

Standard Operating Procedure: Chemical Characterization of Surface Water

Arctic Inventory and Monitoring Network

Stream Communities and Ecosystems Monitoring Protocols

Lake Communities and Ecosystems Monitoring Protocols

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The main Narrative for the Protocol for monitoring Stream Communities and Ecosystems and Lake Communities and Ecosystems for the National Park Service's (NPS) Arctic Inventory and Monitoring Network (ARCN) is available from the NPS ARCN website (<http://science.nature.nps.gov/im/units/arcn>).

SOP: Chemical Characterization of Surface Water

Version 1.0 (November 2017)

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Introduction

This Standard Operating Procedure (SOP) describes the methods for collecting, filtering, and preserving stream and lake water samples for chemical analysis. This SOP is a component of both the Stream Communities and Ecosystems Monitoring Protocol (O'Donnell and Miller 2017a (in review)) and the Lake Communities and Ecosystems Monitoring Protocol (O'Donnell and Miller 2017b (in review)). Tasks associated with this SOP include (1) field preparations, (2) stream water sample collection, (3) lake water sample collection, (4) filtering and preserving water samples, and (5) sample storage and submission to laboratories.

Field Preparations

A wide array of sampling equipment is needed to characterize stream and lake water chemistry. Prior to the onset of the field season, project staff should inventory equipment and sample bottles to insure that there is enough equipment to complete scheduled sampling. Specific sample bottle types, filters, and associated sampling equipment are listed in Table 1.

The following tasks should be completed prior to conducting any field work:

- 1) All HDPE and amber glass sample bottles should be acid washed and cleaned prior to collecting samples. Project staff can make arrangements for all sample bottles to be washed by the Cooperative Chemical Analytical Laboratory (CCAL) at Oregon State University (<http://ccal.oregonstate.edu/>). As of 2017, CCAL charges \$2 per bottle for acid washing and cleaning.
- 2) Project staff should add laboratory tape to all sample bottles (125-mL amber glass, 500- and 250-mL HDPE) and sample syringes (60 cc fitted with 3-way stopcock). Tape should be wrapped all away around each bottle or syringe, as there needs to be enough space to write the date (MM/DD/YY), time (24-hour mode), site ID, and filter status (filtered/unfiltered) on the tape.
- 3) All equipment associated with the Geotech Peristaltic Pump should be checked and tested for functionality. Specifically, project staff should:
 - A) Charge the 12-volt battery for at least 24 hours and then test the battery to ensure it works and can hold a charge.
 - B) Check silicon tubing for areas of wear and tear, and replace any damaged tubing with a new 12 to 15-foot length.
 - C) Inventory the number of capsule filters and order more as necessary.

Table 1. Equipment list for collecting water samples.

Equipment Description	Vendor	Part Number	Purpose
125-mL Amber Glass Bottle	VWR	14235-746	DOC concentration
500-mL HDPE Nalgene Bottle	CCAL or VWR	16059-874	Filtered samples for dissolved constituents
250-mL HDPE Nalgene Bottle	CCAL or VWR	16059-872	Unfiltered samples for particulates
3-way stopcock with luer fittings	VWR	KT420163-4503	Attached to 60-cc syringe for DIC sampling
60 cc luer-lock syringe	VWR	15003-094	DIC concentration
Disposable Capsule Filters (0.45 micron)	Geotech	73050004	Filtering water samples
Silicon Tubing (Size 15)	Geotech	77050000	Tubing for collecting and filtering water samples
Geopump 2	Geotech	91352123	Peristaltic pump used to collect and filter water samples
GF/F Glass Microfiber Filter	VWR	28497-958	Filter for collecting chlorophyll a samples
1000-mL Nalgene Filtering Flask	VWR	29417-048	Flask for filtering chlorophyll a samples
Forceps	VWR	89259-954	Handling chlorophyll a filters
Magnetic Filter Funnels	VWR	28143-548	Funnel for filtering chlorophyll a
Nalgene Vacuum Hand Pump	VWR	54903-808	Pump for manually filtering water or chlorophyll a samples
General Purpose Tape	VWR	89097-990	tape for labeling sample bottles

Note: Vendors can be accessed via the following websites: VWR International (<https://us.vwr.com/>) and Geotech Environmental Equipment, Inc. (<http://www.geotechenv.com/>). CCAL = Cooperative Chemical Analytical Laboratory at Oregon State University (<http://ccal.oregonstate.edu/>)

Surface Water Sample Collection

All stream sampling locations have been identified using GPS coordinates as reported in prior reports (O'Donnell et al. 2015a), peer-reviewed publications (O'Donnell et al. 2016), and the monitoring protocol narrative (O'Donnell and Miller 2017a (in review). Lake study sites have been identified in the Lake Communities and Ecosystems monitoring protocol (O'Donnell and Miller 2017b), based on pilot studies conducted in 2013-2014 (O'Donnell et al. 2015b). For each chemical constituent, CCAL

has provided a minimum and recommended volume of sample needed for analysis <http://ccal.oregonstate.edu/qaqc>). (Table 2).

Table 2. Volume requirements for CCAL analyses.

	Minimum Volume (mL)	Recommended Volume (mL)	Filtered or Unfiltered
Alkalinity	125	250	unfiltered
Anions - Chloride, Sulfate	30	50	filtered
Dissolved Organic Carbon	50	70	filtered
Total Organic Carbon	50	70	unfiltered
Cations, Dissolved – Na, K, Ca, Mg:	40	50	filtered
Nitrogen –			
Total Dissolved Nitrogen:	50	100	filtered
Total Nitrogen:	50	100	unfiltered
Grouped Analyses –			
Ammonia,			filtered
Nitrate + Nitrite,			filtered
Ortho Phosphorous			filtered
Silica:	30	60	filtered
Phosphorous –			
Total Dissolved Phosphorous:	55	110	filtered
Total Phosphorous:	55	110	unfiltered

Stream Water Sampling

The following steps describe the tasks associated with collecting, filtering, and preserving stream water samples from all study sites:

- 1) Upon arrival at the designated sampling location, set-up the Geotech Pump. This involves:
 - A) Plug pump into 12-volt battery
 - B) Connect silicon tubing to peristaltic pump
 - C) Attach 0.45-micron disposable capsule filter to one end of the silicon tubing.
 - D) Insert the other end of the silicon into the stream water, approximately 25-50 cm below the stream surface in a well-mixed location. The designated sampling locations are at least three stream-widths distance above or below any confluences.

- 2) Prior to collecting any samples, run at least two liters of sample water through the capsule filter. This should take between 3-5 minutes, depending on the flow rate of the peristaltic pump.
- 3) Using a fine-tipped Sharpie, label all sample bottles with date (MM/DD/YY), time (HH:MM), Site ID, and filter status (filtered/unfiltered).
- 4) Once two liters have run through the capsule filter, the first water sample can be collected.

Lake Water Sampling

Lake water is collected at two depths: one sample approximately 0.5 m below the lake surface in the epilimnion, and one sample collected at a depth below the thermocline in the hypolimnion. If the lake is well-mixed upon arrival, a single sample can be collected from the epilimnion. For the epilimnion sample, follow the same steps as described above for stream water sampling.

For collection of the hypolimnion, follow these steps:

1. Determine the approximate depth range of the thermocline after collecting temperature profile measurements, as described in SOP: *Field Measurements for the Lake Communities and Ecosystems monitoring protocol*.
2. Using a Van Dorn sampler, collect a water sample from a least one meter below the bottom of the thermocline.
3. Record the depth from which the sample was collected.
4. Collect filtered and unfiltered samples from Van Dorn sampler following procedures described below.

Filtering sample for dissolved nutrient and major ions

- 1) Collect a filtered water sample in the 500-mL HDPE Nalgene bottle. This sample will be analyzed for dissolved nutrients, base cations, and major anions. Follow these steps:
 - A) Rinse the bottle three times by adding 100-mL of sample water to bottle, cap and shake, empty, and repeat two more times.
 - B) After rinsing, fill sample bottle with water sample. Leave approximate $\frac{3}{4}$ to one inch of head-space to allow for volumetric expansion of sample upon freezing.
- 2) Cap sample and then place immediately on ice in a cooler.

Collecting filtered sample for dissolved organic carbon concentration

- 1) Next collect filtered water sample in 125-mL amber glass bottle. This sample will be analyzed for dissolved organic carbon (DOC) concentration. Follow these steps
 - A) Rinse the bottle three times by adding 25-mL of sample water to bottle, cap and shake, empty, and then repeat two more times.

- B) After rinsing, fill sample with water sample. Leave approximately $\frac{3}{4}$ inch of head-space. DOC samples should not be frozen, as glass can break upon freezing.
- 2) Cap sample and then place immediately on ice in a cooler.

Collect unfiltered sample for total nitrogen, phosphorus, and alkalinity

- 1) Before rinsing or collecting an unfiltered sample, remove the disposable capsule filter from the end of the silicon tubing.
- 2) Then, insert silicon tubing into 250-mL HDPE Nalgene bottle to begin the sampling process:
 - A) Rinse the bottle three times by adding 50-mL of sample water to bottle, cap and shake, empty, and then repeat two more times.
 - B) After rinsing, fill sample bottle with water sample. Leave approximate $\frac{3}{4}$ to one inch of head-space to allow for volumetric expansion of sample upon freezing.
- 3) Cap sample and then place immediately on ice in a cooler.

Collect unfiltered sample for dissolved inorganic carbon (DIC) concentration

- 1) DIC samples are collected using the 60-cc syringes with 3-way stopcocks.
- 2) Syringes should be rinsed three time using the following approach:
 - A) Submerge tip of syringe below the stream surface.
 - B) Draw approximately 20-mL of sample water into syringe.
 - C) Withdraw syringe from water, and then pull syringe plunger out to 60-mL mark.
 - D) Shake syringe to rinse, and then expel sample water out through the stopcock.
 - E) Repeat two more times.
- 3) Collect DIC sample using the following approach:
 - A) Submerge tip of syringe below the stream surface.
 - B) Draw approximately 60-mL of sample water into syringe.
 - C) Withdraw syringe from water and pull syringe plunger out as far as possible.
 - D) Hold syringe vertically, with stopcock pointing upward, and tap on syringe to force any bubbles up into headspace.
 - E) Using plunger, expel air out of stop-cock so that there is no head-space and no bubbles in syringe.
 - F) Rotate knob on stopcock to seal off sample in syringe.

- 4) Place sample on ice in cooler.

Collecting sample for chlorophyll a concentration

- 1) Rinse a 500-mL amber HDPE bottle three times with sample water by dipping in stream, capping, shaking and emptying.
- 2) Fill 500-mL amber HDPE bottle and cap until ready to filter.
- 3) Assemble magnetic filter funnel and flask.
- 4) Using forceps, place a GF/F filter on the filtering platform.
- 5) Connect Nalgene hand pump to filter flask.
- 6) Pour 250-mL (approximately half of sample in bottle) through filter funnel, and use hand pump to create vacuum.
- 7) Once all of the sample water passes through the filter funnel, pour the remaining sample water in the amber HDPE bottle into the filter funnel.
- 8) Again, use hand pump to create vacuum and draw water sample through funnel.
- 9) Once all of the water sample has passed through the funnel, use forceps to remove GF/F filter, wrap filter in aluminum foil.
- 10) Label aluminum foil with sample date (MM/DD/YY), sample time (HH:MM), site ID, and the volume of water filtered (e.g. 500 mL).
- 11) Place the chlorophyll- *a* sample (i.e. the filter in the aluminum foil) in a cooler on ice.
- 12) Discard the water in the Nalgene filtering flask.

Sample Storage and Submitting Samples for Chemical Analysis

Most chemical analyses are conducted through CCAL at Oregon State University. Storage and preservation techniques varies depending on the constituents of interest. Here we describe appropriate storage techniques of water samples upon returning from the laboratory, and the optimal time-frame for shipping and submitting samples for chemical analysis.

Prior to shipping water samples to CCAL, samples should be stored appropriate to preserve sample integrity. Filtered samples collected for analysis of dissolved nutrients and major ions should be frozen as soon as possible upon returning from the field. Unfiltered samples for analysis of total nutrients and carbon should also be frozen as soon as possible upon returning from the field. Upon returning from the field, DOC samples (stored in the 125-mL amber glass bottle) should be

immediately refrigerated. DOC samples should never be frozen, as freezing can result in a loss of DOC and alteration of DOC chemical composition (Fellman et al. 2008). Samples should be shipped overnight via FedEx to CCAL. DIC samples should also be refrigerated and then shipped to the CCAL for analysis within 48 hours of returning from the field.

When the project manager is ready to submit samples to CCAL, it is important to coordinate sample custody with the CCAL laboratory manager. The project manager should completely fill out the online sample submission form (Figures 1 and 2) and associated sample submission spreadsheet (Figure 3).

Sample Submission Form

For more information contact Kathy Motter (541-737-5120) or [email us](#).
 Ship samples to CCAL; OSU College of Forestry; 3015 Western Blvd; Corvallis, OR 97331 Attn:CCAL, Laura Hartley

- [Instructions for CCAL Sample Submission \(PDF\)](#)
- [Sample Collection, Handling and Preservation \(PDF\)](#)
- [Volume Requirements Worksheet \(Excel\)](#)
- [Sample Submission Form \(Excel\)](#)

Project *

Phone *

Sample Delivery Date *
 Year Month Day

To ensure timely processing, samples must be received by noon Thursday. [Contact CCAL](#) to make other arrangements.

Number of Samples *

Sample Submission ☐ Fresh ☐ Frozen

Investigator *

E-mail *

Payment Option - None -

Responsible Party

Figure 1. CCAL Submission form (screenshot from <http://ccal.oregonstate.edu/sample-submission-form>).

Additional Services (fees apply)

Are you submitting filtered samples? * ☐ Yes ☐ No

Do you want CCAL to filter your samples? * ☐ Yes ☐ No ☐ N/A

Do you need CCAL to provide prewashed filters? * ☐ Yes ☐ No

Do you need CCAL to provide prewashed bottles? * ☐ Yes ☐ No

If you supply your own bottles, would you like CCAL to wash them before we return them? * ☐ Yes ☐ No ☐ N/A

Other Instructions or Comments

Completed Worksheet File *

No file chosen

Upload a completed [sample submission worksheet](#). Samples must be filtered for some analyses. See [instruction sheet](#) [here](#).

Figure 2. Additional services on the CCAL Submission form.

CCAL Water Analysis Laboratory Sample Submission Form												
Investigator Name: _____												
Project: _____												
E-mail: _____												
Phone: _____												
Sample Delivery Date: _____												
Sample Name or ID	Barcode	Date Collected	Sample Type	Cold or Frozen?	pH	Alkalinity	Conductivity	Suspended Sediment	Dissolved Solids	Organic Carbon	Ammonia Nitrogen	

Figure 3. CCAL Submission spreadsheet.

Literature Cited

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NPS XXXXXX, Month Year (The Fort Collins Support Office will fill out this line for you)

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