to shaft encoder. Connect wires to right-hand white panel on CR500 (red=12V, white=C2/P3, black=G, and clear=G).
- 4) Boot computer, and start PC208. Connect battery pack to CR500. Attach CR500 to the computer using serial cable, SC32A, and an RS232 cable (blue). It goes from the CS I/O port on the CR500 to the data logger port on the SC32A. The terminal/printer port on the SC32A is linked to the printer port on the laptop with the serial cable.
- 5) Click the Connect button on the PC208 menu bar. Go to tools. Make sure the associated program is LOCHO.DLD. Click connect button on tools window. When connected, send the program to the data logger.
- 6) Go to the numeric display window. Enter the observed level reading from staff gage (meters) in the offset window. Monitor display to make sure readings are updated on the frequency set by program.

- 7) Disconnect the link to laptop. Close and lock shelter lid.

Weekly service for CR500

- 1) Attach SM192 to CS I/O on CR500 with blue RS232 cable.
- 2) Wait ten minutes, and then detach cable and close all enclosures.

Annual Shut Down for CR500

- 1) Temperatures will become increasingly colder as fall progresses. After a point, water in the stilling well will freeze. A drop in stage height below 0.1 feet usually accompanies this. In either case, it is time to shut down the gage for the year. First, perform the weekly maintenance as above.
- 2) Disconnect all equipment listed in section b. "Equipment and Supplies". Load everything carefully into pack and return to lab.

Initial Set-up for Stevens gage

- 1) The Stevens gage should be set up in mid to late April. Open Stevens gage stilling well cover (combo: 16-18-24). Remove ice from stilling well when Outlet stage height is just greater than 0.1 foot. This is achieved by carefully chopping with an ice axe or spud bar and by melting with approximately one gallon of boiling water (heated with a backpacking stove).
- 2) Place float and weight in the stilling well, with the cable passing over the external pulley on the Stevens Recorder. The float goes on the left as you are looking towards the creek. Make sure the little balls on the cable fit into the holes in the pulley.
- 3) Place the "D" battery in the blue clock. Movement of the balance wheel should be visible through the inspection window.
- 4) Place clean chart paper on the drum in the recorder. Position the drum and the pen such that the pen writes the stage height on the horizontal axis and the day/time on the vertical axis. Make sure you write the date, time, and stage height reading at the beginning of the chart, as well as in the flume notebook. If flow is on the rising limb of the hydrograph (early season), position the drum so the whole chart is available for recording. This reduces the possibility that the pen will have to skip over the edges of the chart paper. After flow becomes less flashy, you should start the pen in the middle of the chart.

- 5) Replace the recorder cover. Close and lock the cover to the stilling well.

Weekly maintenance for Stevens gage

- 1) Visually read the water level along the staff gage (ft) in the flume, averaging the high and low water surges. Record the value and any adjustments or repairs made to the recorder or flume in the flume notebook.
- 2) Remove the Stevens recorder cover. Tilt pen back and remove chart drum. Replace the chart paper on the drum, and reposition the drum in the recorder. Slide pen carriage back so that the pen will begin recording at the correct time. Each line is equal to two hours. Position the cylinder so the pen will be unlikely to be hung up passing over chart ends, and lock in place. Write the date, time, and stage height on the end of the old chart and the beginning of the new chart. Record the date, time, and stage height in the flume notebook.

Annual Shut Down for Stevens gage

- 1) Temperatures will become increasingly colder later in October. After a point, water in the stilling well will freeze. A drop in stage height below 0.1 feet usually accompanies this. In either case, it is time to shut down the gage for the year. First, perform the weekly maintenance as above, except do not replace the chart paper.
- 2) Remove the battery from the clock. Bring all supplies back to the lab except for the gage, float, weight, and cable.
- 3) Remove the float, cable, and weight from the stilling well and place next to the recorder. Close and lock the stilling well cover.

f. Be aware

The opening and throat of the flume must be clear for the stage height/discharge relationship to be correct. Check frequently (especially during high flows) and remove any obstructions.

The pen carriage rails in the Stevens Recorder may need to be cleaned so the pen can move smoothly along the time axis. Sometimes problems that appear as clock malfunction can be attributed to dirty rails. Lubricate with dry graphite or WD-40.

Usually the Stevens gage pen will last 2-3 seasons. Make sure there are spares in the supply bag located in the Stevens stilling well.

Winter Lake Sampling (*Discontinued in 2002*)

a. Introduction

The lakes in the LVWS freeze over sometime in October. In the field book, note the date and percentage of ice cover of the Loch until frozen completely. Also, note the percentage of ice cover and date each week in the spring until the Loch is ice-free. Due to minimal flow after freezing, lakes become nearly closed basins until the following spring. When ice covered, lake water thermally stratifies, and in-lake biological processes are more likely to influence water chemistry than under summer flow conditions. Take water samples from upper (surface) and lower (hypolimnion) water layers of Sky Pond and the Loch (after boring through ice) bi-monthly during ice covered period.

b. Equipment and Supplies

- Hand-crank peristaltic pump
- 10 meters of acid washed/ DI rinsed tubing
- Sink weight and duct tape
- Orion conductivity/temperature meter
- Butyl gloves, ice axe, ice auger (with spare blades), snow shovel
- 20 ml plastic vial of Lugol's solution (see recipe for Lugol's solution in Appendix E)
- One 2 ml disposable pipette

Sampling set (for each sampling point):

- (1) 500 ml translucent HDPE acid washed (for chemical analysis)
- (1) 60 ml translucent HDPE acid washed (for SiO₂)
- (1) 250 ml brown HDPE acid washed (for raw, unfiltered sample)
- (1) 480 ml baked borosilicate bottle (for DOC, DON, and DOP)
- (1) 125 ml baked borosilicate bottle (for monthly Loch Outlet phytoplankton sample)
- (1) 30 ml syringe for pH (for closed cell pH)

c. Estimated time to complete procedures

For one site, allow 15 minutes to drill hole in ice, and 30 additional minutes to collect samples and conductivity/temperature data.

d. Preparation

Acid-wash the pump tubing before each use (instructions for acid-washing on page 50). Make sure tubing is thoroughly rinsed in DI water. To rinse tube, run DI (at full blast) through it for at least 5 minutes. Drain and spin as much water out of the tubing as possible so it will not freeze during the trip to sampling site.

e. Procedures

- 1) Go to the deepest spot of lake. See bathymetric maps of lakes in Appendix D for locations. Start a hole in the ice with an ice axe. Finish the hole with ice auger. The ice is usually about a meter thick - so do not give up! Sharp blades are necessary. Either have them sharpened, or have a new set on hand before sample day.
- 2) Clear any loose ice out of open water in the hole with shovel and/or rubber gloves.
- 3) Measure the depth of lake and ice with tube to make sure you are over the deepest point of lake. Be careful not to disturb sediments. If you choose a site that is less than half as deep as the deepest point of the lake, abandon it and drill another hole.
- 4) Measure temperature profile of the lake by taking readings every meter. Also, take a reading just above and below the ice layer. Record all data in the field notebook.
- 5) Holding on to one end, drop sample tube into the water through hole. Weight the end of pump tubing so it falls in a straight line (a small bottle filled with sand duct taped to bottom of tube is easy to carry and works very well).
- 6) Collect two water samples from the lake. The first should be labeled "surface" and is collected from just below the bottom of the ice. The second should be labeled "hypolimnion" and is collected 0.25-0.5 m above lake bottom. Before drawing sample, flush pump with at least 45 revolutions of pump handle. Rinse all bottles and syringe 3X before filling (see rinsing procedures in Surface Water Sampling section). To collect the phytoplankton sample, rinse the bottle 3X, fill, dispense 1 ml of Lugol's solution with a disposable 2 ml pipette, and then cap. While one person operates the pump, the other person fills sample bottles. The person holding tube and bottles should wear insulated rubber gloves to keep hands warm and to prevent contamination of sample. Keep bottles insulated if they are in danger of freezing. Record the sample depths, sample times, and names of field technicians in the field notebook.

f. Be aware

Water inside the pump will freeze if not constantly flowing. Once started pumping, do not stop! Difficulty of turning handle and diminished flow is evidence that freezing has begun. You may be able to thaw it by pumping more vigorously from the lake bottom. If this does not work, drain tube, put in plastic bag, and thaw inside your parka.

Prolonged exposure to cold and wind can lead to frostbite or hypothermia. Come prepared with adequate warm clothing, wind protection, hand warmers, and food. Do not ever endanger yourself or the party for a sample. If anyone is in doubt of the party's safety, pack it up and go.

Measuring pH (*Discontinued in 2010*)

a. Introduction

LVWS staff discontinued pH measurement for precipitation and surface water samples at NREL in 2010. The CAL and USFS laboratories measure pH for precipitation and surface water samples, respectively. Therefore, pH measurements at NREL were considered redundant and discontinued.

An important characteristic of water is its acidity. pH is defined as the negative log of the hydrogen ion activity. The standard method for pH measurement uses an H⁺ ion specific electrode that generates an electrical potential across a glass membrane. The pH meter is simply a voltmeter that measures this potential. A stable pH reading is operationally defined as one that does not change by more than 0.01 units in 30 seconds. There are extensive notes on pH measurement and specific hints on the Broadley-James electrode contained in the Instruction Manual for NADP/NTN Site Operation.

b. Equipment and Supplies (located in the NREL A235)

- Lab notebook
- pH meter (TTT85)
- Broadley-James pH electrode
- Calibration buffers: pH 4.00 and pH 7.00
- Quality Control (QC) Check Solution, pH 4.90 ± 0.15
- Fresh deionized (DI) water in squeeze bottle
- 2 ml plastic scintillation vials
- Kimwipes
- Waste beaker

c. Estimated time to complete procedure

Allow 30 minutes for calibration and 1 or 2 samples. Add 5-15 minutes for each additional sample, whether open cup or closed chamber.

d. Preparation

- 1) All solutions to be measured (including standards and check samples) should be at room temperature (within a few degrees).
- 2) Check amount and expiration dates of the standard buffers and QC solution. If needed, order more from the NADP Central Analytical Laboratory by contacting the NADP Site Liaison. It may take several weeks for them to arrive.

e. Procedures

Calibration

- 1) Unplug the LVWS Broadley-James pH electrode from the meter on the LVWS bench. Rinse the probe copiously with DI water.
- 2) Swap probes and turn off the TTT85. Be sure to hit the reset button on the circuit breaker to restore power.
- 3) Rinse the stir bar with DI water and blot dry on a Kimwipe. Add the stir bar to the scintillation vial containing the pH 7.00 buffer. Set the stir plate to the lowest setting and place the vial on the stir plate. Insert the pH probe into the vial so that the red "eye" is completely submerged.
- 4) Press the pH key on the TTT85.
- 5) Press the CAL key - 1. CAL. TEMP. XX.X C appears on the display.
- 6) Press the CAL key again - pH X.XXX BUF1 Y.YYY appears on the display. If necessary, change the pH value of buffer 1 (Y.YYY) (i.e., SHIFT, 7, ., 0, 0, 0, and STORE).
- 7) Wait for a stable measurement. As we record pH to two decimal places (e.g., 4.52), a measurement is considered stable when the hundredths place does not fluctuate. This could take some time (>15 minutes). Don't worry if the meter says that the pH is not 7.00. The calibration procedure will reset the meter.

Once a stable measurement is obtained, press the CAL key. ZERO pH X.XXX CAL1 appears on the display for a short period, then 2.CAL TEMP. X.XX C will be displayed.

- 8) Rinse the pH probe and stir bar with DI water. Blot dry with Kimwipe.
- 9) Place the stir bar in the pH 4.00 buffer vial. Put the vial on the stir plate and insert the pH probe into the buffer solution.
- 10) Press the CAL key again - pH X.XXX BUF2 Y.YYY appears on the display. If necessary, change the pH value of buffer 2 (Y.YYY) (i.e., SHIFT, 4, ., 0, 0, 0, and STORE).
- 11) Wait for a stable measurement (X.XXX) and then press the CAL key. SENS XX.X & CAL2 appears on the display briefly, after 3. CAL TEMP. XX.X C is displayed. The sensitivity should be between 97.5 and 102.5. If not, re-calibrate starting with the pH 7.00 buffer.
- 12) Press the pH key to return to a measuring state. Be sure to rinse the probe and stir bar between samples.

Check solution and sample measurement

- 1) Rinse a vial with DI, then rinse the vial with QC check solution before filling with QC check solution.
- 2) Be sure to rinse the probe and stir bar with DI and then blot dry.
- 3) Immerse the pH probe in the QC check solution and wait for stable measurement.
- 4) If stable pH is 4.90 ± 0.15 , record it. If pH is outside of this range, rinse probe with DI water and check QC check solution expiration. If the QC check solution is good, repeat calibration. Measured pH of check solution must be 4.90 ± 0.15 before any samples are measured. If you cannot get a good reading on check solution, the QC check solution likely needs to be replaced. Cleaning and troubleshooting procedures are described in NADP Site Operation Manual. If a probe is not able to read the check solution properly, consult the Lab Manager.
- 5) Remove probe and stir bar from check solution vial and thoroughly rinse with DI water. Blot excess water from probe tip and stir bar with Kimwipe.
- 6) Rinse and fill a vial with the sample to be measured.
- 7) Immerse probe in the sample vial and wait for stable measurement. Once the pH has stabilized to the hundredths place, record measurement on lab sheet/notebook.
- 8) Remove probe from the sample vial, and thoroughly rinse with DI water. Blot excess water from probe tip with Kimwipe. Rinse the stir bar with DI, blot dry, and transfer to next sample vial.
- 9) Repeat steps 6 through 8 for each additional sample. If measuring more than five samples, re-measure QC sample after every fifth cup samples (to check for drift). If QC sample is not 4.90 ± 0.15 , re-measure last five samples if possible.

f. Be aware

The plastic body of the pH electrode is fragile! Be careful not to crack or scratch it. Be especially careful not to allow anything solid to touch the spherical glass membrane at the tip of the probe. It is easily scratched, which ruins the electrode.

The electrical potential being measured is in the millivolt range; therefore the equipment is extremely sensitive to static charge. Stand back and keep motions to a minimum when attempting a measurement.

Alpkem Procedures (*Discontinued in 2015*)

The Alpkem is an instrument that colorimetrically analyzes aqueous solutions for concentrations of different chemicals. NREL's AlpKem can be configured to run ammonium (NH_4^+), nitrate (NO_3^-), and orthophosphate (PO_4^{3-}). Technicians must have proper training from a laboratory manager before attempting to use this instrument.

a. Introduction

Please refer to the "Flow Solution Manual IV" by OI Analytical 2001 for NH_4^+ , NO_3^- , PO_4^{3-} , and total phosphorus (TP; persulfate digest) methods. This manual is located in NREL A256. Modifications to the TP method are supplied by the Hedin lab and are described below.

b. Equipment and Supplies (located in Rm. A256)

- OI Analytical AlpKem Spectrophotometer
- Samples for $\text{NH}_4^+/\text{NO}_3^-/\text{PO}_4^{3-}/\text{Total Phosphorus}$ (KCL/DI matrix)
- Standards (KCl/DI matrix)
- 2-ml analyzer cups and racks
- KCl/DI squeeze bottles
- 8-micron membrane filters
- Reagents (recipes are described in Appendix E)
- Test tubes (TP)
- Linerless caps (TP)
- Oxidizing solution (Potassium Persulfate for TP)
- Autoclave (TP)
- 5 ml pipette and tips (for samples, standards, washes) (TP)
- 1 ml pipette and tips (for oxidizing solution) (TP)

AlpKem Reagents

NH_4^+	NO_3^-	$\text{PO}_4^{3-}/\text{TP}$
KCl/DI Carrier	DI Carrier	PO_4^{3-} Color Reagent
NH_4^+ Working Buffer	NO_3^- Color Reagent	Dowfax
Sodium Salicylate/Sodium Nitroferricyanide	NO_3^- Buffer (NH_4Cl) (check filter for clogs)	DI Carrier
Hypochlorite (use fresh bleach)	Cadmium Reduction Column	Potassium Persulfate

c. Preparation

- 1) Allow samples and standards to reach room temperature by setting on counter while setting instrument up.
- 2) Make sure all of the reagents are full, and your standards, reagents, and DI are fresh.
- 3) Turn on the computer from the power strip and follow the set-up procedures detailed below.
- 4) The water and $\text{NH}_4^+/\text{NO}_3^-$ waste must be collected and disposed of as hazardous waste. Consult the lab manager if you questions regarding hazardous waste disposal. DO NOT ALLOW THE PINK AND GREEN WASTES TO MIX UNDER ANY CIRCUMSTANCES! Mixing these substances will produce noxious gasses.
- 5) Be sure the correct channels are set up for your particular needs.

d. Procedures

Ammonium/Nitrate Directions

- 1) Check that the instrument is configured for $\text{NH}_4^+/\text{NO}_3^-$: The line from the sampler should be connected to the "T" where the NH_4^+ sample line and the NO_3^- pull through line meet. The debubbler on the channel 3 detector ($\text{NH}_4^+/\text{PO}_4^{3-}$) should be connected to one line labeled "NH₄ from debubbler" and another line labeled "NH₄ to spec". If not, see the section: Switching the AlpKem from PO_4^{3-} to $\text{NH}_4^+/\text{NO}_3^-$.
- 2) Remove NO_3^- color reagent and NH_4^+ salicylate-nitroferricyanide bottles from the fridge. Place the NO_3^- color reagent in a warm water bath to warm up to room temperature.
- 3) Check that the sampler wash waste is flowing into the sink.
- 4) Turn on compressed air at round black knob on bottom of regulator.
- 5) Turn on main power switch and make sure NH_4^+ heater is on. Let the sampler initialize.
- 6) Open Winflow 4.0 software. If software is already open, exit and reopen. This causes the sample probe to go into the wash reservoir.
- 7) Empty and refill the large DI water bottle.

- 8) Lock down the pump platens and pull the engaging levers straight up for all the pump tubes labeled NH₄⁺ and NO₃⁻ plus "to sampler wash", "from sampler wash", and "sample pull through".
- 9) Press the "run stop" button on the pump, the display should read -50.0.
- 10) Connect the sampler wash and NO₃⁻ carrier lines to the large DI wash bottle (be sure to connect to the ports as labeled: the sampler wash will not flow properly if connected to the port labeled NO₃⁻ carrier).
- 11) Connect the NH₄⁺ lines: buffer, hypochlorite, and salycilate, to the NH₄⁺ manifold startup solution.
- 12) Connect the NO₃⁻ lines: color reagent and buffer, to the NO₃⁻ rinse bottle.
- 13) Let pump for 10 minutes and check for leaks.
- 14) Discard old hypochlorite solution and make fresh (12 ml bleach and 178 ml DI water).
- 15) Move the NO₃⁻ buffer line to the buffer bottle.

Condition the cadmium column

- 1) Place the column, syringe with tube to fit column, open specimen cup of NO₃⁻ buffer, and open cup of 0.2% CuSO₄ on the bench within easy reach.
- 2) Draw about 1 ml of buffer into the syringe and remove all air bubbles from the tube. Break the tubing connection on the column and elevate the connector end slightly until a drop of liquid appears at the tube end.
- 3) Hold the syringe plunger end up and depress the plunger until a drop of buffer appears at the connector end.
- 4) Connect the syringe to the column without introducing any air.
- 5) Place the free end of the column into the buffer cup and slowly depress the plunger to expel the air from the free end of the column.
- 6) Transfer the free end to the cup of CuSO₄ and draw up about 2-4 ml.
- 7) Depress the plunger slightly to release any tension on the liquid in the column and transfer the end to the cup of buffer.

- 8) Draw up 3-5 ml of buffer, and then depress the plunger slightly to release any tension on the liquid in the column.
- 9) Remove the end from the buffer, place the column, tubing and syringe flat on the bench, then disconnect the syringe and connect the two ends of the column together.
- 10) Take the column and syringe to the sink and rinse with DI water. Put the buffer and CuSO₄ cup away and wipe the bench with a wet sponge. The NO₃⁻ buffer contains NH₄⁺, which can contaminate your samples!

Connect the cadmium column to the instrument

- 1) Make sure there are no bubbles in the nitrate cartridge (about 10 minutes after moving the NO₃⁻ buffer line to the buffer bottle).
- 2) Press the "run stop" button on the pump, press the "mode" button 4 times, the display should read "2.0", press the "run stop" button again, this puts the pump speed to minimum.
- 3) Break the connection in the line between the "to column" and "from column" ports on the NO₃⁻ cartridge.
- 4) Break the tubing connection on the column and note which end will connect to the line from the "to column" port on the cartridge. Elevate the other end of the tubing until a drop of liquid forms at the end. Wait until a drop forms on the end of the "to column" line and connect it to the column without introducing any air.
- 5) Connect the other end of the column to the "from column" line on the cartridge.
- 6) Press the "run stop" button on the pump, press the "mode" button 3 times, the display should read "-50.0", press the "run stop" button again, this puts the pump speed back to normal.
- 7) Move the NO₃⁻ color reagent line to the color reagent bottle.
- 8) Move the NH₄⁺ reagent lines to their respective reagent bottles.
- 9) Make sure the line from the sampler is completely clear of all other lines and the reagent bottles so the sample probe can move freely.
- 10) Let the system pump at least 30 minutes before beginning a sample run.

Setting up a sample run

Press the sample table button on the main tool bar in Winflow4.

Type in "cup #", "name" and "type" for each sample and standard to be analyzed. Refer to the typical sample table on page 7 and the notes below.

Cup Numbers

Positions 1-20 are the large tubes at the back of the sampler and are used for standards, checks and baselines (washes). The instrument can sample from these cups up to 6 times each.

There are 3 racks for the 2 ml sample cups. The one on the left (closest to the sampler wash cup) holds cup numbers 101-190. The middle rack holds cup numbers 201-290 and the rack on the right holds number 301-390. These cups should only be sampled one time each.

Sample Name

Sample names can be anything that fits in the field. However, the standards used in the calibration curve (anything labeled "C" in the "type" column) must be named exactly the same as they are named in the calibrant table in the method file.

To view the calibrant table, click the "edit method" button on the main toolbar, click file, open, and select the correct method file. Consult the lab manager for the correct method file. The calibrant table is the last page of the method file.

The format for naming calibration standards is: X/Y where X is the concentration of NH₄⁺ and Y is the concentration of NO₃⁻. No leading zeros on values less than 1 and no decimal points except for fractional concentrations.

Type

SYNC - This is always the first cup in a run, it is a high standard (usually top standard) which will yield a large peak to let the software know the sample peaks have started.

C - indicates a calibration standard to be included in the calibration curve. Do not use this for internal standards or checks unless you want them included in the calibration curve.

RB - indicates a baseline (wash). The instrument will use these peaks to correct for baseline drift so they should always be a 0 ppm standard.

U - unknown. Should be used for all samples, checks, and internal standards.

After the calibration curve, the basic pattern should be 10 samples, 1 standard, 10 samples, and 1 baseline. Repeat to a maximum of about 80 samples. Larger sets should be broken into multiple runs. Sample runs should always end with a baseline.

Other columns in the sample table

R = Number of replicate samples to be taken from the cup. Should be set to 1.

Dil = dilution factor of the sample, usually 1.

Wt = weight of the sample, usually 1.

After the sample table is prepared, be sure to save it.

Starting a sample run

- 1) Click the collect data button on the main toolbar. The software will ask for an operator name and ID, type in your initials for both. The software will then ask for a sample table name and a method name. Consult the lab manager for the correct method. Select the correct file names and press OK. The software will ask for a filename for the results with the default being the same as the sample table with an .rst extension. Select or type in a file name and press OK. The software will not allow you to overwrite or append and existing file.
- 2) The data collection window will appear on the screen. Press the “play” button to start the data collection. At this point, the software will monitor the baselines for 60 minutes and then start sampling.
- 3) Debubble both flow cells by pinching and releasing the outflow tubing. Repeat until no bubbles appear.
- 4) Pour standards and samples into the cups and place in the sampler. Get at least 20 cups poured before starting the sampler.
- 5) Check baselines for stability and drift, should be less than 500 micro-absorbance units.
- 6) If there are any peaks or jumps in the baseline traces, Press the “stop” button. The software will ask if you want to stop, press yes. Press the “rewind” button and then the “play” button.
- 7) Press the “fast forward” button to begin sampling.
- 8) The first NO_3^- peak will appear about 75 seconds after the first sample is drawn. The first NH_4^+ peak will appear after about 250 seconds.

Instrument shutdown

- 1) Press the “run stop” button on the pump to stop the reagent flow.
- 2) Disconnect the cadmium column from the NO_3^- cartridge and connect the two ends together. Be careful to minimize the amount of air let into the column.
- 3) Connect the “to column” and “from column” lines together.
- 4) Press the “run stop” button on the pump to restart the flow.
- 5) Move the NO_3^- lines to the NO_3^- rinse bottle and the NH_4^+ lines to the NH_4^+ manifold startup solution bottle. Let pump about 10 minutes.
- 6) Disconnect all the lines and let the system pump until all the liquid is out of the instrument, about 15 minutes.
- 7) Press the “run stop” button to stop the pump and turn off the main power switch to the instrument.
- 8) Push the engaging levers on all the pump platens to horizontal and disconnect one end of each platen from the pump.
- 9) Empty the NH_4^+ waste into the proper hazardous waste container.
- 10) Empty the NO_3^- waste into the proper hazardous waste container.
- 11) Empty and discard the sample cups and tubes. Rinse the sampler racks with DI water and set on the bench to dry.
- 12) Return the NO_3^- color reagent and NH_4^+ salicylate-nitroferricyanide bottles to the fridge.
- 13) Refrigerate the standards if the instrument will be used the next day or freeze them if it will be longer.
- 14) Wipe down the instrument and benches with a moist sponge.
- 15) Turn off the ball valve on the compressed air.

Switching the AlpKem from PO_4^{3-} to $\text{NH}_4^+/\text{NO}_3^-$

- 1) Make sure the PO_4^{3-} waste container is empty. The waste goes in the bottle on the bottom shelf of the acid cabinet in room A258.
- 2) Disconnect the “ PO_4 waste from spec” line from the outflow tube of the channel 3 ($\text{PO}_4^{3-}/\text{NH}_4^+$) detector and connect the “ NH_4 waste from spec” line in its place.
- 3) Disconnect the “ PO_4 to spec” line from the bottom connection on the debubbler on the channel 3 detector and replace it with the “ NH_4 to spec” line.
- 4) Disconnect the “ PO_4 from debubbler” line from the top connection on the debubbler and replace it with the “ NH_4 from debubbler” line.
- 5) Turn the PO_4^{3-} heater off and the NH_4^+ heater on.
- 6) Disconnect the sampler line from pump tube labeled “ PO_4 sample” and connect it to the “T” where the “ NH_4 sample” line and the “ NO_3 sample pull thru” line meet.

Orthophosphate/Total Phosphorus Directions

Orthophosphate

- 1) All glassware and bottles used should be acid washed before beginning.
- 2) Check that the instrument is configured to run PO_4^{3-} . The line from the sampler should be connected to the pump tube labeled “ PO_4 sample” and lines labeled “ PO_4 to spec” and “ PO_4 from debubbler” should be connected to the channel 3 debubbler. If not, see the section: “Switching the AlpKem from $\text{NH}_4^+/\text{NO}_3^-$ to PO_4^{3-} ”.
- 3) Empty the large DI water bottle and fill with 1.2 M HCl from the acid bath. Let it sit for at least 15 minutes. Carefully pour the acid back into the acid bath, rinse 6 times with DI, and fill with DI.
- 4) Dissolve 1.8 grams ascorbic acid in about 70 ml DI water in a 100 ml volumetric flask. Dilute to 100 ml with DI water.
- 5) Check sampler wash waste reservoir under bench to right of instrument. Empty into sink if more than half full.
- 6) Turn on main power switch and make sure PO_4^{3-} heater is on.
- 7) Open Winflow 4.0 software. If software is already open, exit and reopen. This causes the sample probe to go into the wash reservoir.

- 8) Lock down the pump platens and pull the engaging levers straight up for all the pump tubes labeled PO₄³⁻ plus "to sampler wash" and "from sampler wash".
- 9) Press the "run stop" button on the pump, the display should read -50.0.
- 10) Connect the sampler wash line to the port labeled sampler wash on the large DI water bottle. Connect the PO₄³⁻ color reagent line to the port labeled NO₃⁻ carrier on the large DI water bottle (be sure to connect to the ports as listed: the sampler wash will not flow properly if connected to the port labeled NO₃⁻ carrier).
- 11) Connect the "PO₄ Dowfax" line to the dowfax bottle.
- 12) Let the system pump for 15 minutes and check for leaks.
- 13) Prepare the color reagent by adding the following stock solutions to the color reagent bottle IN ORDER and mixing after each addition:
 - 150 ml 5N sulfuric acid
 - 15 ml antimony potassium tartrate solution
 - 45 ml ammonium molybdate solution
 - 90 ml ascorbic acid solution
- 14) If there are no leaks, move the PO₄³⁻ color reagent line to the color reagent bottle.
- 15) Let the system pump 15 minutes before running samples.

Setting up a sample run

Press the sample table button on the main tool bar in Winflow4.

Type in "cup #", "name" and "type" for each sample and standard to be analyzed. Refer to the typical sample table on the page 5 and the notes below.

Cup Numbers

Positions 1-20 are the large tubes at the back of the sampler and are used for standards, checks and baselines (washes). The instrument can sample from these cups up to 16 times each.

There are 3 racks for the 2 ml sample cups. The one on the left (closest to the sampler wash cup) holds cup numbers 101-190. The middle rack holds cup numbers 201-290 and the rack on the right holds number 301-390. These cups can be sampled up to 4 times each.

Sample Name

Sample names can be anything that fits in the field. However, the standards used in the calibration curve (anything labeled "C" in the "type" column) must be named exactly the same as they are named in the calibrant table in the method file.

To view the calibrant table, click the "edit method" button on the main toolbar, click file, open, and select the appropriate method. Consult the lab manager for the correct method. The calibrant table is the last page of the method file.

Type

SYNC - This is always the first cup in a run, it is a high standard (usually top standard) which will yield a large peak to let the software know the sample peaks have started.

C - indicates a calibration standard to be included in the calibration curve. Do not use this for internal standards or checks unless you want them included in the calibration curve.

RB - indicates a baseline (wash). The instrument will use these peaks to correct for baseline drift so they should always be a 0 ppm standard.

U - unknown. Should be used for all samples, checks, and internal standards.

After the calibration curve, the basic pattern should be 10 samples, 1 standard, 10 samples, and 1 baseline. Repeat to a maximum of about 80 samples. Larger sets should be broken into multiple runs. Sample runs should always end with a baseline.

Other columns in the sample table

R = Number of replicate samples to be taken from the cup. Should be set to 1.

Dil = dilution factor of the sample, usually 1.

Wt = weight of the sample, usually 1.

After the sample table is prepared, be sure to save it.

Starting a sample run

- 1) Click the collect data button on the main toolbar. The software will ask for an operator name and ID, type in your initials for both. The software will then ask for a sample table name and a method name. Consult the lab manager for the correct method. Select the correct file names and press OK. The software will ask for a filename for the results with the default being the same as the sample table with an .rst extension. Select or type in a file name and press OK. The software will not allow you to overwrite or append an existing file.

- 2) The data collection window will appear on the screen. Press the “play” button to start the data collection. At this point, the software will monitor the baselines for 60 minutes and then start sampling.
- 3) Debubble the flow cell by pinching and releasing the outflow tubing. Repeat until no bubbles appear.
- 4) Pour standards and samples into the cups and place in the sampler. Get at least 20 cups poured before starting the sampler.
- 5) Check baselines for stability and drift, should be less than 500 micro-absorbance units.
- 6) If there are any peaks or jumps in the baseline traces, Press the “stop” button. The software will ask if you want to stop, press yes. Press the “rewind” button and then the “play” button.
- 7) Press the “fast forward” button to begin sampling.

Instrument shutdown

- 1) Move the “PO₄ color reagent” line to the “NO₃ carrier” port on the large DI water bottle. Let the system pump for about 10 minutes.
- 2) Disconnect all the lines and let the system pump air for about 15 minutes or until all the liquid is out of the instrument.
- 3) Press the “run stop” button to stop the pump and turn off the main power switch to the instrument.
- 4) Push the engaging levers on all the pump platens to horizontal and disconnect one end of each platen from the pump.
- 5) Pour the unused color reagent into the PO₄³⁻ waste container.
- 6) Empty the PO₄³⁻ waste into the container in the acid cabinet in A258.
- 7) Empty and discard the sample cups and tubes. Rinse the sampler racks with DI water and set on the bench to dry.
- 8) Refrigerate the standards if the instrument will be used the next day or freeze them if it will be longer.

- 9) Wipe down the instrument and benches with a moist sponge.

Switching the AlpKem from NH₄⁺/NO₃⁻ to PO₄³⁻

- 1) Make sure the NH₄⁺ waste container is empty. The waste goes in the bottle on the floor by the sink.
- 2) Disconnect the “NH₄ waste from spec” line from the outflow tube of the channel 3 (PO₄³⁻/NH₄⁺) detector and connect the “PO₄ waste from spec” line in its place.
- 3) Disconnect the “NH₄ to spec” line from the bottom connection on the debubbler on the channel 3 detector and replace it with the “PO₄ to spec” line.
- 4) Disconnect the “NH₄ from debubbler” line from the top connection on the debubbler and replace it with the “PO₄ from debubbler” line.
- 5) Turn the NH₄⁺ heater off and the PO₄³⁻ heater on.
- 6) Disconnect the sampler line from the “T” where the “NH₄ sample” line and the “NO₃ sample pull thru” line meet and connect it to the pump tube labeled “PO₄ sample”.

Total Phosphorus

Methods for total phosphorus are taken from the Hedin lab at Cornell. This is a modification of the total nitrogen method with a few slight differences. By analyzing samples for orthophosphate (PO₄³⁻) and total phosphorus (TP), dissolved organic phosphorus (DOP) can be calculated by simple subtraction.

Be sure the test tubes and threads are free of chips and cracks since contents may be lost during autoclaving. Set autoclave for liquid cycle, 250 F, 50 min. using only the cycle 4 button. If system is set for a different cycle, please see Dan Reuss (lab manager).

- 1) Pipette 5 ml of standards, samples, washes, and duplicates into acid washed and oven dried borosilicate glass test tubes.
- 2) Add 1 ml of potassium persulfate oxidizing solution to each tube (12.5 g potassium persulfate to volume in a 250 ml volumetric, adjust recipe depending on sample size).
- 3) Tightly cap the tubes with acid washed linerless caps and arrange in autoclavable racks.
- 4) With remaining persulfate, make up a 1:5 mixture of potassium persulfate to di in 1000 ml flasks (80 ml persulfate to 400 ml di). Two flasks should be enough for 1 run of 90 samples or 2 smaller runs. This is to be used in place of di in the sampler wash line. Be

sure to leave plenty of head space (1/2 of flask) so oxidant does not overflow in autoclave. Use foil and autoclave tape to seal the flasks.

- 5) Place racks with tubes and sealed flasks in metal pans in autoclave.
- 6) Fill the pans with a di water bath to the depth of the solution in the flasks and tubes. This will minimize leaks due to rapid changes in temperature and pressure.
- 7) Turn on the power to the autoclave and allow to warm up for ~10 min.
- 8) Press the 4 button twice to start the autoclave cycle.
- 9) Once cycle is finished, crack door 1 inch and allow slow cool for 10 min.
- 10) Use caution when taking samples and flasks from autoclave as solutions are extremely hot. Allow samples to cool to room temperature for immediate run or place in cooler and run within 24 hours.
- 11) Follow same procedures to run samples on AlpKem as for Orthophosphate (only difference is instead of di for sampler wash use 1:5 persulfate solution from autoclave.)

Shimadzu TOC-V Procedures (*Discontinued in 2011*)

For the analysis of non-purgeable organic carbon (NPOC) and total nitrogen (TN) in stream, lake and precipitation waters.

i. Introduction

The Shimadzu TOC-V instrument measures the amount of total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) in water. Non-purgeable organic carbon (NPOC) can also be measured when the POC accessory is installed. “Oxidative combustion-infrared analysis” is a widely used TOC measurement method that has been adopted by the JIS and other international standards. By installing the optional TN unit, total water-borne nitrogen (TN) can be measured, using the principles of “oxidative combustion-chemiluminescence.” As LVWS water samples are filtered prior to analysis, the resultant concentrations are operationally defined as dissolved organic carbon (DOC) and total dissolved nitrogen (TDN).

Methods can be found in: JIS K-0102 “Industrial Waste Water Testing”, JIS K-0551: “Total organic carbon (TOC) testing methods for ultra-pure water”, U.S. Pharmacopoeia 23, EPA 415.1, EPA 9060A, ASTM D2575, Standard Methods for Examination of Water and Waste Water 5310B. Refer to the Shimadzu user manual in A256.

e. Equipment and Supplies (located in room A256)

- Shimadzu TC TN Auto-Analyzer
- Filtered/acidified DOC/DON/DOP samples
- Calibration standard (6 ppm C / 2 ppm N)
- Check sample (3 ppm C / 1 ppm N)
- 2 M HCl
- 40 ml clear sampler vials
- Parafilm

f. Preparation

- 1) Allow samples and C and N stocks to reach room temperature by setting on counter while setting instrument up.
- 2) Open the two valves on the air tank (main valve to tank and the on/off valve connected to the blue air line which goes to instrument.)
- 3) Turn on the power to the instrument (bottom right corner).

- 4) Load the correct template file (consult the lab manager for the correct template file) and save as a new file with today's date (e.g., lvws_2010Mar18). Connect the instrument to the PC and allow to warm-up by clicking on the lightning bolt button.
- 5) Make up fresh calibration standard, check sample and carbonate removal check sample:

Calibration Standard (6 ppm C/2 ppm N)	Check Sample (3 ppm C/1 ppm N)
In 500 ml volumetric flask add: 3 ml organic C 1 ml N 20 ml 2M HCl And fill to meniscus with DI	In 1000 ml volumetric flask add: 3 ml organic C 1 ml N 40 ml 2M HCl And fill to meniscus with DI

g. Procedures

Use the following procedures when working from the template sample table:

- 1) Each row will be assigned a specific sample and must be named according to the sample site and date. For example "LO_NORM_031215" refers to a Loch.O normal sample from Dec. 15, 2003. Be sure to name all samples, washes and checks in the empty "sample name" column. The "vial" number is the sample table must correspond with the location of the sample in the sample tray.
- 2) Prepare the first twelve sample vials in the sample tray according to the following table. These vials will be used to wash the machine and determine calibration curves.

Vial	Contents
1	DI
2	Calibration Std.
3	Calibration Std.
4	DI
5	Calibration Std.
6	Calibration Std.
7	Check Std.
8	DI
9	Check Std.
10	DI
11	Check Std.
12	DI

- 3) Fill the 40 ml sampler vials with at least 15 ml of analyte and note the position of each sample in the tray. Cover all sampler vials with parafilm to prevent evaporation and contamination. Along with field blanks, field dupes, and an occasional lab dupe (every

20 samples), be sure to insert a DI (wash) and check (3C/2N) after every 10 samples. DI wash and check samples should be included in the template file. End the run with a wash and check.

- 4) Fill a brown 480 ml acid washed borosilicate bottle with check solution and insert the small tube protruding from the front left corner of the Shimadzu into the bottle. This is vial number 0.
- 5) Once the sample table has been set-up and everything looks in place, start the machine by hitting the “start” button, which looks like a traffic light signal. Click “shut down instrument”, “standby”, “OK”, “external acid addition OFF”, and “start”.

Use the following procedures if you need to set up a sample table from scratch:

Setting up calibration curves

- 1) Set-up the calibration curves. “File”, “new”, “calibration curve” (for NPOC).
- 2) Choose “edit calibration points manually” and “dilution from a standard solution”.
- 3) Change “analysis” to NPOC, select “zero shift” off, “multiple injections” on, and name the curve according to the run date and particular curve. For example “031215NPOC”.
- 4) Choose NPOC “acid addition” to be 2.0%. There is no acid addition for the TN method.
- 5) Create NPOC calibration curve using “Edit Calibration Point Parameters” page. The “injection volume” should be changed to 150 µl. From top to bottom, standards should read 6, 3, 1.5, 0.75, 0. This is accomplished by clicking “add”, typing “0” in the “Standard Solution Concentration” box, “1” in the “Auto Dilution” box, and “OK”. Next, type “6” in the “Standard Solution Concentration” box, “1” in the “Auto Dilution” box, and “OK”. Continue this process using 6 as the “Standard Solution Concentration” and by increasing the “Auto Dilution” box number to dilute the four top standards to the ones listed above.
- 6) Select to use default settings and **do not** enable history log.
- 7) Repeat the above steps for the TN curve. The “injection volume” should read 150 µl. From top to bottom, TN standards should read 0, 0.25, 0.5, 1, 2. This is accomplished by clicking “add”, typing “1” in the “Standard Solution Concentration” box, “1” in the “Auto Dilution” box, and “OK”. Next, type “2” in the “Standard Solution Concentration” box, “2” in the “Auto Dilution” box, and “OK”. Continue this process using 2 as the “Standard Solution Concentration” and by increasing the “Auto Dilution” box number to dilute the 1 top standard to the concentrations listed above. This set-up allows the instrument to pull 6 and 3 for NPOC from vial #2, 1.5 and 0.75

for NPOC from vial #3, 0 and 0 for NPOC and TN from vial #4, 0.25 and 0.5 for TN from vial #5, and 1 and 2 for TN from vial #6.

Setting up method

- 1) Select “file”, “new”, “method”.
- 2) For “analysis” choose “NPOC/TN” and name the method. For example “LVS031215” for stream samples or “LVPPT031215” for precipitation samples.
- 3) Browse for the NPOC calibration curve you just created and open.
- 4) You can go through the “injection parameters wizard” or choose to skip this option. **Do not** check “USEPA” or “History Log”.
- 5) Repeat these steps to locate and select the TN calibration curve.

Setting up sample table

- 1) From blank sample table with cursor on row 1, select “insert”, “auto generate”, choose method you just created, select 3 samples for the “number of samples” box, make sure “start vial” is 1, change sample name to “DI”, and click “next”.
- 2) Click “next” on the “Perform Calibrations” page and “Insert Control Samples” page without changing any options.
- 3) From the “Sparging / Acid Addition” page, make sure to change the “vial” column related to the 3 DI samples to read “1”. This will tell the instrument to pull 3 samples of DI from vial #1. Click “OK”.
- 4) From the next blank row, choose “insert”, “calibration curve”, choose NPOC curve you recently set-up for the run, click “open” and change the vial numbers column to “2,2,3,3,4”. Click “OK”.
- 5) From the next blank row, choose “insert”, “calibration curve”, choose TN curve you recently set-up for the run, click “open” and change the vial numbers column to “4,5,5,6,6”. Click “OK”.
- 6) From the next blank row, choose “insert”, “auto generate”, select the method you just created and add the number of samples you will run and the “start vial” number. Clear the “sample name” field and click “OK”.

- 7) Each row will be assigned a specific sample and must be named according to the sample site and date. For example "LO031215" refers to Loch.O from Dec. 15, 2003. Be sure to name all samples, washes and checks in the empty "sample name" column.
- 8) Along with field blanks, field dupes, and an occasional lab dupe (every 20 samples), be sure to insert a di (wash) and check (3 ppm C/1 ppm N) after every 10 samples. Also be sure to end the run with a wash and check.
- 9) Once the sample table has been set-up and everything looks in place, hit the "start" button, which looks like a traffic light signal. Be sure to check the "external acid addition" **off**.

Shimadzu TOC-L Procedures (*Discontinued in 2017*)

The Shimadzu TOC-L analyzer began use in the NREL EcoCore in 2011. From January 2017, LVWS samples for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) are analyzed by the USFS Rocky Mountain Research Station lab as one of our routine weekly analyses. The directions below are a quick start guide for using the Shimadzu TOC-L to analyze water samples for DOC and TDN.

- Take standards out of fridge and allow them to reach room temperature while setting up the machine
- Turn on machine (power button; not “Start” button)
- Connect to machine through software on laptop
 - This enables machine to warm up everything and go through its check cycles
- Create calibration curve:
 - For NPOC
 - System: TOC-TN
 - Normal
 - Dilution from standard solution
 - Analysis: NPOC
 - Clear default name and ID
 - Calculation method: linear regression
 - Uncheck zero shift
 - Check multiple injections
 - Name the file: DATE_LVWS_NPOC
 - Accept defaults on page 4, click next
 - First calibration point: zero concentration
 - 0,0; 10,1; 10,2; 10,3; 10,5; 10,10
 - Injection volume 100 ul
 - Accept defaults on page 6
 - For TN
 - System: TOC-TN
 - Normal
 - Dilution from standard solution
 - Analysis: TN
 - Clear default name and ID
 - Calculation method: linear regression
 - Uncheck zero shift
 - Check multiple injections
 - Name the file: DATE_LVWS_TN
 - Accept defaults on page 4
 - First calibration point: zero concentration
 - 0,0; 5,0.5; 5,1; 5,2; 5,3; 5,5
 - Injection volume 100 ul

- Accept defaults on page 6
- Create method:
 - System: TOC-TN
 - Analysis: NPOC/TN
 - Manual dilution=1
 - Number of determinations=1
 - Clear default name and ID
 - Name the file: DATE_LVWS_NPOC_TN
 - For NPOC
 - Find calibration curve for NPOC
 - Accept defaults on pages 4 and 5
 - For TN
 - Find calibration curve for TN
 - Accept defaults on pages 4 and 5
 - Pharmaceutical on page 6=none
- Create sample table:
 - Right click → insert multiple samples
 - From today's method
 - # samples=68
 - No sample name, no sample ID
 - Uncheck insert calibration curves/control samples
 - Insert 3 qwater samples, all from vial 1
 - Insert std 5/2 in vial 2
 - Insert standard curve NPOC
 - Insert standard curve TN
 - 0 mg/L all come off vial 3 (Qwater)
 - Rest of them pull off vial 0 (10/5 standard)
 - Fill out each row with sample name, click on carousel to make sure vial # is correct
 - Run std 5/2, then qwater, then std 10/5, then di
 - Run 12 samples, then one lab dupe of last of the 12
 - Then run a std, then a qwater
 - Repeat this process till all samples are entered in the sample table
- After last lab dupe of last batch of samples, run qwater, then std 5/2, then std 10/5, then di
- Fill vials with samples and put in tray
 - Use ~15 ml of sample for each vial, more for qwater vial 3 (almost full)
- Make standards using acid washed glassware
 - Bottle 0: 10/5 std (200 ml bottle)
 - 5/2 std (1000 ml bottle)
 - Find standard concentration calculations recipe version 2 on desktop of laptop
 - **Take 30 seconds to empty the volumetrics
- Check big waste bottle on floor; dump if >1/2 full

- Dump and refill DI container in left side of machine; make sure it's mostly full
 - Use qwater if it was used to make standards
- Dump and refill DI container outside machine on left side of tray
 - Use qwater if it was used to make standards
- Make sure magnet is on top of carousel
- Check pressure of ultrazero air at tank; should be no less than 300 psi
- If software says machine is READY, click START
- Check shut down instrument after done
- Clean up:
 - Acid wash volumetrics and std bottles
 - Acid wash vials
 - Rinse, soak, air dry caps

Appendix J: LVWS Watershed Staff

The LVWS program staff is made up of a Principal Investigator, co-Principal Investigator(s), Program Manager, technicians, programmers, graduate students, undergraduate students, and collaborators.

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