AOS PROTOCOL AND PROCEDURE: SWC – WATER CHEMISTRY SAMPLING IN SURFACE WATERS AND GROUNDWATER

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See configuration management system for approval history.

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Change Record

REVISION	DATE	ECO #	DESCRIPTION OF CHANGE
A	07/21/2015	ECO-03068	Initial release of merged protocols (Supersedes NEON.DOC.000694, NEON.DOC.001190 and NEON.DOC.001219 which are now OBSOLETE)
B	02/16/2016	ECO-03483	• Baseline review from FOPs • Updated GW section
C	05/16/2016	ECO-03871	• Minor update to GW section – setting the depth of pump in the well
D	02/07/2017	ECO-04367	• 2016 updates following FOPS training and reviews • Updated template • River stationID changed to 'c0', no longer 'rs' • Updated shipping info and data entry • Updated field replicate strategy • Titration replicates on ALK only. Lake ALK/ANC only conducted at buoy station(s) • GW ANC not collected • Updates to Gran titration instructions • Changes to under ice sampling
E	01/10/2018	ECO-05285	• Conductivity not needed on shipping manifest • Clarification that grid side of filter is down for POM • Added instructions for titration in sites with pH > 8.1 • Added additional methods for groundwater sampling based on yield of well • Added instructions for partial sample collection priorities
F	04/29/2019	ECO-06084	• D18/19 needle sampling method added • Groundwater prioritization updated • Groundwater filtering in field added • Groundwater pH in field added • Updated label size to match ASI and SDG sizing • Added titration upload steps • Add Van Dorn
G	11/04/2019	ECO-06280	• Update to new format • ANC only collected monthly • Updated titration cartridges
H	12/17/2021	ECO-06712	• Updated GW sections: added suggestions for co-scheduling with water clarity, directions on sensor

			positioning, additional pre-field guidance, data examples, recording low-flow water level during purge, and post-field data check • Remove GW and SW PCN sampling • Updated to new template
J	12/19/2022	ECO-06924	• Added information to capture the addition of field and lab blanks for general chemistry.
K	01/02/2025	ECO-07103	• Use handheld pH to collect pH measurement if multisonde pH probe is not operating properly. • Included information on when to do a 3-point pH calibration for field pH measurements. • Change in ALK/ANC bottles to amber glass with phenolic lined cap • Change in RAW sample bottles from 250 mL to 500 mL • Replace groundwater bailer method with use of peristaltic pump. Update groundwater sampling decision tree. • For SI records, use primary stationID (i.e. ss) • Updated to template NEON.DOC.050006 Rev M

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1 OVERVIEW

1.1 Background

This document describes the required protocols for conducting field sampling of water chemistry in lakes, non-wadeable rivers, wadeable streams, and groundwater. Water chemistry involves both the physical properties of water, as well as the substances within the water. It is influenced by a multitude of factors such as local geology, rainwater chemistry, and other atmospheric and terrestrial inputs such as dust and allochthonous compounds. Water is a unique compound due to its physical properties such as bonding, electronic structure, and chemistry. Its structure imparts a fundamental ability to hold chemical constituents. Further, the character of water can change as a function of physical and biological processes, namely retention, redox reactions, evaporation and adsorption, and metabolism. Thus, water chemistry varies spatially and temporally, depending on the watershed characteristics, primary surface and sub-surface hydrologic flowpaths, and the turnover time of the water. The character of the water chemistry allows one to determine the quality of a water body, the influence on biotic assemblages, and the overall ecosystem function and health.

Lake, stream, and ground water chemical parameters include concentration, load, and yield. Concentration is the amount of a constituent in a volume of water (e.g., mg/L). Load is the total amount of a constituent transported per unit time:

$$L = CQ$$

Where: L = Load (mg/s)

C = Concentration (mg/L)

Q = Discharge (L/s)

Loads are typically calculated on an annual basis (e.g., Kg/year). Constituent yield is the transported load per unit of drainage area (e.g., Kg/Ha/year), and is useful in comparing loads from watersheds of differing sizes.

Water chemistry provides valuable information to help inform scientists, managers, and decision makers about the response of the aquatic ecosystem to natural and anthropogenic changes. Therefore, characterizing lake and stream water chemistry can provide an early warning sign of ecosystem degradation resulting from contaminant inputs, nutrient additions, sediment runoff, and overuse of the resource (Nevers & Whitman, 2007). Sources of such impacts may be far-ranging and include atmospheric deposition, contamination from the watershed, industrial or residential development, waste disposal, water level control, mining, herbicide use, timber production, building of dams and levees, and non-native species invasions (Nevers & Whitman, 2007). Aquatic biota can tolerate small changes in chemistry; however, large shifts in chemistry can have dramatic effects on the biotic community structure and function through processes such as nutrient uptake and retention. Long-term observations provide an effective means of keeping track of impacts and ecological status (water quality).

1.2 Scope

This document provides a change-controlled version of Observatory protocols and procedures. Documentation of content changes (i.e., changes in particular tasks or safety practices) will occur via this change-controlled document, not through field manuals or training materials.

1.2.1 NEON Science Requirements and Data Products

This protocol fulfills Observatory science requirements that reside in NEON's Dynamic Object-Oriented Requirements System (DOORS). Copies of approved science requirements have been exported from DOORS and are available in NEON's document repository, or upon request.

Execution of this protocol procures samples and/or generates raw data satisfying NEON Observatory scientific requirements. These data and samples are used to create NEON data products and are documented in the NEON Scientific Data Products Catalog (RD[03]).

1.3 Acknowledgments

The surface water component of this protocol is derived from the United States Geological Survey, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water Resources Investigations, Book 9, Chapter A4, Version 2.0, 9/2006.

The groundwater component of this protocol is derived from the Environmental Protection Agency Report: Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures (Puls, R.W., and Barcelona, M.J., 1996, Report EPA/540/S-95/504) and the United States Geological Survey, National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey TWRI Book 9, Chapter A4, Version 2.0, 9/2006), and the laboratory of Dr. George Kling, University of Michigan.

The laboratory component of this protocol is derived from the U.S. Geological Survey Techniques of Water Resources Investigations, Book 9, Chapter A6., sec 6.6, Version 2.0, 9/2006 Chapter A6.6, Version 4.0, 9/2012.

2 RELATED DOCUMENTS AND ACRONYMS

2.1 Applicable Documents

Applicable documents contain higher-level information that is implemented in the current document. Examples include designs, plans, or standards.

AD[01]	NEON.DOC.004300	EHS Safety Policy and Program Manual
AD[02]	NEON.DOC.004316	Operations Field Safety and Security Plan
AD[03]	NEON.DOC.000724	Domain Chemical Hygiene Plan and Biosafety Manual
AD[04]	NEON.DOC.050005	Field Operations Job Instruction Training Plan
AD[05]	NEON.DOC.004104	NEON Science Data Quality Plan

2.2 Reference Documents

Reference documents contain information that supports or complements the current document. Examples include related protocols, datasheets, or general-information references.

RD[01]	NEON.DOC.000008	NEON Acronym List
RD[02]	NEON.DOC.000243	NEON Glossary of Terms
RD[03]	NEON.DOC.002652	NEON Data Products Catalog
RD[04]	NEON.DOC.001271	AOS/TOS Protocol and Procedure: DMP – Data Management
RD[05]	NEON.DOC. 002906	Datasheets for AOS Protocol and Procedure: SWC – Water Chemistry Sampling in Surface Waters and Groundwater
RD[06]	NEON.DOC.003282	NEON Protocol and Procedure: SIM – Site Management and Disturbance Data Collection
RD[07]	NEON.DOC.002792	AOS Protocol and Procedure: DEP – Secchi Disk and Depth Profile Sampling in Lakes and Non-Wadeable Streams
RD[08]	NEON.DOC.001646	General AQU Field Metadata Sheet
RD[09]	NEON.DOC.001152	NEON Aquatic Sample Strategy Document
RD[10]	NEON.DOC.004257	Standard Operating Procedure: Decontamination of Sensors, Field Equipment, and Field Vehicles
RD[11]	NEON.DOC.001197	AOS Protocol and Procedure: BAT – Bathymetry and Morphology of Lakes and Non-Wadeable Streams
RD[12]	NEON.DOC.004362	NEON Preventive Maintenance Procedure: AIS Groundwater Level Sensor
RD[13]	NEON.DOC.001199	AOS Protocol and Procedure: SDG – Surface Water Dissolved Gas Sampling
RD[14]	NEON.DOC.001886	AOS Protocol and Procedure: ASI – Stable Isotope Sampling in Surface and Ground Waters
RD[15]	NEON.DOC.003044	AOS Protocol and Procedure: AMC – Aquatic Microbial Sampling
RD[16]	NEON.DOC.005224	AOS/TOS Protocol and Procedure: SCS – Shipping Ecological Samples and Equipment
RD[17]	NEON.DOC.005277	AOS Protocol and Procedure: GAG – Staff Gauge

2.3 Acronyms

Acronym	Definition
A/R	Acid-rinsed
ALK	Alkalinity
ANC	Acid Neutralizing Capacity
ASR	Analytical Services Request
C/B	Cleaned and burned
^oC	Degrees Celsius
DI	Deionized
DO	Dissolved Oxygen
FIL	Filtered Chilled
GF/F	Grade F Glass Fiber Filter
GW	Groundwater
H_2SO_4	Sulfuric acid
ha	Hectare
HDPE	High-density polyethylene
kg	Kilogram
L	Liter
lb/in	Pounds per inch
m	Meter
M	Molar
m^3	Cubic meter
mg	Milligram
mg/L	Milligrams per liter
meq/L	Milliequivalents per liter
mL	Milliliter
µS/cm	Microsiemens per centimeter
mph	Miles per hour
MAD	Maximum Allowable Drawdown
N	Normal
OW	Observation Well
P&P	Procedure and Protocol
PSI	Pounds per square inch
PPE	Personal Protective Equipment
RAW	Raw Untreated
s	Second
SOP	Standard Operating Procedure
SPC	Specific Conductance
µS/cm	Microsiemens per centimeter
USGS	United States Geological Survey

2.4 Definitions

Active Layer: The ground layer above the permafrost that seasonally freezes and thaws.

Alkalinity: The buffering capacity of a water body, or the ability of solution to neutralize acids to maintain a fairly stable pH, which is important for agriculture, wastewater, contamination determination, ecosystem health etc. Good water buffers include compounds such as bicarbonates, carbonates, and hydroxides, which combine with H^+ ions to prevent acids from building up in a solution.

Acid Neutralizing Capacity (ANC): Measure of the overall (total) buffering capacity of water or the ability to neutralize acid and maintain a constant pH. Acid neutralizing capacity is similar to alkalinity, but is measured on an unfiltered water sample, rather than a filtered one.

Conductivity: A measurement of the electrical conductance per unit distance in an aqueous solution.

Depth to Water Table: Measurement from top of the PVC well casing to the water table.

Epilimnion: Top layer of water of a stratified lake, denoted by highest temperatures and least dense water in the summer.

Fulcrum: Software tool used to create NEON electronic data entry applications.

Headspace: A gaseous space above a closed liquid sample.

High Yield Well: Groundwater wells with a recharge at a rate greater than 100 mL/min.

Hydrograph: A diagram depicting the change in discharge (m^3) over a given time (s).

Hypolimnion: The dense bottom layer of a stratified lake that sits below the thermocline. This layer is denoted by cooler summer temperatures and slightly warmer winter temperatures relative to the Epilimnion.

Low-yield Well: Groundwater wells with a recharge at a rate less than 100 mL/min.

pH: A measure of the acidity or basicity of an aqueous solution.

Recharge Rate: The rate at which the well water is replenished in a well during pumping.

Sample Depth: Measurement from top of PVC to the inlet at the top of the QED pump.

ServiceNow: Software tool used for problem/incident tracking and resolution.

Specific Conductance: The conductivity measurement at 25°C.

Thalweg: The deepest part of a stream channel.

Thermocline: The vertical section of the lake where the rate of decrease in temperature with increasing depth is greatest. The denser and cooler layer below the thermocline is defined by the hypolimnion. The warmer upper layer is termed the epilimnion.

Total Depth of Well: Measurement from top of PVC to bottom of the well.

Water Column Height: Measurement from top of water to the bottom of the well.

3 METHOD

The field protocol used by NEON for collecting **surface water** chemistry samples follows the general requirements set forth by the 2011 USGS National Water-Quality Assessment (NAWQA) Program and the Arctic LTER standard operating procedures (SOP). The field protocol used by NEON for collecting **groundwater chemistry** samples in small (2-in diameter) shallow (<100 ft depth) groundwater observation wells follows the general procedure for minimal drawdown sampling detailed by EPA report Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures (Puls and Barcelona, 1996). Sample handling and preparation portions of this protocol follow the general requirements set forth by the USGS National Water-Quality Assessment (NAWQA) Program (USGS 2006) the Quality-control design for surface-water sampling in the National Water-Quality Assessment Program (USGS 1997). This protocol describes the collection, field processing, preservation, and storage (if applicable) of total and dissolved nutrients samples, as well as anions, cations, and general chemistry (i.e., conductivity and pH). Additionally, samples are collected for alkalinity and acid neutralizing capacity (ANC) and are measured at the Domain Support Facility to reduce the error associated with changes in the chemical composition of a sample due to chemical dissolution or precipitation as well as the loss of CO_2.

The sampling strategy for surface water is specific to the type of waterbody. The strategies for sampling wadeable streams, non-wadeable streams (i.e., rivers), lakes, and groundwater are outlined below.

The majority of the NEON **wadeable stream** sites are shallow and narrow, rendering the use of isokinetic (i.e., sampling at same velocity as the stream) samplers for depth-integrative sampling impractical. Thus, the following protocol outlines the use of a dip sampling method in the main section of streamflow (i.e., thalweg). This method assumes the stream channel is completely mixed. In streams, the water chemistry sampling location should be located, when possible, approximately 1 meter downstream of the downstream sensor set (sensor set 2), so that the sensor measurements can be validated with stream water chemistry samples.

In **lakes and rivers**, sampling occurs 5 m from the buoy (if sampling from a boat) and at the buoy location for dock-mounted buoys. In lakes and rivers, sample collection depends on lake depth and stratification, as detailed below (Figure 12). For all lakes and rivers, one sample is taken at 0.5 m below the surface of the water at the buoy location. If the lake is stratified at the time of sampling, an additional sample will be collected from the hypolimnion at the buoy. Note that if lake inflow and outflow streams are present, samples are collected just downstream of the inflow and outflow infrastructure, following the wadeable stream sampling design.

Groundwater samples are collected at all types of aquatic sites. Samples are limited in both bouts per year and number of wells sampled due to current limitations in the budget to support higher resolution sampling. For **groundwater** sampling, samples are budgeted on a basis of an average of one sample per well per year at each site, for a total of 8 samples per year per site. **Due to the limited number of samples available, a subset of 4 wells will be sampled twice per year at all sites with greater than 4 groundwater wells (Table 14).** Three wells will be sampled twice per year at sites that only have 3 wells

(TOMB, BLWA, and WALK), for a total of 6 samples per year per site. For rivers and wadeable streams, the four sampling wells are selected in an attempt to cover all the following categories: upstream, downstream, right bank, and left bank. Preference is also given to wells that are closer to the surface water chemistry sampling locations. For lakes, the four sampling wells are selected with two on the inflow side and two on the outflow side of the lake. Consistent sampling of the same four wells will allow for evaluation of seasonal responses in groundwater constituent concentrations. Periodic changes to the selected subset of wells may occur throughout the life of the Observatory and are guided by various parameters (i.e., changes in hydrologic conditions (dry wells, changes in hydrologic flow paths) or infrastructure (damaged wells)).

Standard Operating Procedures (SOPs) of this document provide detailed step-by-step directions, contingency plans, sampling tips, and best practices for implementing this sampling procedure. To properly collect and process samples, field technicians **must** follow the protocol and associated SOPs. Use NEON's problem reporting system to resolve any issues associated with implementing this protocol.

The value of NEON data hinges on consistent implementation of this protocol across all NEON domains, for the life of the project. It is therefore essential that field personnel carry out this protocol as outlined in this document. In the event that local conditions create uncertainty about carrying out these steps, it is critical that technicians document the problem and enter it in NEON's problem tracking system.

Quality assurance is performed on data collected via these procedures according to the NEON Science Data Quality Plan (AD[05]).

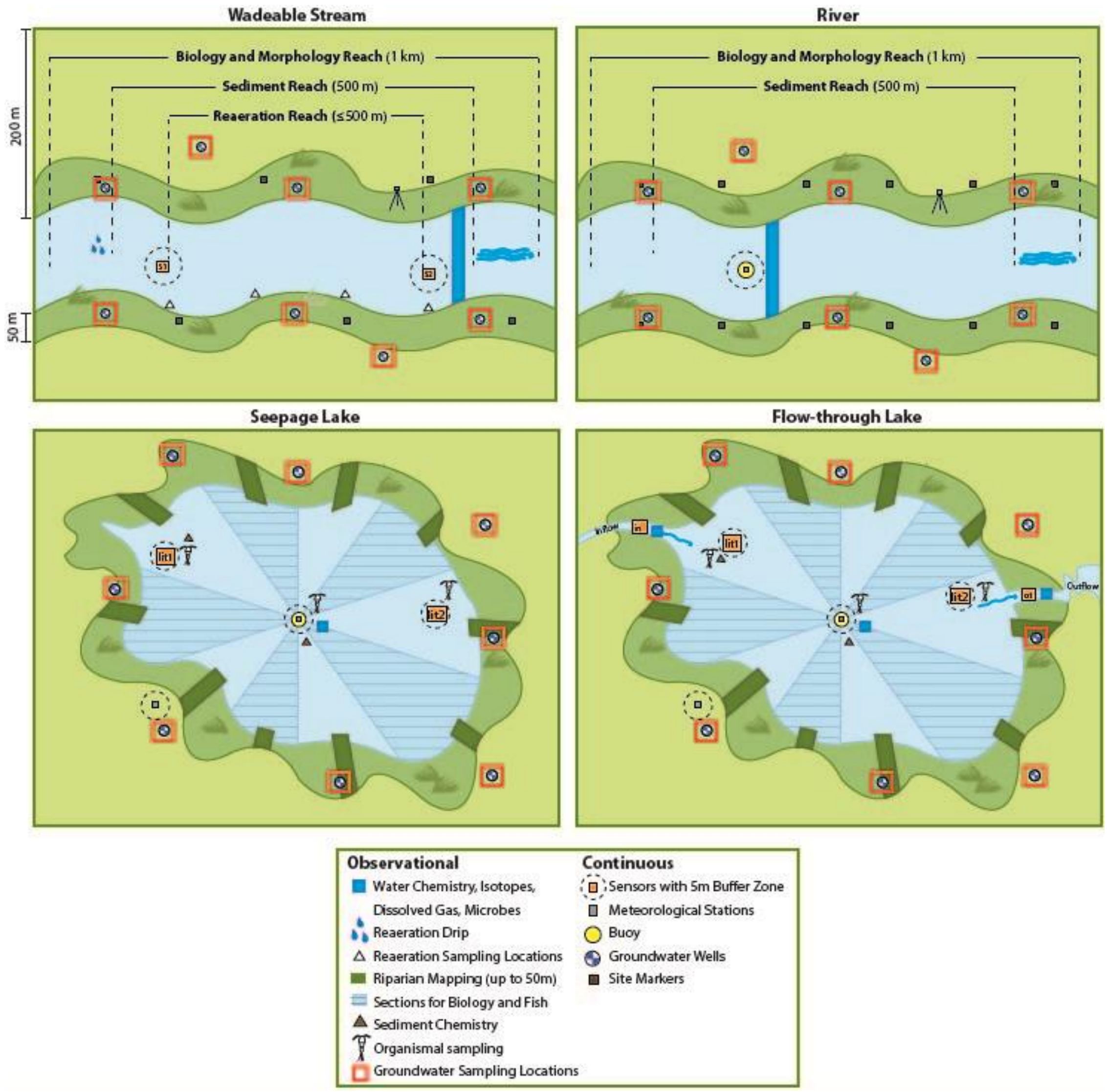


Figure 1. Generic site layouts for wadeable streams, rivers, and lakes surface water and groundwater sampling locations. Seepage lakes are lakes with no true inflow and outflow, while flow-through lakes have a true inflow and outflow.

4 SAMPLING SCHEDULE

4.1 Sampling Frequency and Timing

When applicable, chemistry samples should be collected on Tuesday to coincide with other National chemistry sampling efforts. Sample timing is described below and should follow site-specific timing guidelines found in the Domain Specific Sampling Design documents (**Table 14**).

Wadeable stream and river water chemistry sampling occurs up to 26 times per year, with 12 monthly samples and 14 flow-weighted samples. **Lake** water chemistry samples are collected 12 times per year (approximately monthly and during shoulder seasons to capture ice-on and ice-off events). **Groundwater** chemistry samples are collected twice per year from a subset of wells, selected on a site-by-site basis. Groundwater chemistry samples shall be collected within +/- 2 days of the surface water chemistry sampling event. Sample timing should follow site specific timing guidelines found in the Domain Specific Sampling Design documents (**Table 14**).

Table 1. Sampling frequency for Water Chemistry Sampling in Surface Waters and Groundwater procedures on a per SOP per plot type basis.

SOP	Site Type	Bout Duration	Bouts Per Year	Remarks
SOP B	Stream/ River	1 day	26	Sampling dates are synchronized with the Staff Gauge, Surface Water Dissolved Gas, and Aquatic Stable Isotope protocols. Surface water aquatic microbial samples are collected monthly (streams) and bimonthly (rivers). See Domain Specific Sampling Design documents for site-specific sampling dates (**Table 14**).
	Lake	1 day	12	Sampling dates are synchronized with the Staff Gauge, Surface Water Dissolved Gas, and Aquatic Stable Isotope protocols. Surface water aquatic microbial samples are collected bimonthly. See Domain Specific Sampling Design documents for site-specific sampling dates (**Table 14**).
SOP B.5	All - GW	1-2 days	2	Sampling dates are synchronized with Aquatic Stable Isotope and Surface Water Chemistry protocols. See Domain Specific Sampling Design documents for site-specific sampling dates (**Table 14**).

Scheduling Considerations

- Coordinate with aquatic stable isotope samples and surface water dissolved gas (surface water chemistry only) on each sampling event. For a subset of the surface water chemistry sampling events surface (monthly collections in streams and bimonthly in lakes and rivers), surface water microbial samples will also be collected. Ensure there is enough time to process all samples within the defined processing period.

It is NOT advised to collect field samples on Friday given shipping and support facility laboratory processing requirements.

- Lab and field blanks for nutrient analysis should be collected once per year **per site**.
- Lab and field blanks for general chemistry should be collected once per year **per domain.**
- **Replicates for external analysis:** NEON will quantify environmental variability by collecting additional surface water samples for external analysis **Table 2**.

Table 2. Summary of the number of blank and replicate bouts per year by analyte type and site type. Nutrient samples are .NUT and Gen Chem samples are .RAW and .FIL.

Type	Per Domain	Per Site	
		Stream/River	Lake
Blanks - Nutrients	-----	1	1
Blank - Gen Chem	1	-----	-----
Replicates – Nutrients	----	2	1
Replicates – Gen Chem	----	1	1

- Remember to account for these replicates when ordering consumable supplies.
- Replicate sample collection should be spread throughout the sampling season to capture different hydrological and biological conditions, where applicable.
- Field Science is not required to collect dissolved gas and stable isotope replicates on the same day as water chemistry replicate collection if there are timing/logistical constraints.
- In stratified lakes, replicate sampling events should occur during periods when the lake is NOT stratified.
- No replicates are collected from groundwater wells given limited volumes available.

Replicates for alkalinity laboratory processing: *One additional titration will be completed,* at a minimum of every 10 samples per site.

Field Work and Laboratory Processing*:* *After alkalinity and ANC samples are collected from a given location, the following points are critical with respect to timing:*

- Keep samples cold until they are processed in the laboratory.
- Process titration samples in the laboratory as soon as possible.
  - *(Ideally) Process titration samples within 24 h of collection.*
  - *(Required) Process titration samples within 72 h of collection.*

- ANC is only collected monthly.
- **Coordinating groundwater activities:** Due to the extremely sensitive nature of the groundwater sensor pressure readings to changes in position, sensors should be removed from the wells as infrequently as possible. The activities that require sensor removal include groundwater chemistry sampling, redevelopment, sensor swap, and quarterly maintenance including water clarity checks (see RD[12]). To minimize disturbance to the sensor, perform the quarterly water clarity checks on the same day as groundwater chemistry sampling when possible.

4.2 Criteria for Determining Onset and Cessation of Sampling

The timing of sampling allows researchers to assess aquatic biogeochemistry cycles, and therefore timing depends on the dominant driver(s) of nutrient flux within each system. Timing of sampling is site-specific and determined by rules developed using historical meteorological, physical, and environmental data ice on- ice- off dates, including lake levels, stratification, discharge, and riparian greenness (see RD[08]).

For example, **wadeable streams** with little or no flow during the summer dry-season or completely frozen streams during the winter are sampled more intensively during wet periods. Systems with a snowmelt-dominated or storm-dominated flow regime are sampled more intensively during time periods of high flow, when most of the nutrients are moving through the system and sampled sporadically during times of base flow. Stream systems heavily influenced by autumn leaf fall and winter rains are more heavily sampled in autumn and winter. **Rivers** are sampled approximately twice monthly with more intensive sampling occurring during high flow periods.

Lakes that stratify are sampled just before and after turnover in spring and autumn. Other higher intensity sampling may occur following a major storm event. Lakes that do not stratify and the remaining samples of stratified systems are taken approximately every month throughout the year when conditions allow. When sampling during the winter, the last winter sample shall be collected within 1 month prior to the annual average ice-off date. The first spring/summer sample shall be collected within 1 week after ice-off, assuming safe access conditions to the lake. Ice-off in lakes is defined by the permanent loss of ice in spring from the center of the lake. Ice-on in lakes is defined by the permanent ice coverage in the central part of the lake.

Groundwater sampling dates are guided by the hydrologic cycle of the system that the site is located in. Samples are targeted for the early spring when precipitation events begin to increase the groundwater flow rate towards the streams; and for late fall when the production of surface constituents have had sufficient time to infiltrate into the groundwater. The timing of these seasons is site dependent but will occur based on the streams' cumulative discharge with the first bout occurring when the stream is between 20-30% and the second bout occurring when the stream is between 70-80% of the predicted annual cumulative discharge based on historic discharge data. The timeframe for collecting samples will range from a 2-week to a 2-month time window in which a groundwater chemistry sampling event will be aligned with a surface water chemistry bout. This range is dependent on the discharge characteristics unique to each stream. Lake sites are sampled following a similar approach for timing and are sampled in the spring and fall with groundwater sampling dates linked to surface water chemistry sampling events. Date ranges for sampling are provided in the site-specific sample strategy document (**Table 14**).

4.3 Timing for Laboratory Processing and Analysis

For external laboratory analysis, general surface water samples should be chilled immediately and processed (i.e., filtered) as soon as possible, preferably within 4 hours, and shipped to the water chemistry lab within 24 hours, when possible, to ensure sample integrity. Samples must be shipped for external analysis within 72 hrs. Nutrient samples are frozen immediately and shipped for external analysis within 2 months.

For internal laboratory analysis, samples for alkalinity and ANC should be kept on ice or refrigerated at 4°C ± 2°C until you are ready to process. Samples must be brought to room temperature before processing. Laboratory analysis should be completed within 24 hours, when possible. Samples analyzed after the 24 hours window will be flagged. The maximum allowable time between sample collection and analysis is 72 hours.

4.4 Sampling Timing Contingencies

If surface water sampling must be rescheduled, reschedule as soon as possible. If sampling is:

1. Rescheduled within 14 days of the scheduled sampling date, proceed with the reschedule and no additional action is necessary.
2. Rescheduled > 14 days from the scheduled sampling date, submit an IS/OS Schedule Change Request.
3. Cancelled completely, submit an incident ticket.

If groundwater sampling must be rescheduled, reschedule as soon as possible. If sampling is:

1. Rescheduled within the sampling window specified in the site-specific sample strategy document (**Table 14**) AND it is rescheduled within 2 days of a surface water chemistry bout, proceed with the reschedule and no additional action is necessary.
2. Rescheduled outside of the site-specific sampling window or cannot be rescheduled within 2 days of a surface water chemistry bout, submit an IS/OS Schedule Change Request.
3. Cancelled completely, submit an incident ticket.

When unexpected field conditions require deviations from this protocol, the following field implementation guidance must be followed to ensure quality standards are met:

Table 3. Contingency decisions for Water Chemistry Sampling in Surface Waters and Groundwater.

Delay/ Situation	**Action**	**Outcome for Data Products**
Minutes - Days/ Unsafe weather conditions	If weather conditions deteriorate and conditions become unsafe: • **All sites** - e.g., approaching thunderstorm, • **wadeable stream** - rapid increase of water level in the stream, • **lake/non-wadeable stream** – e.g., becomes too windy (>20 mph) and has unsafe wave heights (e.g., >1 m) to hold the boat stationary over a sampling point), Action: 1. Return to shore and wait in a safe location for 30 min 2. If conditions improve, resume sampling 3. If not, return to the Domain Support Facility and sample at another time.	No adverse outcome.
Hours/ Wadeable stream, Unsafe for wading	If stream conditions are too high to safely wade into the thalweg: 1. **Sample from stream side, only if** the following are true: • the stream is well mixed due to the high flows, • AND you are not sampling in a dead zone or back eddy 2. **If you cannot sample,** reschedule.	No adverse outcome.
Hours/ Wadeable stream, ice-covered	If wadeable stream is: • ice-covered but still flowing: if safe, break ice and sample • has thick ice that is hard to break: bring a shovel, ice-chisel, or other tool • unsafe to break ice: move to a nearby sampling location that is safe and sample. If you sample > 10 m from sampling location, record alternate location information in Fulcrum app.	No adverse outcome.
Hours/ Lake frozen, navigable by boat	If the lake surface has a layer of ice on it, but you are able to safely navigate the boat through the ice, continue to sample as normal.	No adverse outcome.
Hours/ Lake frozen, safe to walk on	If the lake surface is frozen and safe to walk on (minimum of 15 cm thickness for walking and 20 cm thickness for use of UTV/snowmobiles, etc.): • make a hole in the ice and proceed with sampling.	No adverse outcome.
Hours/ Lake inflow and outflow in winter sampling	During winter, lake sites with inflow and outflow stream sampling locations should follow stream ice recommendations.	No adverse outcome.
Minutes - Hours/ Sediments stirred up or added chemical constituents	If sampling stirred up sediments or added chemical constituents to the water within the past hour: • Wait 5-10 minutes to allow the water to clear and disturbance to pass.	No adverse outcome.

Delay/ Situation	Action	Outcome for Data Products
Minutes- Hours – DI system broken	For site specific equipment – rinse sampling equipment with source water prior to sampling. For equipment shared across sites – purchase distilled water to rinse equipment, then rinse sampling equipment with source water prior to sampling.	Potentially reduced data quality.
Hours/ Not able to process water samples on site	If water samples cannot be processed on site (due to field conditions, time limits, etc.), collect water samples in two 4 L jugs, keep on ice, process as soon as possible. Requirements: 1. The filtration should be completed within 4 hours and no more than 6 hours. Data processed after 4 hours will be flagged. Samples must be kept cold (~4°C) and dark to reduce nutrient transformation. Water jugs must be shaken before sampling or filtration for RAW/POM samples to re-suspend particulates and homogenize water.	No adverse outcome.
Hours/Sampling location shallow or disturbed	If sampling location is too shallow or has been too disturbed to obtain a clean sample: • Sample in a nearby location where water is deep enough to obtain a clean, sediment free, sample. • If sampling in a new location, record alternate location with GPS and note in Fulcrum app.	No adverse outcome.
Hours/Multisonde pH probe not functioning properly	If multisonde pH probe is not operating properly during planned water chemistry collections, surface water field pH should be measured at the site using the handheld pH meter (freshly calibrated).	
Hours/ Low water	Low Water Situation Examples: • Low water levels rendering some habitat dry • Flow is so low that the stream appears to be a series of pools not connected by surface water Actions: 1. Continue sampling in the water chemistry sampling locations provided the sample bottle can be filled without disturbing sediments. Be sure to note the state of water level in the data collection app.	No adverse outcome.
Hours/ Wells dry during low flow	When sampling a groundwater well following the low-flow method, if the well goes dry at the lowest flow rates: If another well has water, sample the alternate well. Otherwise, purge the original well dry and plan to return within 24-48 hours to sample	No adverse outcome.

Delay/ Situation	Action	Outcome for Data Products
	via the low flow method. Contact Science to discuss the deviation in expected sampling method.	
Hours/ on site filtration not possible	If temperatures are below freezing and filtration equipment is not functional on site: Collect samples and filter in a sheltered area, such as the field vehicle or return to the Domain Support Facility for filtration.	No adverse outcome.
Days-Months/ Water body entirely dry or frozen	If the water body is entirely dry or frozen solid so there is no water to sample: 1. Complete Sampling Impractical Record for the primary stationID (i.e. ss for streams). 2. Reschedule sampling until water is available for sampling.	No adverse outcome.
Days-Months/ Groundwater when steam sampling not possible	If site conditions dictate that **stream** sampling is not possible due to the stream being dry: Then postpone the **groundwater-sampling** event until flow returns in the stream.	No adverse outcome.
Days-Months/ Groundwater pump freezing	If temperatures are below freezing and water in the **groundwater** pump discharge line is freezing: 1. Stop sampling. Complete Sampling Impractical. 2. Reschedule the sampling bout when ambient temperatures are above freezing and with surface water sampling. Since GW sampling occurs at most twice a year, the events should be timed with above freezing weather conditions.	No adverse outcome.
Days-Months/ Groundwater level below bottom of well	In some locations, the **groundwater** level will drop below the bottom of the well either seasonally (e.g., Taiga and Tundra sites) or in periods of drought, which are likely to occur at some point during the life of the Observatory. Under these conditions sampling of groundwater is not possible and the timing of the sampling bout or the wells to be sampled should be reevaluated by Science.	No adverse outcome.
Days-Months/ Standing water surrounding groundwater well	Though **groundwater** wells are generally sited for slightly elevated locations, times will occur when standing water surrounds the base of the well. For Tundra and Taiga locations, water may be collected up to 3 meters from the well using the needle method where active layer water is not exposed at the surface. For all other sites, postpone sampling until the ground near the base of the well is free of standing water.	No adverse outcome.

Delay/ Situation	Action	Outcome for Data Products
Days-Months/ Groundwater with seasonal permafrost thawing	For sites that have the "generation" **of groundwater** resulting from seasonal thawing of permafrost, Sampling is targeted for times when the permafrost is sufficiently thawed to allow for collection of groundwater samples.	No adverse outcome.
Damaged groundwater well	If a groundwater well is damaged (i.e., casing is broken internally) or bent: **Do not try to sample this well.** It is likely that the pump may get stuck inside the well due to the limited tolerance between the pump and well casing. If this condition is observed sample an alternate well and submit a trouble ticket for a new permanent well to be selected for sampling.	No adverse outcome.
Days-Weeks/Surface sampling reschedule	If surface water sampling must be rescheduled and can be rescheduled within 14 days of the originally scheduled sampling dates, reschedule event. No additional action is needed.	No adverse outcome.
Weeks/Surface sampling reschedule	If surface water sampling must be rescheduled but cannot be rescheduled within 14 days of the originally scheduled sampling, submit an IS/OS Schedule Change Request.	Potentially reduced data availability
Days-Weeks/ Groundwater sampling reschedule	If groundwater sampling must be rescheduled and can be within the sampling window specified in the site-specific sample strategy document and within 2 days of a surface water chemistry bout, proceed with the reschedule. No additional action is necessary.	No adverse outcome.
Weeks/ Groundwater sampling reschedule	If groundwater sampling must be rescheduled and cannot be rescheduled within the site-specific sampling window and within 2 days of a surface water chemistry bout, submit an IS/OS Schedule Change Request.	No adverse outcome.
Cancelled/Surface or groundwater	If surface or groundwater sampling is cancelled completely, submit an incident ticket.	Reduced data availability

4.5 Missed or Incomplete Sampling

Sampling according to the schedule is not always possible, and multiple factors may impede work in the field at one or more sampling locations in a given bout. For example:

- Logistics – e.g., insufficient staff or equipment
- Environment – e.g., deep snow, flooding, inclement weather, or
- Management activities – e.g., controlled burns, pesticide application

Instances such as those listed above must be documented for scheduling, tracking long-term sampling location suitability, and informing end users of NEON data availability. Some types of missed sampling bouts are due to events that should be recorded in the Site Management App; refer to the Site Management and Event Reporting Protocol for more detail (RD[06]).

Missed or Incomplete Sampling Terms

Terms that inform Missed or Incomplete Sampling include:

- **Protocol Sampling Dates**: Bout-specific sampling dates (Appendix C, **Table 14**).
- **Scheduled Sampling Dates**: Bout-specific sampling dates scheduled by Field Science and approved by Science. These dates coincide with or are a subset of the Protocol Sampling Dates.
- **Missed Sampling**: Incidence of *scheduled sampling* that did not occur. Missed Sampling is recorded at the same resolution as data that are ordinarily recorded.
- **Sampling Impractical**: The field name associated with a controlled list of values that is included in the data product to explain a Missed Sampling event – i.e., why sampling did not occur.
- **Rescheduled**: Missed Sampling is rescheduled for another time within the *protocol sampling dates*, resulting in no change to the total number of sampling events per year.

The documentation that must accompany missed sampling depends on the timing, subsequent action, and the audience appropriate for numerous scenarios (**Figure 2**). Additional site-specific guidance can be found in the Site Sampling Design documents (**Appendix D**).

Figure 2. The documentation to account for a Missed Sampling event. Blue diamonds contain decision making questions and blue rectangles indicate required actions. Missed Sampling events may also require a Data Quality flag and/or creation of a Site Management record.

To Report Missed or Incomplete Sampling:

1. Missed or Incomplete Sampling must be communicated to Science by a Service Now Incident if:
   a. Surface water sampling cannot be rescheduled within 14 days of the originally scheduled sampling dates (**Table 14**).
   b. Groundwater sampling cannot be rescheduled within the site-specific sampling window **and** within 2 days of a surface water chemistry bout.
2. For Missed Sampling that is Rescheduled, there are some cases that require approval by Science and Operations (**Figure 2**).
3. Consult **Figure 2** to determine required actions if scheduled activities are delayed or canceled. This protocol is the ultimate source of information should any discrepancy exist between this document and other summary materials – e.g., the 'Scheduled Field Activities – Delays and Cancellations' spreadsheet linked via the SSL.
4. Create a Fulcrum record for each Missed Sampling event in the field.
5. For each Missed Sampling record, the **Sampling Impractical** field must be populated in the mobile collection device (**Table 4**).
   a. For each **Sampling Impractical record, use the primary stationID (i.e., 'ss' for streams).**

Table 4. Protocol-specific Sampling Impractical reasons entered in the Fulcrum application. If more than one is applicable, choose the dominant reason sampling was missed.

Sampling Impractical reason	Description
High water velocity	High water velocity
Location dry	Location dry
Location frozen	Location frozen
Location snow covered	Location snow covered
Low-yield groundwater	Used when groundwater fails to return to the well within 48hrs of purge.
Other	Sampling location inaccessible due to other ecological reason described in the remarks

Water Chemistry sampling is scheduled to occur at all prescribed sampling locations according to the frequency and timing described in Section 4, Appendix C, and Table 14. Ideally, sampling will occur at these sampling locations for the lifetime of the Observatory (core sites) or the duration of the site's affiliation with the NEON project (gradient sites). However, sampling may be shifted from one location to another when a sampling location is compromised. In general, a sampling location is compromised when sampling becomes so limited that data quality is significantly reduced. If a sampling location is only temporarily impacted, following sampling contingency steps (**Table 3**). If the sampling location is believed to be permanently compromised, submit an incident ticket.

4.6 Estimated Time

The time required to implement a protocol will vary depending on a number of factors, such as skill level, system diversity, environmental conditions, and distance between sample plots. The timeframe provided below is an estimate based on completion of a task by a skilled two-person team (i.e., not the time it takes at the beginning of the field season). Use this estimate as framework for assessing progress. If a task is taking significantly longer than the estimated time, a problem ticket should be submitted. Please note that if sampling at particular locations requires significantly more time than expected, Science may propose to move these sampling locations.

Table 5. Estimated staff and labor hours required for implementation of Water Chemistry Sampling in Surface Waters and Groundwater. More time may be required at sites with multiple sampling stations, such as a stratified lake or a lake with inflows and outflows.

SOP	Estimated time	Suggested staff	Total person hours
SOP A.1: Preparing for Data Capture	0.5 h	1	0.5 h
SOP A.2: Preparing for Sampling	0.5 h	1	0.5 h
SOP A.3: Labels and Identifiers	0.5 h	1	0.5 h
SOP B: Field Sampling	1 h per bout (Streams) 2 h per bout (Lakes and Rivers) 8-10 h per bout (GW)	1-2	1 h per bout (Streams) 4 h per bout (Lakes and Rivers) 16 h per bout (GW)
SOP C.5: Titrations	0.75 h per sample	1	0.75 h per sample
SOP D: Data Entry and Verification	0.5 h per bout	1	0.5 h per bout
SOP E: Sample Shipment	0.75 h per bout	1	0.75 h per bout

5 SAFETY

This document identifies procedure-specific safety hazards and associated safety requirements. It does not describe general safety practices or site-specific safety practices.

Personnel working at a NEON site must be compliant with safe field work practices as outlined in the EHS Safety Policy and Program Manual (AD[01]) and Operations Field Safety and Security Plan (AD[02]). Additional safety issues associated with this field procedure are outlined below. If an employee witnesses any unsafe conditions or uncontrolled hazards that present an imminent danger, they should immediately take action to stop work and report such conditions to their manager. Employees must also report all workplace injuries, illnesses, incidents, or releases to the environment as soon as possible, regardless of the severity.

Activities in streams should only be performed when flow conditions are safe. Do not attempt to wade a stream where velocity x depth is ≥ 10 ft^2/s (0.93 m^2/s). For non-wadeable streams, field workers should consult site-specific safety plans for safety guidelines. When working around ice, refer to (AD[02], Section 10.3 Winter Water Safety. Do not attempt to walk on frozen lake if depth of ice is less than 6" (15 cm) or operate UTV or snowmobile on frozen lake if depth of ice is less than 8" (20 cm). Use caution and good judgment to carefully evaluate site conditions including ice strength. Local guidelines from natural resource officials, property owners or hosts, and domain managers should be consulted regarding work on ice, prior to deploying employees and equipment. Do not continue if the risk is too great.

Acid must be stored in acid-safe containment cabinets in compliance with the Domain Chemical Hygiene Plan and Biosafety Manual (AD[03]). Wear nitrile gloves and eye protection when dispensing acid.

In addition to standard safety training provided by NEON, the following safety requirements are sought:

1. Due to site-specific hazards that may be encountered, technicians may perform GPS positioning around the lake, and measurements for inflow and outflow, without dismounting from the vessel. In addition, technicians are required not to put hands and feet in waters where alligators are present and to make sure a safe distance from hazards is maintained.
2. All personnel must be wearing a personal flotation device prior to entering the boat.
3. All employees shall have access to a form of communication with other team members such as a two-way radio.
4. Technicians should be aware of any site-specific hazards and of the waters of that location (e.g., flooding, high velocity water, freezing, etc.).
5. Technicians should be aware of air and water temperatures and bring appropriate equipment and supplies (i.e., insulated waterproof gloves).

6. If personnel or loads will be on ice while performing their task for greater than 2 hours, all loads should be multiplied by 2 to determine safe ice thickness. Refer to (AD[02], Section 10.3 Winter Water Safety.
7. Access to Safety Data Sheet shall be available for work with chemicals associated with this protocol.

6 PERSONNEL

6.1 Training Requirements

All technicians must complete protocol-specific training as required in the Field Operations Job Instruction Training Plan (AD[04]). Additional protocol-specific required skills and safety training are described here.

Personnel shall be trained in making water chemistry measurements and associated safety procedures.

All personnel required to operate a boat shall be trained through a NEON Safety approved program. All others shall be aware of boating safety procedures.

All personnel are required to take the groundwater sampling test on the SharePoint training page.

6.2 Specialized Skills

Where applicable, personnel will be licensed to operate a boat and able to safely handle a motor and drive a boat.

7 STANDARD OPERATING PROCEDURES

SOP Overview

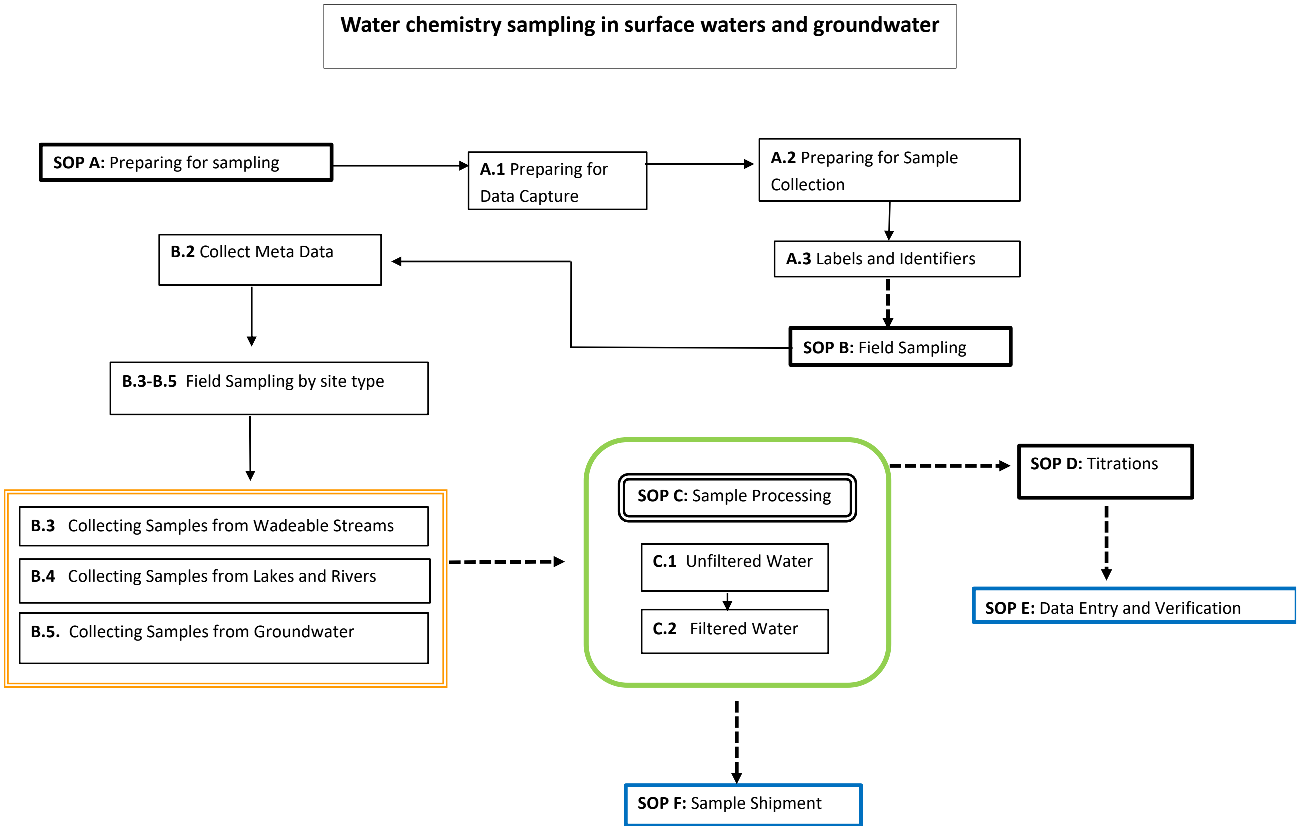


Figure 3. High level workflow diagram that visually shows how the Water Chemistry Sampling in Surface Waters and Groundwater SOPs are sequentially connected.

SOP A Preparing for Sampling

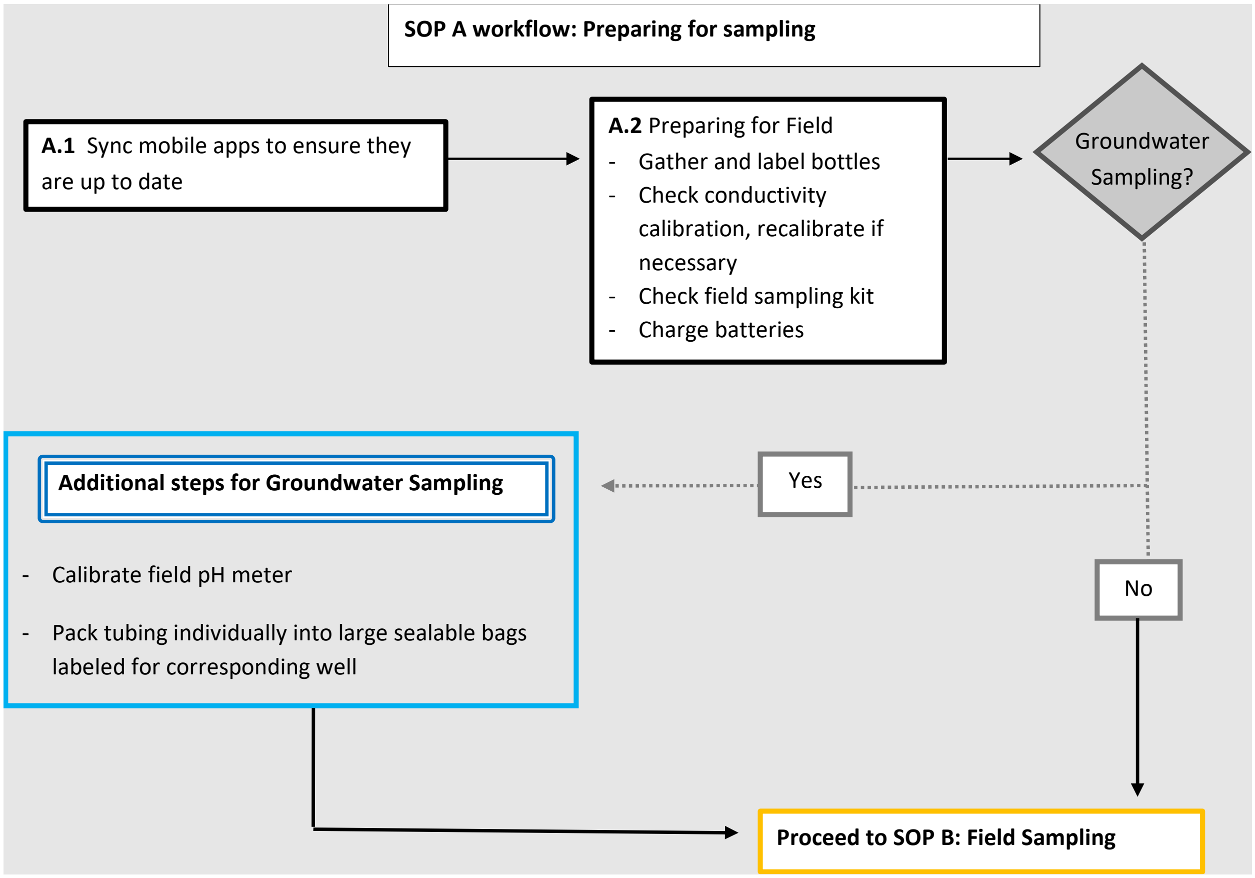


Figure 4. Workflow diagram of SOP A: Preparing for Water Chemistry Sampling in Surface Waters and Groundwater.

A.1 Preparing for Data Capture

Mobile applications are the preferred mechanism for data entry. Mobile devices should be fully charged at the beginning of each field day, whenever possible.

However, given the potential for mobile devices to fail under field conditions, it is imperative that paper datasheets are always available to record data. Paper datasheets should be carried along with the mobile devices to sampling locations at all times.

A.2 Preparing for Sample Collection

<u>**All Sampling Location Types**</u>

1. Check the water chemistry field sampling kit to make sure all supplies are packed and ensure all batteries are charged.

2. Check the hand-held conductivity calibration and recalibrate if necessary. We suggest the conductivity sensor should be calibrated monthly. See Conductivity Sensor User's Manual. Be sure when calibrating and using the conductivity meter that the holes at the top of the sensor are completely covered. (Note: DO will be calibrated every use, at the actual site). Maintain DO Sensor tip and/or refill electrolyte solution in tip on a monthly schedule. Pressure does not need to be calibrated.

3. Prepare the appropriate bottles and collection devices based on the type of water samples being collected (**Figure 5**, **Figure 6**). *Note: prepare 2 sets of bottles; the second set will be used as a backup.

    a. GWC: If low sample volume is expected for groundwater, plan to collect the FIL sample in a 250 or 500 mL bottle.

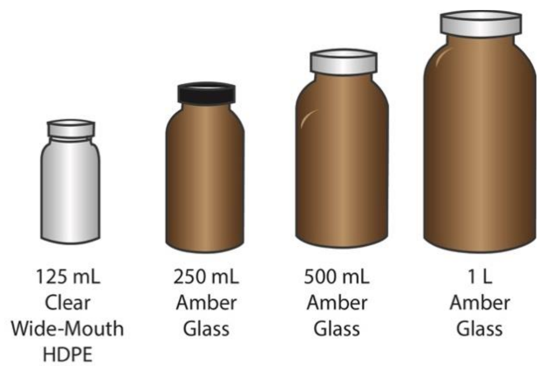


Figure 5. Water chemistry bottle types.

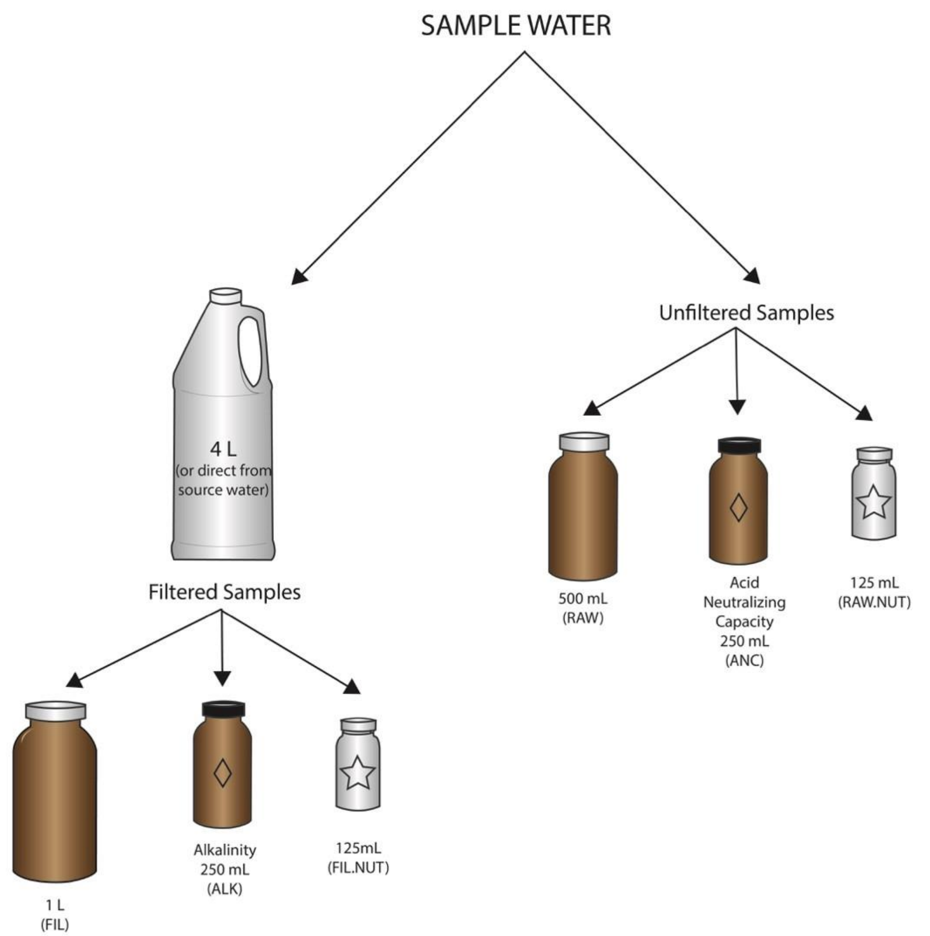


Figure 6. Flowchart of Water Chemistry Sample Collection and Filtration. A ◊ Indicates 250 mL, glass sample bottles with phenolic lined cap that remain at the Domain Support Facility for titration analysis. ☆ Indicates 250 mL HDPE, wide-mouth sample bottles that are frozen (-20°C) immediately. ANC is only collected monthly. Letters in parenthesis indicate the sample type that corresponds to the chemistry labels (see **Figure 8**).

4. **Additional steps if collecting Lab/Field Blanks – QC checks (Once per year per site for nutrient samples and once per year per domain for general chemistry (Table 7). Lakes should collect replicates during non-stratified periods.)**

Lab and field blanks are collected to capture potential contamination that may occur in the lab and field while collecting and processing samples. Always use lab grade DI-water.

a. **Lab blank (LB)** – Collected in the lab prior to leaving for the field. This should be done at the same time as filling the DI transport bottle that will be taken out to the field for the RAW and FIL field blanks.

   i. RAW Lab blank

1) Rinse a clean 125 mL HDPE (nutrients) and/or 500 mL amber glass (general chemistry) sample bottle(s) 3 times with lab-grade DI water collected from the Support Facility Millipore DI system (just like a stream sample).

ii. For Nutrient blank:

1) Fill bottle to below the shoulder (~100 -120 mL of water).

2) Freeze as normal.

3) Example ID: PRIN.ss.20220813.RAW.NUT.LB

iii. For General Chemistry blank:

1) Fill bottle to below the shoulder.

2) Overnight blank to external facility with stream samples and field blanks

3) Example ID: PRIN.ss.20220813.RAW.WC.LB

iv. You do not need to collect a FIL lab blank.

v. If 2 sites are visited in one day for field blanks, only one lab blank is required. (e.g., SUGG and BARC or PRLA and PRPO).

b. **Field blanks (FB)** – Collected in the field.

i. Take at least 2.5-3 L lab grade DI (from Millipore DI water system in Support Facility lab) in a triple rinsed transport container to the field at the time of nutrient sampling as part of the water chemistry bout.

1) The transport bottle should be a dedicated lab-grade DI transport bottle.

2) This transport bottle should remain clean. Never insert tubing into this transport bottle.

ii. Field blanks should be processed at the same location as the sample water.

1) If ambient water is processed at another location (i.e., returned to the domain lab or processed on boat ramp), the field blank processing and collection should occur where the ambient samples are processed. However, the DI water should still be taken into the field to replicate the sample journey.

iii. Collect:

1) RAW Nutrient field blank

a) Rinse a clean 125 mL HDPE sample bottle 3 times with DI prior to collecting blank sample.

b) Pour water directly into RAW Blank HDPE bottle, leaving headspace for freezing. Fill bottle to below the shoulder (~100-120 mL of water).

c) Example ID: PRIN.ss.20220813.RAW.NUT.FB

2) RAW General Chemistry field blank

a) Rinse a clean 500 mL amber bottle 3 times with DI prior to collecting blank sample.

b) Pour water directly into RAW Blank bottle. Fill bottle to the shoulder.

c) Example ID: PRIN.ss.20220813.RAW.WC.FB

3) FIL field blank

a) Collect field FIL blank prior to collecting water samples.

b) Triple rinse a transfer container with the lab-grade DI. The transfer container should be a clean container, such as a clean graduated cylinder. Never use the transport DI bottle as your transfer container because we do not want to contaminate our dedicated transport container.

c) Transfer DI water to the pre-rinsed transport container to prepare for filtration.

d) Insert clean tubing into the transport container.

e) Run a minimum of 100 mL of DI water through clean tubing.

f) Once tubing has been rinsed, attach a new capsule filter, and run 100 mL through the capsule filter.

g) Collect the Nutrient FIL sample:

1. Rinse the 125 mL sample bottle 3 times with filtered, lab-grade DI water.
2. Fill FIL blank HDPE bottle with ~ 100-120 mL of water, leaving a small amount of headspace for freezing.
3. Example ID: PRIN.ss.20220813.RAW.NUT.FB

h) Collect the General Chemistry FIL sample:

1. Rinse the 1-L glass bottle 3 times with filtered, lab-grade DI water.
2. Fill 1L amber bottle completely (NO HEADSPACE).
3. Example ID: PRIN.ss.20220813.RAW.WC.FB

i) Once you collect the field blanks, you can re-use the capsule filter to collect the FIL sample. Be sure to rinse capsule filter and tubing with sample water prior to rinsing the .FIL bottle and collecting sample.

5. **<u>Additional Steps for Groundwater sampling only:</u>**

a. Calibrate pH prior to each sampling bout.

i. Ensure that the temperature sensor is connected. This is indicated on the display by TP. The pH meter will automatically compensate for temperature when a temperature sensor is connected.

- Calibrate the sensor according to the two-point Conventional Calibration procedure as described in the pH manual. For the two-point calibration, use either pH 4 and 7 buffers or pH 7 and pH 10 buffers depending on historical pH at your site. If the historical pH at your site is close to 7, calibrate the sensor according to the three-point Conventional Calibration procedure. Make sure buffer solution has not expired and is not reused.

If the pH meter is off by ≥0.1 pH units, recalibrate pH meter following the manual.

b. Remove batteries from the pH meter between bouts.

c. Between wells, immerse the pH combination electrode in reference electrolyte (KCl 3 mol/L).

d. Prior to the next measurement, rinse the combination electrode with the test sample or deionized water.

e. Store the clean combination electrode in the watering cap that is filled with reference electrolyte (KCl 3 mol/L). If the liquid in the watering cap has dried up, condition the combination electrode in reference electrolyte (KCl 3 mol/L) for at least 24 hours.

6. Pack tubing individually into large sealable bags labeled for the corresponding well.

   a. If tubing is either missing or damaged, take new spare tubing from the bucket of tubing. In the first round of sampling, the tubing will need to be cut for each well (detailed in SOP B.5).

A.3 Labels and Identifiers

Barcodes and pre-printed labels are useful for minimizing transcription errors and tracking samples from the domain support facility (DSF) to external locations. **All field samples must use a barcode and all samples being shipped from the DSF must have a barcode.** Although it is always acceptable to use barcodes, in some cases barcodes are absolutely required (**Table 8**).

All barcodes and pre-printed labels need to be applied to dry containers for 30 mins before use. Type I (prefix A, plus 11 numbers) are for all field samples and any non-cryo applications; they have a tolerance from 4°C to 105°C and still scan. Type II (prefix B, plus 11 numbers) are the large size cryo safe barcodes usable on most cryo samples (rated for liquid nitrogen). Labels are waterproof but should be filled out before getting wet to ensure ink is dry.

1. Prepare final sample containers by affixing one Type I (FIL and RAW) and Type II (FIL.NUT, RAW.NUT, and lab and field blanks if applicable) adhesive barcode label to each bottle used to contain each sample. Adhesive barcode labels should be applied to dry, room temperature containers in advance of their use in the field (at least 30 minutes prior but may be applied at the start of the season).

a. Barcode labels should be oriented such that it is possible to scan them; the scanner will not work on a curved surface. This means aligning the barcode lengthwise along a vial, *not* horizontally wrapping around a vial.

b. Barcode labels must be associated with a unique sample and each barcode must be mapped to one sample in the database. Barcodes are unique, but are not initially associated with a particular sample, so you are encouraged to adhere barcode labels to needed containers in advance.

neon Type I barcode
A00000000061

neon Type II barcode
B00000000061

Figure 7. An example of a Type I and Type II barcode. These large-size, field-tolerant barcodes have a prefix of 'A' (Type 1) and B (Type II) followed by 11 numbers.

a)

SampleID :________________________
(siteID.stationID.YYYYMMDD.sampleType)
Sample Type: FIL RAW

b)

SampleID :________________________
(siteID.stationID.YYYYMMDD.sampleType)
Sample Type:
ALK (Filtered) **ANC** (Unfiltered)

Figure 8. Blank NEON Chemistry Labels for a) the External Analytical Laboratory and b) Internal NEON Domain Support Facility Measurements

2. Attach pre-printed labels (**Figure 8a,b**) to bottles (**Figure 5**).
3. Determine the sampleID based on the location, date, and sample type (**Table 6**, **Table 7**).
4. Use permanent marker to fill out pre-printed labels (**Figure 8**) before going into the field. Note that there are two different labels depending on whether the samples will be shipped to the external analytical chemistry laboratory (**Figure 8a**) or will be analyzed at the Domain (**Figure 8b**).

Table 6. SampleID format.

<table>
<tr><th colspan="5">SampleID format: siteID.StationID.date.sampleType</th></tr>
<tr><th>Part of sampleID</th><th>Location</th><th colspan="2">Location Specifics</th><th>ID</th></tr>
<tr><td>siteID</td><td colspan="4">4-letter site code</td></tr>
<tr><td rowspan="13">stationID</td><td>Stream</td><td colspan="2">All</td><td>ss</td></tr>
<tr><td rowspan="3">River</td><td colspan="2">Not Stratified</td><td>c0</td></tr>
<tr><td rowspan="2">Stratified</td><td>Top layer below surface</td><td>c1</td></tr>
<tr><td>Bottom layer below surface</td><td>c2</td></tr>
<tr><td rowspan="4">Lake</td><td colspan="2">Not Stratified</td><td>c0</td></tr>
<tr><td rowspan="3">Stratified</td><td>Top-layer: Epilimnion</td><td>c1</td></tr>
<tr><td>Middle: Thermocline</td><td>c2</td></tr>
<tr><td>Bottom-layer: Hypolimnion</td><td>c3</td></tr>
<tr><td rowspan="2">Lakes with permanent inflows and outflows</td><td colspan="2">Inflow stream</td><td>in</td></tr>
<tr><td colspan="2">Outflow stream</td><td>ot</td></tr>
<tr><td>Groundwater</td><td colspan="2">Well number</td><td>w1- w8</td></tr>
<tr><td colspan="3">Sample collected elsewhere from the normal location</td><td>re</td></tr>
<tr><td>Date</td><td colspan="4">YYYYMMDD</td></tr>
<tr><td rowspan="5">sampleType</td><td colspan="3">Filtered</td><td>FIL</td></tr>
<tr><td colspan="3">Filtered Nutrients</td><td>FIL.NUT</td></tr>
<tr><td colspan="3">Raw/Unfiltered</td><td>RAW</td></tr>
<tr><td colspan="3">Raw Nutrients</td><td>RAW.NUT</td></tr>
<tr><td colspan="3">Alkalinity</td><td>ALK</td></tr>
</table>

<table>
<tr><th colspan="5">SampleID format: siteID.StationID.date.sampleType</th></tr>
<tr><th>Part of sampleID</th><th>Location</th><th colspan="2">Location Specifics</th><th>ID</th></tr>
<tr><td>siteID</td><td colspan="4">4-letter site code</td></tr>
<tr><td rowspan="14">stationID</td><td>Stream</td><td colspan="2">All</td><td>ss</td></tr>
<tr><td rowspan="3">River</td><td colspan="2">Not Stratified</td><td>c0</td></tr>
<tr><td rowspan="2">Stratified</td><td>Top layer below surface</td><td>c1</td></tr>
<tr><td>Bottom layer below surface</td><td>c2</td></tr>
<tr><td rowspan="4">Lake</td><td colspan="2">Not Stratified</td><td>c0</td></tr>
<tr><td rowspan="3">Stratified</td><td>Top-layer: Epilimnion</td><td>c1</td></tr>
<tr><td>Middle: Thermocline</td><td>c2</td></tr>
<tr><td>Bottom-layer: Hypolimnion</td><td>c3</td></tr>
<tr><td rowspan="2">Lakes with permanent inflows and outflows</td><td colspan="2">Inflow stream</td><td>in</td></tr>
<tr><td colspan="2">Outflow stream</td><td>ot</td></tr>
<tr><td>Groundwater</td><td colspan="2">Well number</td><td>w1- w8</td></tr>
<tr><td colspan="3">Sample collected elsewhere from the normal location</td><td>re</td></tr>
<tr><td colspan="3">Acid neutralizing capacity</td><td>ANC</td></tr>
<tr><td colspan="3">Dissolved inorganic carbon and pH (D18/19 only)</td><td>DIC</td></tr>
</table>

Table 7. SampleID format and frequency for blanks and replicates. Add ID to end of sample ID.

	SampleID modifiers for replicates and blanks			
Sample Type	**Location Specifics**	**ID**	**Example**	**Frequency**
Replicate	First Replicate of Sample (primary)	Leave as is	PRIN.ss.20220813.RAW	
	Second Replicate of Sample	.2	PRIN.ss.20220813.RAW.2	• Gen Chem - Once per year per site • Nutrients – ○ Twice per year per stream/river site ○ Once per year per lake site
	Third Replicate of Sample	.3	PRIN.ss.20220813.RAW.3	
Lab Blank	Lab – unfiltered (RAW.WC.LB or RAW.NUT.LB)	.LB	PRIN.ss.20220507.RAW.WC.LB PRIN.ss.20220507.RAW.NUT.LB	• General Chemistry - Once per year per domain • Nutrients - Once per year per site
Field Blank	Field – unfiltered DI (RAW.WC.FB or RAW.NUT.FB)	.FB	PRIN.ss.20220507.RAW.WC.FB PRIN.ss.20220507.RAW.NUT.FB	
	Field – filtered DI (FIL.WC.FB or FIL.NUT.FB)	.FB	PRIN.ss.20220507.FIL.WC.FB PRIN.ss.20220507.FIL.NUT.FB	

Table 8. Sample types and labels used. sampleID format is siteID.stationID.YYYYMMDD.sampleType.

Sample Type	Description	sampleID	Fulcrum App	Container Type	Labeling Used	Lab Analysis Location
Filtered Sample	Filtered water	PRIN.ss.20170712.FIL	SWC: Water Chemistry	1 L amber glass bottle	Barcode I & Pre-printed label	External Lab/Chilled

Sample Type	Description	sampleID	Fulcrum App	Container Type	Labeling Used	Lab Analysis Location
Filtered Nutrient Sample	Filtered water	PRIN.ss.20170712.FIL.NUT	SWC: Water Chemistry	125 mL clear wide mouth bottle	Barcode Type II & Pre-printed label	External Lab/Frozen
Raw Sample	Unfiltered water	PRIN.ss.20170712.RAW	SWC: Water Chemistry	500 mL amber glass bottle	Barcode I & Pre-printed label	External Lab/Chilled
Raw Nutrient Sample	Unfiltered water	PRIN.ss.20170712.RAW.NUT	SWC: Water Chemistry	125 mL clear wide mouth bottle	Barcode Type II & Pre-printed label	External Lab/Frozen
DIC	Filtered GW from Bubble Free Method (D18/19 only)	OKSR.w1.20170801.DIC	SWC: Water Chemistry	60 mL amber glass bottle	Barcode I & Pre-printed label	External Lab
Alkalinity Sample	Filtered water	PRIN.ss.20170712.ALK	SWC: Water Chemistry	250 mL (site-specific size) amber glass bottle with Phenolic lined cap	Barcode I & Pre-printed label	Domain Lab
ANC Sample	Unfiltered water	PRIN.ss.20170712.ANC	SWC: Water Chemistry	250 mL (site-specific size) amber glass bottle with Phenolic lined cap	Barcode I & Pre-printed label	Domain Lab

Sample Type	Description	sampleID	Fulcrum App	Container Type	Labeling Used	Lab Analysis Location
Nutrient Lab Blank[a]	Unfiltered water	PRIN.ss.20170712.RAW.NUT.LB	SWC: Water Chemistry	125 mL clear wide mouth bottle	Barcode Type II & Pre-printed label	External Lab/Frozen
Nutrient Field Blank – Filtered[a]	Filtered water	PRIN.ss.20170712.FIL.NUT.FB	SWC: Water Chemistry	125 mL clear wide mouth bottle	Barcode Type II & Pre-printed label	External Lab/Frozen
Nutrient Field Blank – Unfiltered[a]	Unfiltered water	PRIN.ss.20170712.RAW.NUT.FB	SWC: Water Chemistry	125 mL clear wide mouth bottle	Barcode Type II & Pre-printed label	External Lab/Frozen
General Chem - Lab Blank[b]	Unfiltered water	PRIN.ss.20170712.RAW.WC.LB	SWC: Water Chemistry	500 mL amber glass bottle	Barcode I & Pre-printed label	External Lab/Chilled
General Chem - Field Blank – Filtered[b]	Filtered water	PRIN.ss.20170712.FIL.WC.FB	SWC: Water Chemistry	1 L amber glass bottle	Barcode I & Pre-printed label	External Lab/Chilled
General Chem -Field Blank – Unfiltered[b]	Unfiltered water	PRIN.ss.20170712.RAW.WC.FB	SWC: Water Chemistry	500 mL amber glass bottle	Barcode I & Pre-printed label	External Lab/Chilled

a Collected once per year per site.
b Collected once per year per domain.

SOP B Field Sampling

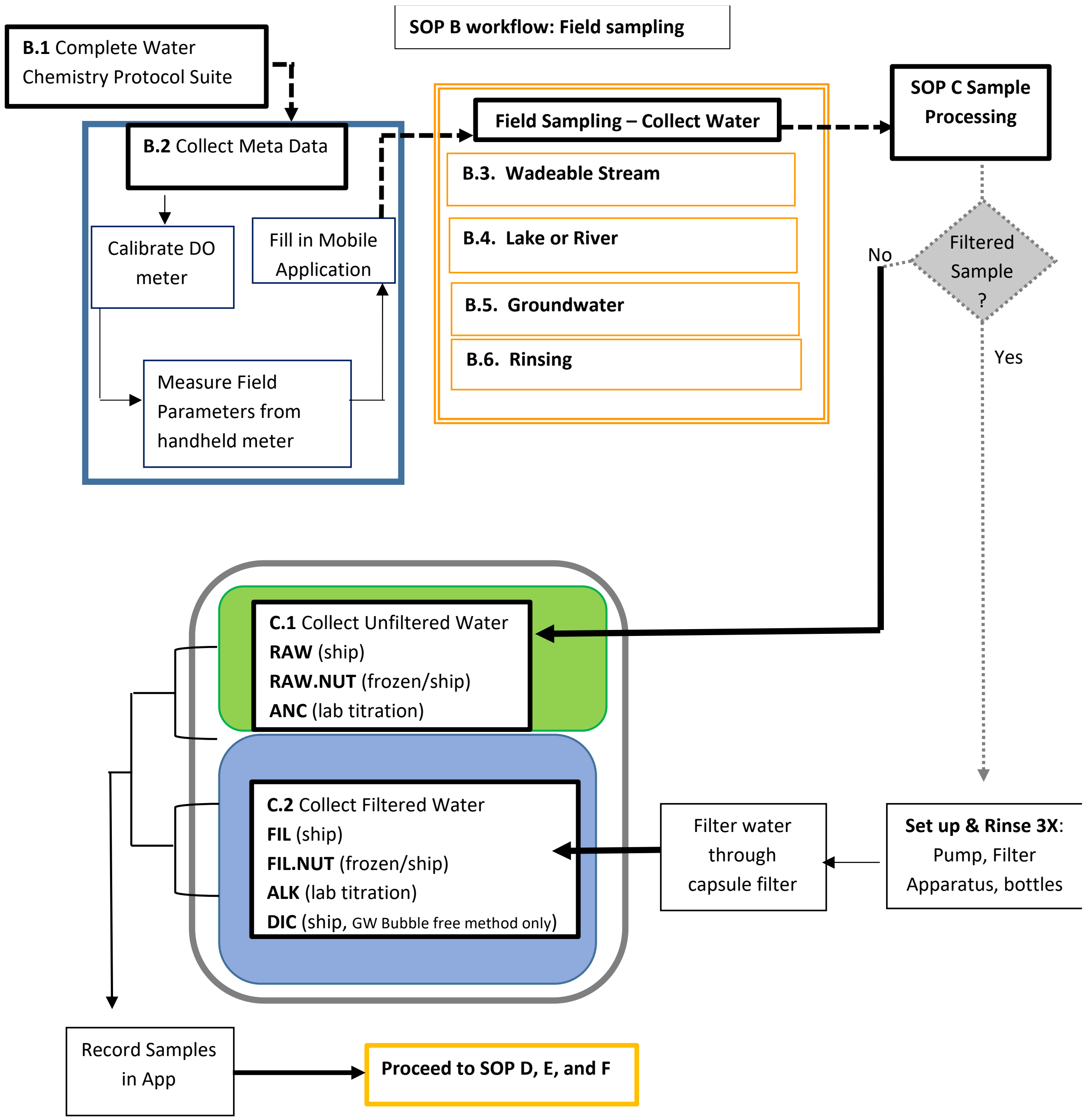


Figure 9. Breakout workflow diagram of SOP B: Field Sampling.

B.1 Spatially and Temporally Linked Protocols

Synchronized protocols and SOPs include:

- AOS Protocol and Procedure: SDG – Surface Water Dissolved Gas Sampling (RD[13])
- AOS Protocol and Procedure: ASI - Stable Isotope Sampling in Surface and Ground Waters (RD[14])
- AOS Protocol and Procedure: AMC – Aquatic Microbial Sampling (RD[15])

Surface water chemistry samples are collected at the same time and place as surface water dissolved gas and aquatic stable isotopes. Aquatic microbes are collected in coordination with the surface water chemistry suite during monthly sampling events in streams and every other month in lakes and rivers. Groundwater chemistry samples are collected at the same time and place as groundwater stable isotopes.

B.2 Metadata for All Water Chemistry Samples

In the field, fill out the General AQU Field Metadata Mobile App or Field sheet (RD[07]) before collecting samples. You only need to fill out one AQU Field Metadata record per **SITE** per day.

1. Calibrate the DO sensor at the field site. DO <u>MUST</u> be calibrated at the actual site.
2. For each station, complete the mobile application or datasheets for Water Chemistry Sampling in Surface Waters and Groundwater (RD[05]). Record the date and the time of day (use local, military time; ex. 13:46) that samples were collected.
3. For surface water, measure and record water temperature, Specific Conductance, DO, DO percent saturation, and barometric pressure at time of sample collection on the mobile application or datasheets for Water Chemistry Sampling in Surface Waters and Groundwater (RD[05]). For groundwater, these measurements (and field pH) will be collected during the pre-sampling purge.
   a. If the multisonde pH probe is not operating properly, surface water field pH should be measured using the handheld pH meter (freshly calibrated) to get a pH reading. NOTE: Handheld pH probe will need to equilibrate to the water temperature. More time is needed in very cold water.
   b. Specific conductance should be measured as temperature-corrected conductivity at 25°C, whenever possible. Ensure conductivity measurements are on the appropriate temperature-corrected and unit setting (i.e., setting SPC, µS/cm).
   c. The conductivity sensor is located in the black plastic above the metal guard, so ensure probe is completely submerged in the water or the measurements will be inaccurate (**Figure 10**).

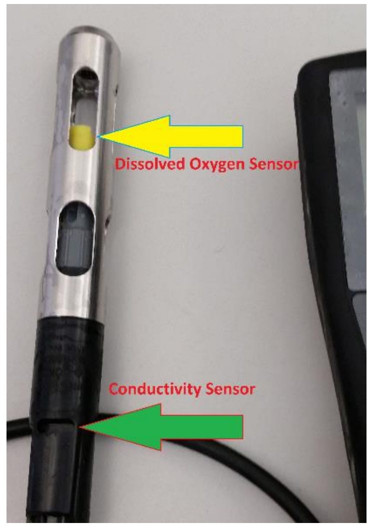


Figure 10. Picture of handheld meter showing location of sensors on probe.

B.3 Collecting Samples from Wadeable Streams

1. ALWAYS sample in the THALWEG with the bottle opening pointed upstream and into the main flow of water (**Figure 11**). To ensure you are not sampling surface particles or film, hold cap over bottle opening while you lower the bottle to ~10 centimeters below the surface.
    a. You may step into the stream but minimize bed disruption as you walk. Collect samples UPSTREAM from where you are standing.

Figure 11. Cap bottle when lowering to not sample surface film. Remove cap ~10 cm below surface.

2. Rinse the collection and sample bottles and caps with the appropriate sample water (i.e., use filtered water to rinse filtered samples):
    a. Raw samples: bottles to be rinsed with **raw** sample water (**Figure 6**):

- 4 L jug(s) (can be used for filtered samples if needed, see below)
- RAW - 500 mL burned amber glass bottle for external lab
- RAW.NUT – 125 mL wide-mouth, HDPE
- ANC - 250 mL amber glass bottle with Phenolic lined cap – ***to be analyzed at the Domain Support Facility**.

i. To rinse RAW samples: (NOTE: You may also use the field pump to pump water out of the stream and into your bottle if water depths are very low making it impossible to collect with the sample bottle directly from the stream. Make sure the end of the tubing is not too close to the stream bed. Pump water slowly and reduce oxygenation as much as possible).

1) Hold the cap in your hand when the cap is not on the bottle (setting the cap down increases risk of contamination).
2) With cap loosely on bottle, lower the collection bottle under the water surface (approximately 10 cm below the surface) so that the opening of the bottle faces upstream.
3) Remove the cap and allow stream water to fill approximately $^{1}/_{5}$ of the collection bottle.
4) Cap bottle under water.
5) Remove bottle from stream and shake.
6) Discard water downstream.
7) Repeat 2 more times.

b. Filtered samples: bottles to be rinsed with filtered sample water.

- FIL – 1 L burned amber glass bottle for external lab
- FIL.NUT – 125 mL wide-mouth, HDPE
- ALK - 250 mL amber glass bottle with Phenolic lined cap – ***to be analyzed at the Domain Support Facility**.

i. To rinse filtered samples:

1) DO NOT use raw water to rinse filtered samples.
2) Proceed to SOP C for instructions on filtering samples.

3. Fill the RAW collection bottles by placing the bottle 10 cm below the water surface with the opening pointed upstream (**Figure 11**) or pump water directly out of the stream from 10 cm below the water surface. If using pump, make sure the end of the tubing is not too close to the stream bed.

a. Be sure to loosely cap bottle while lowering the bottle 10 cm below surface so as not to collect surface film.

b. Remove cap and allow container to fill, keeping the container horizontal to the stream.

c. Recap bottle under stream.

d. Leave headspace in RAW and RAW.NUT bottles.

When possible, always fill raw samples in the field. However, if it is necessary to fill raw collection bottles away from site, you may collect a SEPARATE jug to be subsampled for RAW samples.

Keep samples cool by placing them in a cooler with ice or frozen ice packs until processing.

Proceed to C.2 Sample Processing of Filtered Samples.

B.4 Collecting Samples from Lakes and Rivers

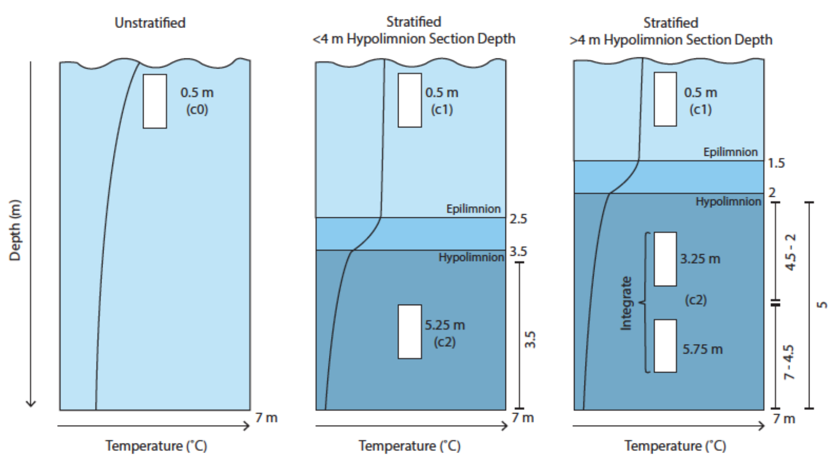
B.4.1 Determine Sampling Depth Based on Stratification Conditions

1. Move to the sampling location.
2. Determine if you need to collect a non-integrated or integrated.
    a. Take one sample at a 0.5-meter depth at buoy station (Kemmerer should be placed with top at 0.25 m and bottom at 0.75 m) below the surface of the water. For more details, see **'Field Sampling –Lakes and Rivers'** below.
    b. Is the lake thermally stratified at buoy station? Use the Secchi Depth App to determine sampling depths and stratification. If the secchi depth app is not available, use the decision tree:
        i. If NO, do not take any more samples.
        ii. If YES, evaluate the **hypolimnion** section depth (i.e., hypolimnion thickness) at the buoy, calculated using the secchi disk app. If you are not using the secchi depth application, ensure you are calculating the hypolimnion section depth (i.e., hypolimnion thickness), NOT the maximum lake depth and NOT the depth that the hypolimnion starts (**Figure 12b**).
            1) If hypolimnion section depth (i.e., hypolimnion thickness) is <2 m, do not take any more samples.
            2) If hypolimnion depth/thickness ≥2 m but ≤4 m, then collect a sample from the midsection of the hypolimnion depth.
            3) If hypolimnion depth/thickness >4 m, then divide the hypolimnion depth by 2 and collect a sample in the midsection of both those layers. Integrate the samples from the hypolimnion into 1 sample. For an integrated sample, the fulcrum app will auto

populate the hand-held depth profile measurements from the depth closest to the uppermost composite depth.

3. Note the maximum depth of the lake or non-wadeable stream on the datasheet. If the lake or non-wadeable stream is stratified, also note the upper and lower depth of each section for each integrated sample (Z_{upper}, Z_{lower}) to enable the total depth per section to be known (**Figure 12**). Note: Do NOT include the metalimnion (AKA thermocline zone) in your depth measurements for c1 and c2 subsections (i.e., the upper depth of the hypolimnion is the bottom of the metalimnion; **Figure 12**).
4. During winter sampling:
   a. Core through the ice. Ensure safe conditions (See Section 5 Safety).
   b. Determine the total depth of water below the ice.
   c. Take samples from below the ice as per an unstratified lake or non-wadeable stream.
      i. A minimum of 0.5 m of water below the ice is required to sample.
      ii. If < 0.5 m of water depth is available in the central (buoy) location, then move to a location that is within 10 m of the original location and note the new GPS location.

a)



b)

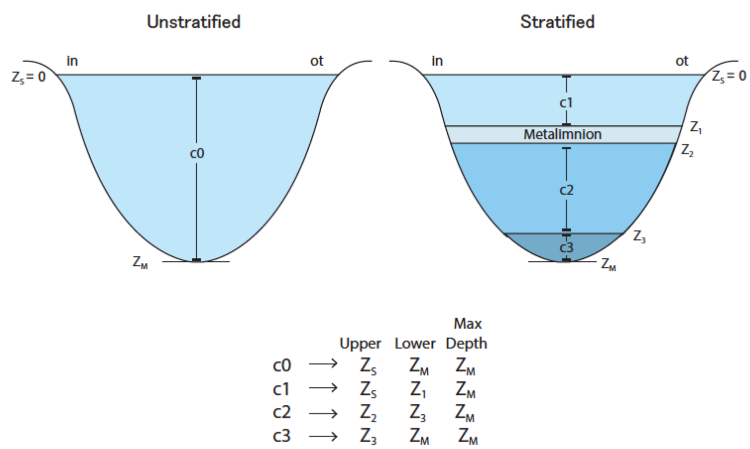


Figure 12. Example of an unstratified and stratified lake water column **a)** sampling depths with placement of thermocline and **b)** identification of upper and lower section depths. In deep lakes, 2 thermal stratifications may occur, creating 3 sections. Note, hypolimnion sampling is determined by the hypolimnion section depth (i.e., thickness). If hypolimnion thickness is < 4m, collect one sample at midpoint of hypolimnion. If hypolimnion thickness is > 4 m collect an integrated sample.

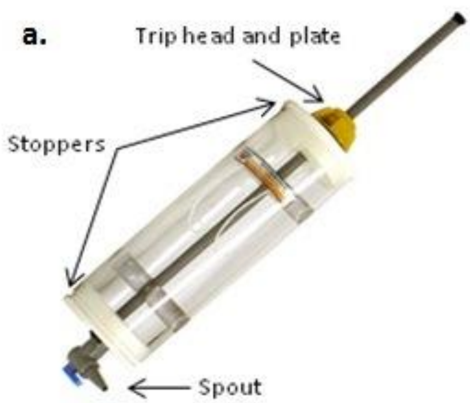
5. Determine if you need to collect inflow and outflow samples:
   a. Is there a true (i.e., flow-through) inflow and outflow to the lake?
      i. If No, do not take any more samples.
      ii. If Yes, collect samples sampled just downstream of the inflow and outflow infrastructure, following the wadeable stream sampling protocol.

B.4.2 Field Sampling – Lakes and Rivers

1. Take the water sample from the windward (the upwind) side of the boat to lessen any contamination from the boat.
    a. Care must be taken to avoid contaminating the sample with re-suspended bed sediment. Such contamination may be minimized by anchoring the boat upwind (or upstream) of the sampling site and using an anchor line 2-3 times as long as the depth of the lake or stream. If sediments are disrupted, wait until the area has cleared before sampling.
    b. Sample ~5m away from buoy if using a boat (not required for dock mounted buoy).
2. Record the date and the time of day (use local, military time; ex. 13:46) that samples were collected in the Mobile Application or Surface Water Chemistry Field Sampling Datasheet (RD[05])
3. Record DO, water temperature, barometric pressure, and specific conductance. Be sure to gently jiggle the DO probe while collecting DO readings in non-flowing water.
4. Rinse the Kemmerer by dunking it in the water body to be sampled 3 times. Keep the tubing spout “Open” during rinsing.
5. Prepare Kemmerer for sampling and check the knot at the bottom of the sampler for tightness and size. The knot should be sufficiently large so that it will not pull through the central tube of the sampler. Do not touch the inside of the Kemmerer.
6. Cock the sampler by pulling the trip head into the trip plate by holding the top and bottom stoppers and giving a short, hard pull to the bottom stopper.
7. Tips for deeper lakes: The Kemmerer can be set to a “half-cocked” position that will still hold open but is easier to trigger. After following the directions above to have the Kemmerer fully cocked, take one white stopper in either hand, and slowly but firmly push them together. Make sure your hands are outside of the stoppers because it is easy to push past the half-cocked position and slam the Kemmerer shut. If done correctly, you will feel a definitive click, but the Kemmerer will still be fixed open. This setting is important for deeper sample depths, as it is difficult to trigger the Kemmerer closed and you cannot feel or see whether it tripped until you pull it to the surface.
8. Ensure the spout is CLOSED.
9. Holding the rope securely in one hand, lower the Kemmerer sampler gently, allowing it to fall to the desired depth with the other hand. Be sure you hold the messenger securely on the rope (**Figure 13b**). Depth markings should be pre-marked on the rope.
    a. If the messenger will not stay closed around the rope, check the spring in the messenger.
10. In swiftly moving rivers, a Van Dorn water sampler can be used in place of a Kemmerer. If a Kemmerer is used it is suggested to drop the Kemmerer slightly up current so that when the

Kemmerer gets to the correct sampling depth, the messenger can be dropped as it is passing by the sampling location.

11. When the desired depth is attained, drop the messenger to release the clamps and seal the sampler. In deep lakes, you may need to drop the messenger with some force to release the clamps.
12. Retrieve the sampler from the water column. Water is dispensed into the appropriate containers/sample bottles through the spout (**Figure 13a**).
13. Repeat steps 1 through 12 for each sample.



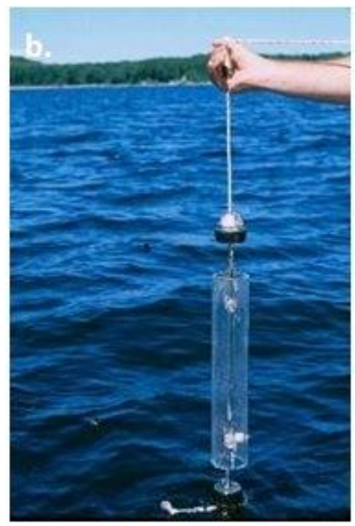


Figure 13. Illustration of Kemmerer sampler for water sampling (a). Illustration of how the Kemmerer is lowered into the water by holding the rope and messenger (b)

14. Rinse the collection bottles and caps with the appropriate sample water (i.e., use raw sample water for unfiltered samples and use filtered water to rinse filtered samples) (NOTE: you may fill two 4 L jugs to be used for all raw and filtered water in SOP C):
    a. Raw samples: bottles to be rinsed with <u>**raw**</u> sample water (**Figure 6**):
        - 4 L jug(s) (can be used for filtered samples if needed, see below)
        - RAW – 500 mL burned amber glass bottle for external lab
        - RAW.NUT – 125 mL wide-mouth, HDPE
        - ANC - 250 mL amber glass bottle with Phenolic lined cap – ***to be analyzed at the Domain Support Facility**.

        i. <u>To rinse raw samples:</u>
            1) Hold the cap in your hand (setting the cap down increases the risk of contamination).

2) Fill approximately $^{1}/_{5}$ of the collection bottle with water from the Kemmerer.

3) Cap bottle and shake.

4) Discard water away from the area you are sampling (other side of the boat or downstream of any current).

5) Repeat 2 more times.

b. Filtered samples: bottles to be rinsed with filtered sample water.

- FIL – 1 L burned amber glass bottle for external lab
- FIL.NUT – 125 mL wide-mouth, HDPE
- ALK - 250 mL amber glass bottle with Phenolic lined cap – ***to be analyzed at the Domain Support Facility**.

i. To rinse filtered samples:

1) Use **filtered** water to rinse filter sample bottles. DO NOT use raw water.

15. Proceed to SOP C for instructions on filtering sample water to be used for rinsing and collection.

B.5 Collecting Samples from Groundwater

Several groundwater extraction methods are used by NEON for obtaining groundwater samples from the wells. The best method for a given site will vary with site conditions and should be selected based on the decision tree described in the following section and discussions with NEON Science. The low-flow method is the preferred and most common method used by NEON domains. Alternative methods may be used when the low-flow method is not practical for given site conditions, including minimum purge sampling and purging to dryness. Sites in permafrost regions will always use a needle and syringe to sample directly from the active layer, which is the ground layer above the permafrost that seasonally freezes and thaws.

Decontamination

While working in groundwater wells, special attention is required to avoid contamination. Decontaminate all materials (or use dedicated materials) between wells according to the procedures described in the following sections. Always work on wells with known or suspected contamination issues last to minimize the chances of cross-contamination.

Groundwater Sensor Considerations

The groundwater pressure sensor is extremely sensitive to minor changes in sensor position. Remember to check the sensor position both before and after sampling. The paint on the sensor cable should align with the metal docking ring (**Figure 14a**). Ensure the docking ring sits flush with the PVC collar (**Figure 14b**). Any misalignment should result in a trouble ticket notifying AIS Staff to provide science evaluation/guidance.

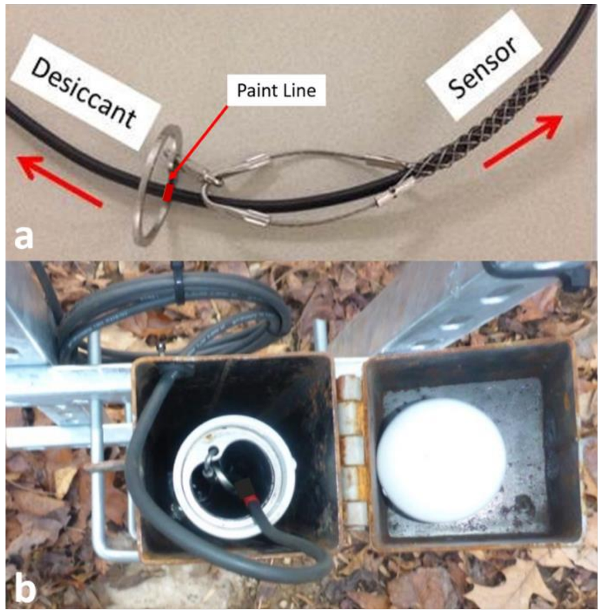


Figure 14. Correct cable position for groundwater sensors. a) Cable paint should align with the metal docking ring. b) The metal docking ring should sit flush within the PVC collar.

B.5.1 Determine Best Sample Method and Sampler Type

NEON uses four distinct sampling methods and 3 sampler types for groundwater chemistry (**Figure 16**). Sites with permafrost will always use the **needle method** which uses a needle and syringe to sample the active layer**.** For non-permafrost sites, the most appropriate method is determined from the recharge rate and current water column height of a given well. Recharge rate is the rate at which water is replenished when removed or discharged from a well. When a static water level is reached during continuous pumping, the recharge rate is equal to the pump discharge rate. Water column height informs how much water is currently in the well.

Wells that recharge at a rate greater than 100 mL/min are considered high yield wells and are sampled via the **low-flow method**. Most NEON sites will use the low-flow sampling method. When the water column height is adequately thick (> 0.5m), the low-flow method is conducted using the QED bladder pump. In cases where the water column height is shallow (< 0.5m), the peristaltic pump is substituted for the QED bladder pump.

Some NEON wells are low-yield wells (defined here as wells with recharge rates lower than 100 mL/min). Pumping low-yield wells using the traditional low-flow method is inappropriate because it will cause enough drawdown that the well will run dry over the course of sampling. In this case, the **minimum purge method** or **purge dry method** may be advised.

Use the following decision workflow for determining which method is most appropriate for a given well. In most cases, the appropriate groundwater sampling method can be determined prior to going into the field. Note that some sites might need to use multiple sampling methods at various times of the year due to water table elevation changes throughout the season. Sampling methods may also vary between wells with differing water levels or recharge rates at a single site. When in doubt, contact Science for help determining the appropriate sampling method.

Decision Workflow:

1. Sites located in tundra or taiga ecosystems will always use the **needle method.** If the well is in domains 18 or 19, proceed to section B.5.3.4 Needle Method. Otherwise, proceed to step 2.
2. Prior to the field:
   a. For non-permafrost sites, start by reviewing the historical groundwater records on the NEON data portal or in your groundwater metadata records on the N-drive to see what sampling methods have been used in the past.
      i. Most wells can be expected to use the same method throughout their lifespan, but further investigation will inform whether that method is still the most appropriate.
      ii. In cases where multiple methods have been used for a single well, be prepared to use either method in the field by packing all necessary materials.
   b. If available, review discharge/recharge rates from past sampling events to determine if the wells are high or low-yield.
      i. High-yield wells correspond to static discharge rates >= 100 mL/min
      ii. Low-yield wells correspond to static discharge rates < 100 mL/min
   c. Determine water column height by examining recent sensor L0 pressure data via NEON's IS Data Quality Monitoring Dashboard (DQ Blizzard) (**Figure 15**).
      i. Pressure is displayed in kilopascals. 1 kPa is equal to roughly 0.1m of water above the sensor.
      ii. With few exceptions, the pressure sensor is located 0.5 m from the well bottom for deep wells (greater than 3 m deep), and 0.2 m from the well bottom for shallow wells (less than 3 m deep).
      iii. Estimate water column height by adding the depth of water above the sensor to the sensor distance from the well bottom.
         1) Example 1: If a shallow well shows recent pressure readings around 1 kPa, we can infer that there is 0.1 m of water above the sensor. If the sensor is 0.2m above the well bottom, then the water column height of roughly 0.3 m.
         2) Example 2: If a deep well shows recent pressure readings around 51 kPa, we can infer that there is 5.1 m of water above the sensor. If the sensor is 0.5m above the well bottom, then the water column height of roughly 5.6 m (**Figure 15**).

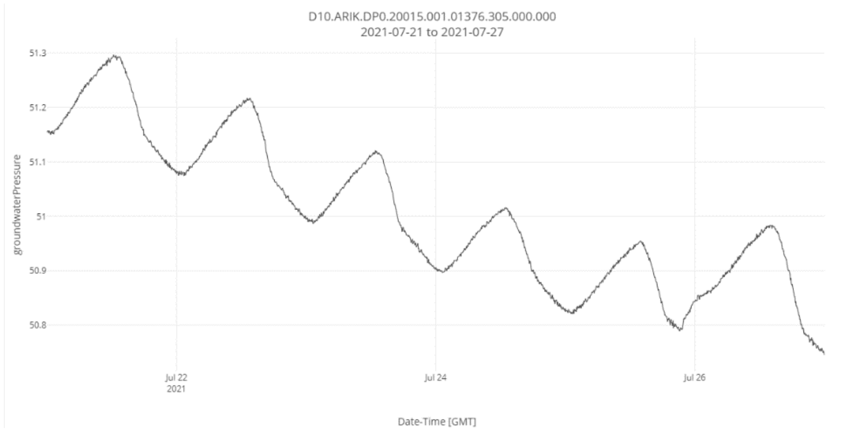


Figure 15. DQ Blizzard plot for groundwater pressure for an individual well over a 1-week period. Pressure is roughly 51 kPa indicating that there is about 5.1 m of water above the sensor. If the sensor is 0.5m from the well bottom, then the water column height is roughly 5.6m.

d. Use the decision tree in **Figure 16** to determine probable sampling method and sampler type.

i. If the well has been sampled consistently with discharge/recharge rates >100 mL/min in the past, plan to use the low-flow method (B.5.3.1 Low-flow Method).

1) Plan to sample using the QED groundwater bladder pump for water columns > 0.5 m.

2) Plan to sample using the peristaltic pump for water columns < 0.5 m.

ii. If the well is known to be low-yield (discharge/recharge rates <100 mL/min):

1) Plan to use the purge dry method (B.5.3.3 Purge Dry Method) for water columns <0.5 m.

2) Discuss with Science if the minimum purge method (B.5.3.2 Minimum Purge Method) is appropriate if the water column is > 0.5 m.

3. In the field:

a. If a well is dry, attempt to sample an alternate well if available. If no alternate well can be sampled, create a sampling impractical record for the originally scheduled well.

b. Determine water column height as described in section B.5.2 Locate well and assess water depth.

c. Calculate recharge rate as described in section B.5.2 Locate well and assess water depth.

d. Use the decision tree in **Figure 16** to determine the appropriate sampling method. Instructions for calculating the Maximum Allowable Drawdown (MAD) are discussed in section (B.5.3.2 Minimum Purge Method).

i. If the determination aligns with the planned method and sampler type, proceed with sampling.

ii. If the determination does not align with the planned method or sampler type, proceed with the on-site determined method.

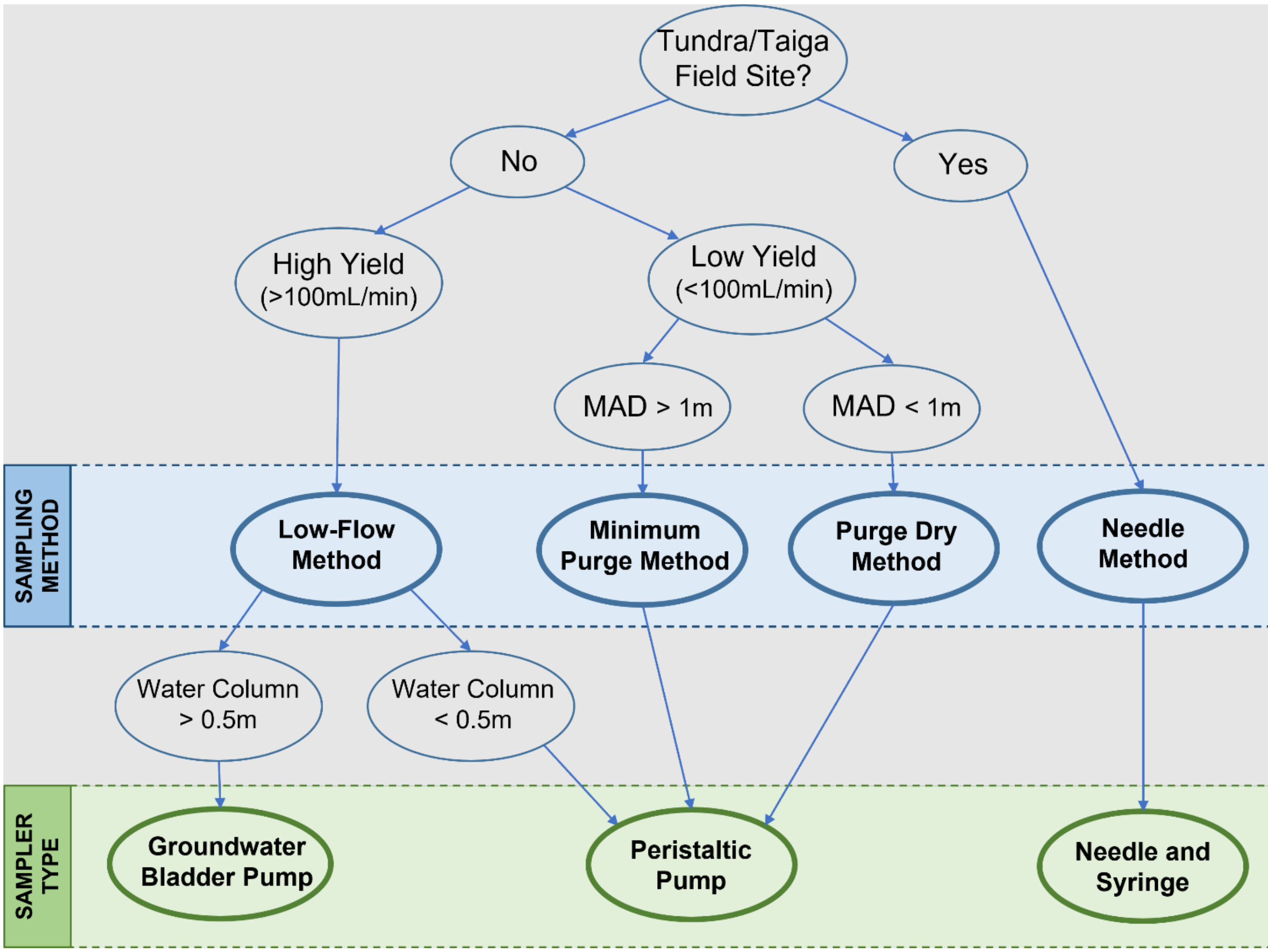


Figure 16. Decision tree for determining appropriate groundwater sampling method and sampler type.

B.5.2 Locate well and assess water depth

1. Locate Well. The NEON groundwater observation wells (OW) will look different depending on site host requirements and may be camouflaged at National Parks sites. Wells can be difficult to locate the first time, therefore a well map with GPS coordinates should be taken to the field the first time.
2. Power down the well by disconnecting the radio from the aquatic interconnect circuit board. Disconnecting the sensor from the cable should be avoided as this can cause damage to the

connection over time. Remember to reconnect the sensors and after finishing work on a well. Always reset the grape to ensure that all data comes back online.

3. Unlock the Well. Open the lock and flip open the protective well lid, then remove the white PVC cap from the well. For snorkel wells, unscrew the PVC cap at the coupler and attach to the unistrut so that the cap is not pulling on the cable.
4. Check that the cable paint position is properly aligned with the metal docking ring. If misaligned, measure the offset between the paint line and the ring prior to realigning. Submit a Data Quality Ticket with this information.
5. Remove the sensor from the well.
   a. Pull the sensor cable and mounting cable out of the well gently to not damage the sensor (they are sensitive to shock).
   b. Place the sensor and coiled sensor cable in clean and dry 5-gallon bucket to help keep the sensor and cable clean. The sensor is fine to be kept out of water.
6. Take key groundwater measurements prior to starting the groundwater extraction process (**Figure 17**).
   a. Measure the **depth to water table** by measuring the depth from the top of the PVC well casing down to the water surface using the water level tape.
      i. Attach the water level tape to the outer steel casing of the well (**Figure 18b**). Turn the water level tape on by turning the dial on the side of the reel, and slowly lower the tape down into the well. The water level tape will give an audible signal when it reaches the water in the well (the knob used to turn the unit on is also the volume control). It's important to "test" for the water level by pulling the water level tape up in the well slowly once you hear the signal and then slowly lowering it back in to the well until you just hear the signal occur again. This will help in dialing in the water surface in the well.
      ii. Note the depth to water and time in the Fulcrum app. Take the reading from the top of the PVC casing. The water level tape is read like a standard ruler or survey tape as shown in **Figure 18c**. The measurement point will differ for standard NEON wells and those fitted with snorkel caps to prevent overflow at flood prone sites. Standard wells should be measured to the edge of the PVC lip (**Figure 18c**). For wells fitted with snorkel caps, unscrew the cap at the coupler and measure on the PVC lip as shown in **Figure 18d**.
      iii. If low-flow sampling is planned, the water tape can remain in the well for the YSI stabilization measurements.
      iv. Wipe down water meter tape with bleach wipes between wells. (Make sure the wipes contain bleach. Note that normal Clorox wipes do not actually contain bleach).

v. If a well is dry, attempt to sample an alternate well if available. If no alternate well can be sampled, create a sampling impractical record for the originally scheduled well.

b. Calculate **water column height.** The app will do this calculation, but if there is an app malfunction and paper data sheets need to be used, follow steps here. Subtract the depth to water table from the total depth of the well (auto-populated field) to get the water column height in the well. (i.e., Depth to Water = 2.27m, Total Depth = 4.03m, Height of water = 1.76m)

Note: To prevent corrosion damage, the battery should be removed from the water level tape between sampling bouts.

7. If the well is known to be a high yield (high recharge rate) well, now is a good time to do the quarterly preventive maintenance water clarity check (see RD[12]) prior to sampling. This will improve data by reducing the total amount of times per year that the sensor needs to be removed from the well. Remaining quarterly maintenance activities such as data log downloads can be performed if convenient, but do not need to happen at this time. Copy any clarity photos to your site folder on the NEON N-drive (N:\Science\Sensor Swap\groundwaterMetadata). Note that you should not perform the quarterly clarity check on low-yield wells in combination with sampling because there may not be enough water volume remaining for the sample.

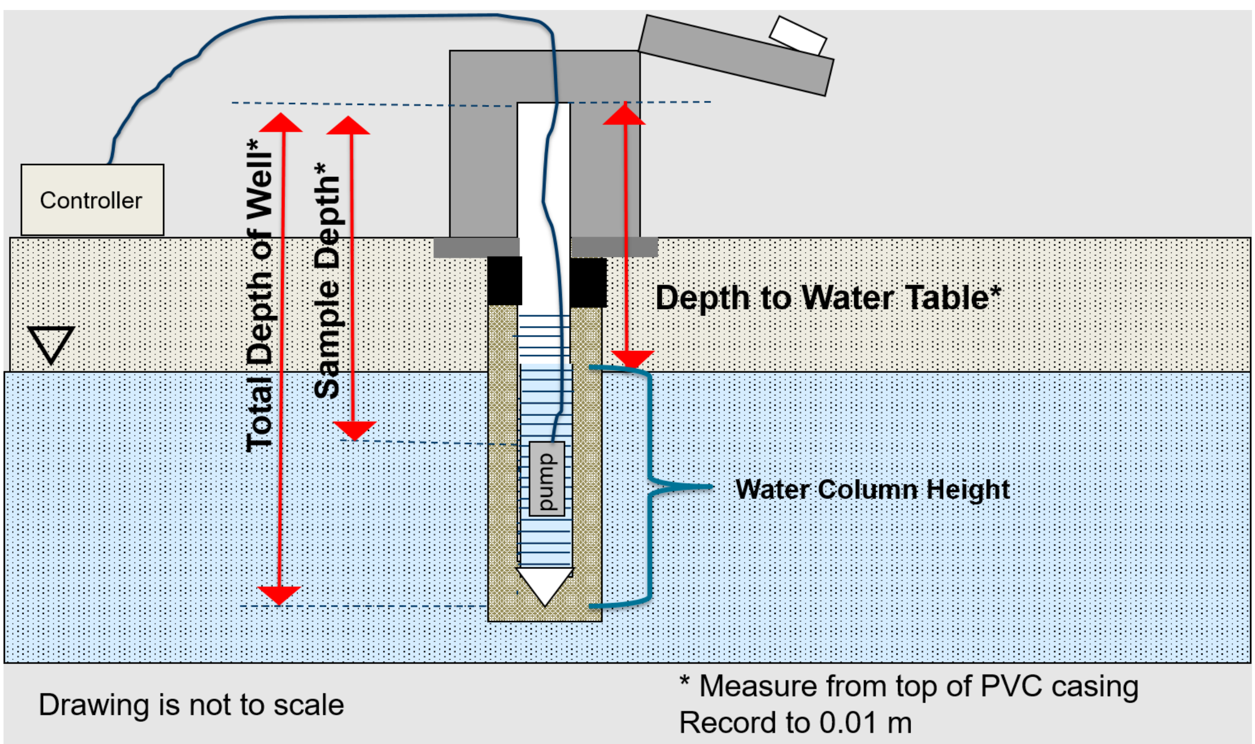


Figure 17. Key groundwater measurements.

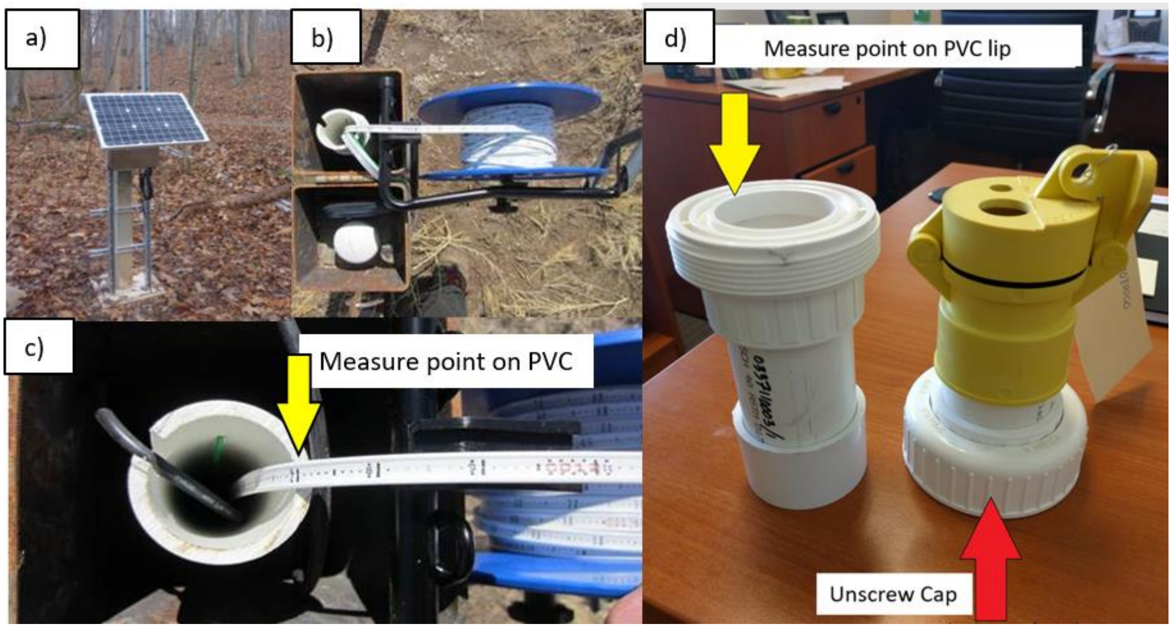


Figure 18. Groundwater well depth measurements (**a**) Standard groundwater well at a NEON site (**b**) Water-level tape attached to outer well casing. (**c**) Reading the depth to water from the water-level tape on standard well. The tapes are marked in "meters" with each foot increment marked in red. Readings are taken at the top of the inner PVC casing. (d) Cap disconnection and measurement point for wells with snorkel cap design.

B.5.3 Extract groundwater from well

B.5.3.1 Low-flow Method

This method is used for high yield wells (recharge rates greater than 100 mL/min). High yield wells should aim to sample using the QED bladder pump where possible. Shallow high yield wells may have better success sampling directly with the peristaltic pump.

1. Calculate water column height as shown in section B.5.2 Locate well and assess water depth).
2. Calculate the sampling depth as follows:

Water Column Height (m)	Sample Location	Sample Depth Calculation
≥ 1.5 m	Top of QED pump should be 1 m below the water surface	(Well Water Surface) + (1 m)
0.5-1.5 m	Top of QED pump should be 0.5 m above the well bottom	(Total Depth of Well) – (0.5 m)
< 0.5 m	End of Peristaltic Pump tubing should be in the middle of the water column	(Total Depth of Well) - (Water Column Height/2)

Note: Measure from top of PVC casing to an accuracy of 0.01 m.

Example 1:
Total Depth of Well = 15.55 m
Depth to Water Table = 5.55 m
Water Column Height = (15.55 – 5.55) = 10.00 m
Sample Depth: (5.55 m + 1 m) = 6.55 m

Example 2:
Total Depth of Well = 7.25 m
Depth to Water Table = 5.85 m
Water Column Height = (7.25 – 5.85) = 1.40 m
Sample Depth: (7.25 m –0.5 m) = 6.75 m

Example 3:
Total Depth of Well = 3.20 m
Depth to Water Table = 2.80 m
Water Column Height = (3.20 – 2.80) = 0.40 m
Sample Depth: (3.20 m – (0.40/2)) = 3.00 m

3. Cut Tubing to Correct Length. (NOTE: Use tubing cutters provided in the well kit to cut tubing, NOT scissors). Tubing will vary with sampler type. If sampling with the QED Bladder Pump, use dual bonded tubing with one line for air delivery to the pump and one line for water discharge from the pump. If sampling with the peristaltic pump, use 0.125 inch inner diameter Tygon tubing.

For all sampler types, the tubing used to sample a well is dedicated to that specific well and should not be used to sample other wells. The first time a well is sampled the tubing will need to be cut to a sufficient length for each well. This length can be relatively unique at each well, depending on the depth to water in each well. It will likely be necessary to cut the tubing in the field after you have measured the water depth. The tubing length needs to be sufficiently long so that there is enough tubing to reach from the sample depth, up the PVC well casing, and then back to the ground to reach either the controller and collection cell or the peristaltic pump. Add at least an extra 2-3m to the length of tubing account for water table elevation fluctuations between bouts (i.e., make sure there is sufficient tubing available if the water table is higher/lower for your next sampling bout) and to account for any tubing trimming in the future.

Steps 4-8 are guidance for **Low-Flow** sampling using the **QED Bladder Pump**. If sampling using the peristaltic pump, proceed to **Step 9.**

4. Set-up the QED Bladder Pump. There are a few components to the sample pump: The sample pump, controller/air compressor, air lines, a battery, and a collection cell (a 1000 mL graduated cylinder or a graduated bucket).

a. Assemble Pump – The pump has push-in style fittings for connecting the air and water lines to the pump. The fitting plate (or "grab plate," a thin metal disk with teeth) can be re-used between sampling events if properly maintained. The grab plate needs to be replaced at the first signs of damage to the teeth or inability to firmly "grab" the tubing. To assemble or change the fitting plate, unscrew the 3-in tall cylinder cap/collar at the top of the pump, remove the top plate (with the "A" and "W" on it), place the fitting plate on the top of the pump with the holes lining up, and then reassemble the pump. Note: make sure that the grab plate has the word "TOP" facing upwards. **Figure 19**(a-d) illustrates this for each step.

b. After sampling, to disassemble or remove the grab plate for future use, remove the collar and top plate and cut the tubing on the side of the grab plate that says "top." Push the cut tubing pieces through the grab plate; this method allows the "teeth" to remain intact and reusable.)

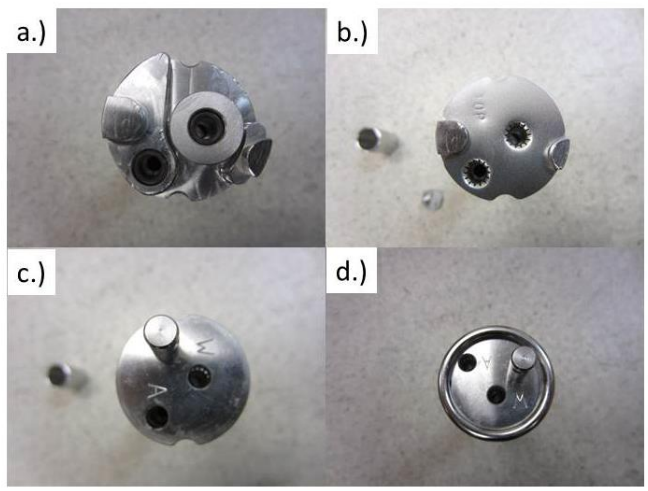


Figure 19. Assembly of the fitting plate at the top of the pump for holding the air and water lines. (**a**) Bare top of pump. (**b**) Fitting/grab plate added ("TOP" must face upwards). (**c**) Top plate added. (**d**) Collar added to lock parts (a-c) together.

5. Attach/Change Air Bladder – The pump uses a bladder to hold water drawn in from the well and compressed air that surrounds the bladder to discharge the water from the pump and out of the discharge lines to the surface. Use a new or dedicated bladder for each well. To replace the bladder, remove the lower portion of the pump (long, metal cuff/housing) to expose the bladder. Cut the old bladder off with scissors and install a new one by sliding the new bladder over the bottom port on the top of the pump. **Figure 20** shows the components of the pump including the bladder.

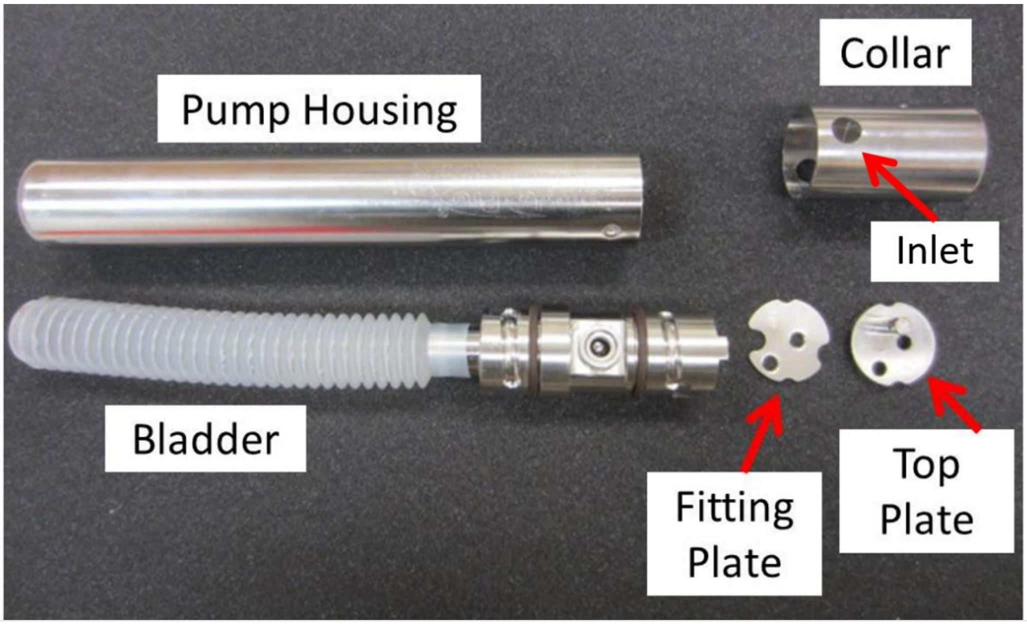


Figure 20. Components of the sampling pump.

6. Attach Tubing Lines and Cable
7. To connect the tubing to the pump, separate the bonded lines for about 15 cm of length and then push each tubing line through the holes in the top of the pump. The top plate is denoted with an "A" for the GREY air-line and a "W" for the CLEAR water-line shown in **Figure 21**. (A good way to keep track of the lines is to remember that you want to SEE the water flowing, so water is the CLEAR line.) The lines should be pushed into the pump top by about 1 cm. A little water dabbed on the ends of the tubing helps facilitate inserting the tubing in the pump. It should be noted that pushing the tubing into the fittings of the grab plate is a little tough and takes a bit of practice. It is sometime easier to first slide the tubing through the cap/collar and top plate and THEN push the tubing into the grab plate/pump. Once the tubing is inserted into the pump, be sure that pump, grab plate, top plate, and collar are all assembled and in the correct (listed) order. Gently but firmly tug the tubing once fully assembled to ensure that the tubing is properly connected.
   a. Attach the post (thread into threaded port) and cable to the pump as shown in **Figure 22**.

Figure 21. Attaching grey air-line and white water-lines to pump (top-right photo shows lines pushed through top plate and "teeth" of grab plate).

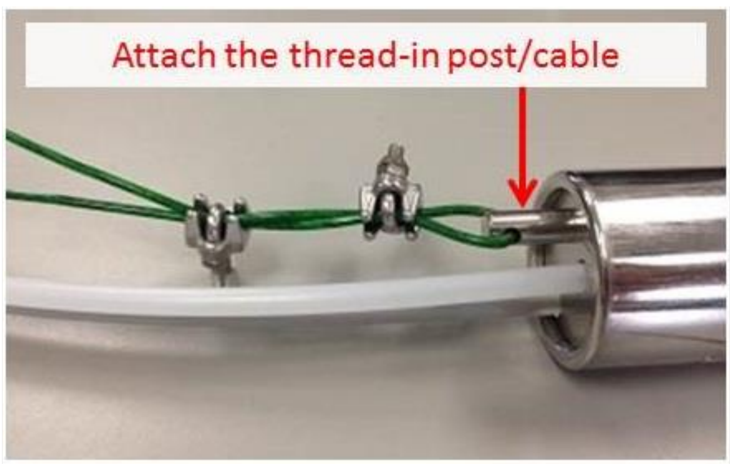


Figure 22. Attach post and cable to the pump via the top plate.

8. Place Pump in Well: Once all tubing is connected between the pump and controller, gently lower the pump into the well holding the assembly by the plastic-coated cable. Lower the pump until the pump is at the correct depth for sampling the well (mark the tubing so that the "correct depth" of the pump can easily be identified by the mark matching with the top of the well casing). Tie the cable off to the metal casing so the pump stays at the desired location. Desired accuracy for setting the pump is +/- 10cm from the specified sampling depth. The inlet for the pump is near the top of the pump (noted by the hole in the side of the pump body) and is the

specific point on the pump to set to the specified depth. When marking the tubing, measure from this point.

9. Set-up the Controller / Compressor / Collection Cell
   a. Connect the blue air-line tubing contained in the controller kit to the AIR OUT port on the controller compressor (**Figure 23**), and then the GREY air-line coming from the pump to the other push-in fitting on the opposite end of the blue air-line. To remove the GREY air-line from the blue air-line pull the thin black collar back toward the brass fitting and pull the tubing out of the push-in fitting (**Figure 24**).

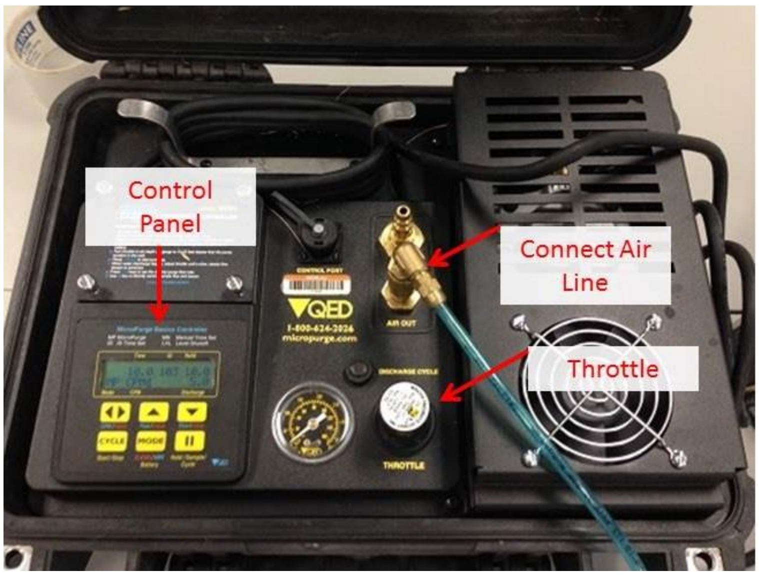


Figure 23. Attach blue air-line to controller.

Figure 24. Attach grey air-line to blue air-line.

b. Place the water discharge line into your collection cell (a 250 – 1000 mL plastic graduated cylinder works well). Place the hand-held water quality probe (YSI PRO2030) into the collection cell (**Figure 25**).

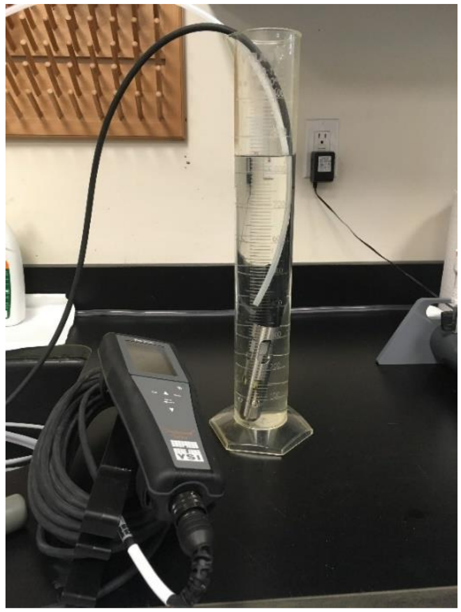


Figure 25. Groundwater Chemistry Collection cell using a 1000 mL graduated cylinder.

c. Operation of the Controller:

i. Once the pump is placed in the well and all the air and water lines are connected to the controller, check to make sure the "throttle" (regulator dial) is turned off – counter-clockwise until it stops.

ii. Connect the controller/compressor to the battery. This will turn the compressor on, but because the pressure throttle is turned down, no air should come out of the controller yet and no water will pump.

iii. Slowly turn the throttle clockwise to begin adding air pressure to the air-line. As a rule of thumb, 1 PSI of air pressure is required to lift water in the pump line 1ft. The max PSI should not be more than 15 PSI over the minimum pressure required to lift the water of 1 psi per 0.42ft of pump depth. After 1-3 minutes, the pump should begin to discharge water in pulses. Record the time that water begins flowing in the data collection app.

The function of the controller is to control the pump functions: the length of time that water is allowed to enter the pump, the length of time that air is sent to the pump to discharge the water in the pump, and the air pressure used to discharge the pump (i.e., compress the bladder in the pump). The regulator dial controls the air pressure. The controller has two main modes of operation for controlling discharge times, displayed on the control panel window. A manual "MN" mode requires the user to specify the length of time desired for each step, and a preset "ID" mode gives predetermined time settings. Pushing the "MODE" button on the controller toggles between the different modes of operation, and the "UP" and "DOWN" arrows show the settings within each mode. Either mode is acceptable to use, but ID mode is easier.

Once a MODE is selected, use the arrows to select a pair of refill and discharge times, indicated on the far right of the control panel window (**Figure 26**). When selecting the pump refill and discharge times, the main aim is to achieve a relatively consistent water discharge rate. Any rate ranging between 100 and 500 mL/min is acceptable, provided it remains relatively continuous (pulsing is expected) and the well water column height is stable. Use the controller to select refill/discharge rates that allow for continuous flow and adjust as needed. Discharge rate is measured by putting the discharge water line into a graduated cylinder and measuring the flow over 30 secs or 1 min intervals periodically through-out the sampling event. Include the total time in this measure, not just the active time of the pump. Ideally once the flow rate is set it will be maintained at this rate for the duration of the sampling event for the well.

Figure 26. Groundwater pump control panel screen. Note the Refill and Discharge times on the right.

<u>**Steps 9-12** are guidance for **Low-Flow** sampling using the **Peristaltic Pump**. If sampling using the QED Bladder pump, proceed to **Step 13.**</u>

10. Set up the peristaltic pump as described in section C.2. and weight the end of the peristaltic pump tubing with stainless steel nuts as shown in **Figure 27**. Then firmly insert a 2-way luer-lock and remove its handle to secure the nuts.

11. Lower one end of the tubing to desired sampling depth, taking care to cause minimal disturbance to the water column. Place the outflow tubing from the peristaltic pump into a graduated cylinder.
12. Use a U-clamp to achieve a steady discharge rate of 100-500 mL/min with minimal drawdown. A Velcro step may help to keep the U-clamp in place.
13. Sampling deep wells using the peristaltic pump may drain the battery over the course of sampling. It is recommended that technicians bring 2 backup batteries with them into the field.

Figure 27. Nuts added to peristaltic pump tubing for weight.

14. Monitor water level and determine recharge rate. Recharge rate is the rate at which the well water is replenished during pumping. Once the water reaches a relatively static level during pumping, the recharge rate is equal to the discharge rate. Water-level within the well should be recorded every 3-5 minutes using the water-level tape. The aim is to select a pumping rate from the well that does not cause the static water level within the well to decline by more than 10% of the value initially noted before pumping started. As an example, if the static water level in the well was measured at 3.25m from the top of the casing prior to turning the pump on, then the decline in the well should be limited to about 0.32m (i.e., measured water depth should not be less than 3.57m from the top of the casing).
    a. If the water depth declines more than the 10% threshold when sampling with the QED bladder pump, then select a decreased discharge rate by either choosing a shorter discharge time on the controller or turning the throttle counterclockwise to decrease the air pressure delivered to the pump. The discharge rate of the effluent water will likely need to be measured a few times prior to achieving the correct settings on the pump.
15. If the water depth declines more than the 10% threshold when sampling with the peristaltic pump, then loosen the U-clamp to decrease the suction.

a. If a static water level cannot be achieved with flow rates below 100 mL/min, then the well is low-yield.

i. Submit a Service Now incident. Low-yield sampling may be advised for the next bout.

ii. For this bout, proceed with sampling via the purge dry method (B.5.3.3 Purge Dry Method). Purge the well at this time and take the YSI measurements.

1) Skip step 14 and collect the groundwater chemistry sample suit after the water column has returned to the original height. This may occur within the same day or take as long as 24-48 hours.

2) If the water has not returned to its original level on the sampling day and it is not possible to return in 24-48 hours, submit a sampling impractical record.

16. Monitor water quality: While the pump is discharging water from the well, monitor the water level and water quality parameters Specific Conductance (µS/cm) and Water Temperature (°C) using the hand-held meter to determine when the water is ready to be collected for sampling.

a. Specific conductance should be measured as temperature-corrected conductivity at 25°C, whenever possible. Ensure conductivity measurements are on the appropriate temperature-corrected and unit setting (i.e., setting SPC, µS/cm).

b. Once you start removing water, take readings from the hand-held meter approximately every 3-5 minutes during the pumping event and record on the sampling sheet in addition to the time and water level. Do not stop the pump between measurements.

c. Once temperature and specific conductance readings stabilize, by varying less than 10% over 3 consecutive readings spaced a minimum of 3 minutes between readings, then the water being discharged from the well is ready to be collected for sampling.

d. If temperature and specific conductance readings do not meet the stabilization criteria after 30 minutes of pumping, you may sample after confirming that three well volumes have been removed.

$$Well\ Volume = (Total\ Well\ Depth - Depth\ to\ Water)\ x\ \pi\ (well\ radius)^2$$

e. Once the criteria in step c or d is met, collect a final set of parameters.

i. Record water quality parameters (SPC, Temp, DO mg/L, and DO %sat) at the time of sampling using the YSI hand-held meter in the data collection app.

ii. Record pH at the time of sampling using the hand-held pH meter in the data collection app.

1) Between wells, immerse the pH combination electrode in reference electrolyte (KCl 3 mol/L).

2) Prior to the next measurement, rinse the combination electrode with the test sample or deionized water.

17. Collect samples: Once the well water is ready to be collected for sampling, it should be collected directly from the water line coming from the pump, not from the collection cell.
18. Filter the samples minimizing the exposure to air as described in section
19. Additional pH Measurements
20. If there is sufficient water remaining, take 2 additional pH measurements. The average of the 3 pH values will be used for the final reported pH. Only take pH replicate measurements if there is additional water available to sample after taking the initial bubble free syringe pH and the rest of the GWC sample suite.
21. B.5.4 Groundwater Sample Rinsing, Field Filtering, and Prioritization.
22. Process samples per SOP C.
23. When removing tubing for the QED bladder pump, tubing can be cut just above the top plate to prevent tube waste.
24. Decontaminate the QED Bladder Pump between wells:
    a. Remove the bladder and place all pump components into a sealed container with 2% bleach. Safety lines can be placed in the same container if you elect to reuse one line.
    b. Shake container and soak for 10 minutes.
    c. Reassemble pump with new or dedicated bladder for each well.
    d. For each well use dedicated tubing for the section that goes into the well.
25. Decontaminate the Peristaltic Pump between wells:
    a. Remove the luer-lock and nuts if reusing between wells.
    b. Place all pump components into a sealed container with 2% bleach. Shake container and soak for 10 minutes.
    c. For each well use dedicated tubing for the section that goes into the well.
26. Wipe down water meter tape with bleach wipes and squirt with DI between wells.

B.5.3.2 Minimum Purge Method

For wells that are low-yield the minimum purge sampling technique may be applicable. Minimum purge sampling works on the assumption that water located above the well screen is stagnant, but water located within the screened interval interacts with the aquifer and is representative of surrounding groundwater chemistry (Puls and Barcelona, 1996; Nielsen and Nielson, 2006). Sample collection using this method is less time consuming because it involves removing the minimum volume needed for sampling while avoiding the stagnant water in the upper well casing. Minimum purge sampling should only be conducted when recharge rates are too low for low-flow sampling and when the water column height is greater than the maximum allowable drawdown described below. If you think that your well qualifies for the minimum purge method, discuss the feasibility with Science prior to attempting for the first time.

1. Requirements for Feasibility

   a. **Volume**

      In order to obtain the necessary groundwater chemistry samples using the minimum purge method, a sufficient volume of water within the screened interval of the well is required. The ideal volume includes: 1) 4L for the full suite of samples; 2) the well volume equivalent to 0.5 m of buffer space; and 3) the volume needed to fill one full tube length for the pump. If available water is insufficient to meet the sample volume requirements, it is acceptable to take a partial sample prioritizing tests in the following order: H2O isotope (RD[14]), FIL, FIL.NUT, ALK, RAW, RAW.NUT. However, it is necessary to discontinue the sampling once maximum allowable drawdown (described below) is reached. If maximum allowable drawdown is less than 1 m, do not use this method.

   b. **Timing**

      This method requires that the pump tubing be placed in the appropriate location within the well water column and left for a minimum of 48 hours prior to sampling (Puls and Barcelona, 1996). This is to allow for background conditions to stabilize after the disturbance created by the pump tubing placement. Due to the timing requirements and the desire for minimal mixing of the water column, this method requires field scientists to know that their wells qualify as low-yield wells prior to the sampling event. Ideally, pump tubing will be placed in low-yield wells in the week prior to scheduled sampling.

2. Methodology

   a. Minimum purge sampling is conducted using the peristaltic pump. Set up the peristaltic pump as described in section C.2.

   b. Calculate the amount of tubing needed to place the pump tubing 0.3m from the bottom of the well, allowing for an extra 1 – 2 m of tubing to stick out above the well top. Deeper wells may require 1/8” inner diameter tubing to appropriately lift the water sample. Use dedicated tubing for each well.

   c. Weight the end of the peristaltic pump tubing with stainless steel nuts as shown in **Figure 27**. Then firmly insert a 2-way luer-lock and remove its handle to secure nuts.

   d. Leaving the sensor in place, lower the tubing to desired depth of 0.3 m from the well bottom at least 48 hours prior to sampling. Take care to cause minimal disturbance to the water column.

e. Secure the tubing in place by attaching it to the sensor cable with a zip tie (**Figure 28**). Tubing with 1/8"ID will fit in the same slot as the cable.

f. Sampling deep wells using the peristaltic pump may drain the battery over the course of sampling. It is recommended that technicians bring 2 backup batteries with them into the field.

Figure 28. Pump tubing secured in place with zip tie.

g. Calculate the **Maximum Allowable Drawdown (MAD)** for a given well. This is the distance between the pump intake and the top of the screened interval minus a 0.5m buffer margin. Consult with Science to obtain screened interval values for your site. If the water level is below the top of the screen, replace the depth to top of screen with depth to water table in the equation as shown below. Depth to the top of the screened interval will require well log information available in Fulcrum.

If water table is above the screened interval of the well:

MAD = depth to pump tubing placement – depth to top of screen - 0.5m

Example 1:
Depth to pump tubing placement = 5 m
Depth to top of screened interval = 2 m
Depth to water table = 1 m
Maximum Allowable Drawdown = 5 m – 2 m - 0.5 m = 2.5 m

If water table is within the screened interval of the well:

MAD = depth to pump tubing placement – depth to water table - 0.5m

Example 2:
Depth to pump tubing placement = 5 m
Depth to top of screened interval = 2 m
Depth to water table = 2.5 m
Maximum Allowable Drawdown = 5 m – 2.5 m – 0.5 m = 2 m
Note: If the calculated MAD is less than 1m, do not use this method and move on to the Purge Dry method.

h. Do not turn the sensor off during minimum purge sampling.

i. Prior to sampling, remove a set volume based on tube length (**Table 9**). Measure and record water temperature, specific conductance (SPC), DO percent saturation, and pH for the discharged water.

   i. Between pH measurements, immerse the electrode in reference electrolyte (KCl 3 mol/L).

   ii. Prior to the next measurement, rinse the combination electrode with the test sample or deionized water.

j. Collect samples immediately following the small volume removal.

   i. To minimize turbidity and disturbance to the water column, samples should be removed at a rate at or below 100 mL/min.

   ii. Filter samples inline per section B.5.4 Groundwater Field Filtering and Prioritization.

   iii. Measure drawdown with the water tape as the sample is being collected and discontinue collection if the MAD is reached.

   iv. If maximum drawdown is met prior to obtaining the full volume needed for the groundwater chemistry suite, prioritize samples as detailed in section B.5.4 Groundwater Field Filtering and Prioritization.

   v. Process samples per SOP C.

Table 9. Volume removed prior to sampling based on tube length for the Minimum Purge method.

Tube Length (m)	0-10	10-12	12-14	14-16	16-18	18-20
Volume (mL)	300	380	440	510	570	640

B.5.3.3 Purge Dry Method

If the minimum purge method is not feasible for a low-yield well, yet there is enough water in the well for a partial sample, the purge dry method can be used as a last resort. This method is not ideal as it has been shown that purging the well to dryness could alter the groundwater chemistry by altering dissolved gas concentrations, redox states, and increasing turbidity potentially inducing fine sediments that may have accumulated at the bottom of the well (Puls and Barcelona, 1996; Nielsen and Nielsen, 2006).

1. Use a peristaltic pump with well-specific tubing to drain the well.
    a. Record the volume of water removed by collecting the entirety of the water discharged in a bucket and measuring the volume of water in the bucket.
    b. Record pre-purge field measurements for pH, Dissolved Oxygen Saturation (%), Specific Conductance (µS/cm), and Water Temperature (°C) in the data collection app.
        i. Between wells, immerse the pH combination electrode in reference electrolyte (KCl 3 mol/L).
        ii. Prior to the next measurement, rinse the combination electrode with the test sample or deionized water.
2. Collect the groundwater chemistry sample suit after the water column has returned to the original height. This may occur within the same day or take as long as 24-48 hours.
3. Start by removing a minimum of 50 mL from well for the field measurements and rinse.
    a. Use a 250 mL graduated cylinder to record pre-sampling YSI and pH field measurements. You may remove the YSI guard for this measurement.
    b. Use the water to rinse the 4L jug then discard.
4. If using the peristaltic pump, sample directly into the sample containers. Filter samples inline per section B.5.4 Groundwater Field Filtering and Prioritization.
5. When obtaining the full sample volume is not possible, prioritize samples as detailed in section B.5.4 Groundwater Field Filtering and Prioritization.
6. Process samples per SOP C.
7. Wipe down water meter tape with bleach wipes and squirt with DI between wells. Make sure that the wipes contain bleach. (Note that normal Clorox wipes do not contain bleach).

B.5.3.4 Needle Method

This method is specifically for Tundra and Taiga domains where liquid water exists close to the surface and frost heave precludes the possibility of obtaining good samples from the wells themselves. This method utilizes a specially designed sampling needle, tubing, and syringe to collect a sample from the active layer, which is the ground layer above the permafrost that seasonally freezes and thaws.

1. In the domain, pre-assemble the 47mm GF/F glass fiber filters in the syringe filter holders.
2. Clean the needle prior to sampling and between wells locations.
    a. Flush the needle several times with DI water.

   b. In cases where the needle holes are severely clogged, flush the holes in the lab with HCL and clear with a hypodermic needle.

3. Assemble the needle, tubing, two three-way stopcocks, and syringe (**Figure 29**). Use individual dedicated syringes and tubing for each well location.

Figure 29. Sampling needle and syringe setup.

4. Take precautions to avoid disturbing the ground surrounding the sample location.
   a. Use the boardwalks and stand downhill of the location when possible.
   b. If taking physical well measurements on the same day, complete the water chemistry sample prior to working on the well.
5. Collect sample
   a. Insert the needle at an angle next to the well infrastructure and sample slightly above the frozen interface (**Figure 29**). Note that the ground will contain pockets with differing levels of saturation. Attempt to sample the inter-tussock areas within a 2 m radius of the well and make sure to avoid areas of standing surface water.
   b. **Bubble-free** sampling will minimize contact between the anoxic sample and the atmosphere which can impact pH, Alkalinity, and DIC. Fill a 140 mL syringe using a bubble-free technique.
      i. Fill a 140 mL syringe using a bubble-free technique.

1) Locate a sampling location with a substantial pocket of water. If any air bubbles are drawn into the syringe, the water pocket is not large enough to collect a bubble-free sample.

2) Once you have located a spot capable of providing a continual stream of water that is void of bubbles, draw in approximately 50 mL of water to the syringe. Ensure that all connections are airtight so that no atmospheric gases are drawn into the syringe.

3) Close the stopcock attached to the tygon tubing to maintain a bubble-free connection to the groundwater and disconnect the two stopcocks.

4) Expel air from syringe (**Figure 30**).

   a) Hold the syringe upside down vertically and expel the air to get rid of the large air bubble in the syringe.

   b) Tap on the syringe to shake any small bubbles off the plunger.

5) Pull in a small amount of air to collect the smaller bubbles you just shook off the plunger and expel the air again. Maintain at least 30 mL of water in the syringe during this step.

Figure 30. Expel air bubbles from the syringe during bubble-free sampling.

6) Re-attach the stopcocks to one another. Make sure that the connection is tight so that air is not introduced.

7) Keep the stopcock attached to the tubing in the OFF position towards the tubing and the stopcock attached to the syringe in the OFF position perpendicular to the in-

line flow of water. This will result in the water coming out of the side port of the stopcock attached to the tubing (**Figure 31**). Expel all but ~5 mL of water from the syringe.

Figure 31. Stopcock position for expelling water during bubble-free sampling.

8) Open the stopcock attached to the tubing and SLOWLY pull the syringe plunger. If you pull too forcefully, you can change the pressure within the syringe and cause dissolved gases to come out of solution and create bubbles. Draw in as much water as needed for sample collection and field measurements. If bubbles are larger than 1-2mm then clear the syringe and start the process again.

9) Indicate instances in the data collection app to inform data users when water table conditions render bubble-free sampling impossible.

c. **ALK**

i. Once you have collected 140 mL of bubble-free sample, use the 47mm syringe filter to filter directly into a 60 mL ALK bottle. Fill the bottle from the bottom up, overflow the container, and cap. DO NOT LEAVE HEADSPACE.

d. **Field pH**

i. Remove the syringe plunger and immediately insert the calibrated pH probe into the remaining water. Within a few seconds there is usually a plateau, followed by a steady rise in pH. The plateau value is what you are aiming to record. Record pH in the data collection app.

1) Discard water.
2) Between wells, immerse the pH combination electrode in reference electrolyte (KCl 3 mol/L).
3) Prior to the next measurement, rinse the combination electrode with the test sample or deionized water.

e. **DIC**

i. Fill the syringe again with 140 mL using the bubble-free technique.

ii. Filter 15 mL through the syringe filter into the 60 mL DIC bottle three times to triple rinse.

iii. Filter the remaining water into the 60 mL DIC bottle from the bottom up. Overflow and cap the bottle. DO NOT LEAVE HEADSPACE. DIC is susceptible to alteration when exposed to air.

f. The remaining samples do not require the bubble-free method and should be prioritized in the following order if available water is insufficient to meet the full sample volume.

i. **H2O Isotope** (RD[14])

ii. **FIL**

1) Use a 250 or 500 mL bottle for low-volume situations rather than sending a partially full 1 L bottle.
2) If using a 250 mL bottle, LEAVE headspace to prevent freezing.
3) A minimum FIL sample is 100 mL.
4) Filter the FIL sample in field directly after sample collection.

iii. **FIL.NUT**

1) Leave headspace to allow for expansion during freezing.

iv. **RAW**

1) Leave headspace to prevent breakage from freezing.

v. **RAW.NUT**

1) Leave headspace to allow for expansion during freezing.

vi. **Remaining Field Measurements**

1) Pour syringe water into a 250 mL graduated cylinder and insert the YSI probe.

2) Record Dissolved Oxygen Saturation (%), Specific Conductance (µS/cm), and Water Temperature (°C) in the data collection app.

vii. **Additional pH Measurements**

1) If there is sufficient water remaining, take 2 additional pH measurements. The average of the 3 pH values will be used for the final reported pH. Only take pH replicate measurements if there is additional water available to sample after taking the initial bubble free syringe pH and the rest of the GWC sample suite.

B.5.4 Groundwater Sample Rinsing, Field Filtering, and Prioritization

1. Rinsing

After recording water quality parameters, sampling method, and approximate volume of water discharged, Rinse collection bottle and cap with the appropriate sample water (i.e., use filtered water to rinse filtered samples)

To rinse: Hold the cap in your hand (setting the cap down increases risk of contamination). Fill water from pump into jug until about 1/5 full, shake to rinse the bottle and discard water away from the well. Repeat 2 more times. For low-volume samples, a modified rinse may be used as described in the specific sampling method sections above.

2. Field Filtering

Particulates within groundwater samples will undergo chemical reactions upon contact with the atmosphere affecting pH, Alkalinity, and DIC. By filtering in the field rather than back at the lab, we can reduce the contributions of particulate materials to the dissolved chemistry.

Filter the FIL, FIL.NUT, and ALK samples in the field as close as possible to the time of collection. Read through the options below to determine the best method for your scenario. See Section C.1 for instructions on setting up the peristaltic drill pump.

a. In-line Field Filtering:

In-line filtering is appropriate for samples collected directly with the peristaltic pump or samples collected with the QED bladder pump in wells with both high recharge rates and low particulate content.

i. For peristaltic sampling, connect the intake end of a capsule filter to the outflow of the peristaltic pump and the outflow end to additional tubing (~7”) that can reach the bottom of the sample bottle.

ii. For QED bladder pump sampling, use an adaptor to connect the peristaltic pump tubing (1/4’’ ID x 3/8’’ OD) intake directly to the QED groundwater pump outflow clear water line. Connect the intake end of a capsule filter to the outflow of the peristaltic pump and the outflow end to additional tubing (~7”) that can reach the bottom of the sample bottle.

iii. Filter directly into the FIL, FIL.NUT, and ALK sample bottles. Overflowing each bottle from the bottom upwards and immediately cap leaving no headspace.

b. Field Filtering with a Flow-through Reservoir:

A flow-through reservoir is used during low-flow sampling with the QED bladder pump to store water in the short period between well water extraction and filtering. This method is useful if the water has high particulate content or longer periods of time between the water exiting the well and it being filtered into the sample bottles.

i. If Sampling with the QED Bladder Pump insert the outflow end of the groundwater sample tubing through an appropriately sized hole drilled into a 1L Nalgene cap (**Figure 32**). Insert the intake of the peristaltic drill pump tubing into a second hole in the cap. Ensure that both tubes are long enough to reach the bottom of the Nalgene bottle when closed. Use parafilm to create an airtight seal between the tubes and cap.

ii. With the cap loose, pump directly from well into the 1L Nalgene container, filling from the bottom up.

iii. Allow the container to overflow, then seal the cap onto the container.

iv. Allow large particulates to settle to the bottom of the Nalgene container and situate the intake of the peristaltic pump tubing above any settled sediment.

v. Start the peristaltic drill pump. Simultaneously run both pumps so that the water line remains at or close to the top of the Nalgene. The goal is for no air bubbles to be in the tubing.

vi. Pump the outflow of the peristaltic drill pump through the capsule filter and through a final tube to fill the FIL, FIL.NUT, and ALK containers from the bottom up. Make sure to rinse this tube with DI between wells.

vii. Particulate heavy water can sometimes break through the internal filter in the capsule. A series of multiple filters in line and a peristaltic pump rate <15 psi can be used if particulates persist in the filtered sample.

viii. For the FIL and ALK containers, overflow the containers then immediately cap leaving no headspace.

ix. For the FIL.NUT samples, pour off the top of the sample to just below the bottle shoulder in order to create headspace to prevent breakage during freezing.

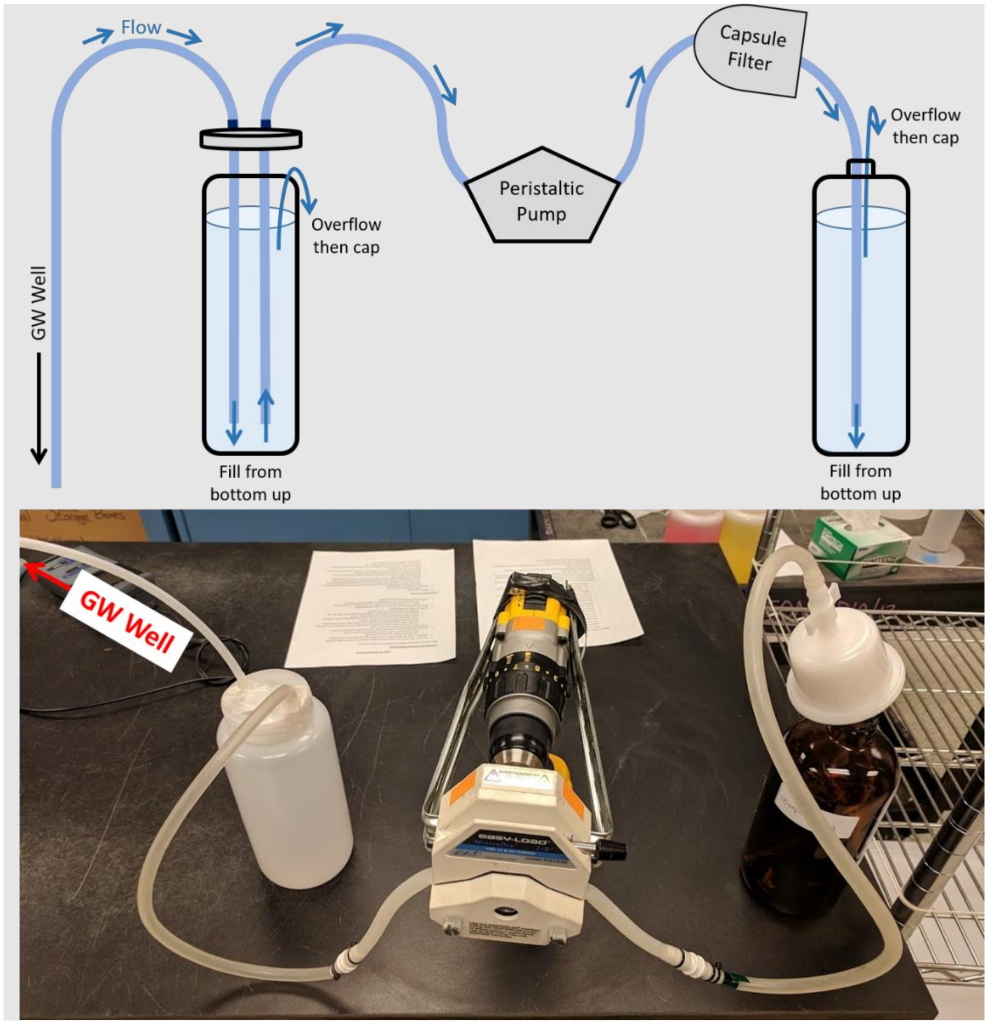


Figure 32. Filtering setup to minimize sample aeration during filtration for low-flow groundwater samples.

c. Field Filtering for the Needle Method

i. The needle method will utilize a **pre-ashed** 47 mm GF/F syringe filter the .DIC, .FIL, .FIL.NUT, and .ALK samples directly into the sample bottles.

ii. Overflow the bottles from the bottom up. Leave no headspace and immediately cap.

3. Sample Prioritization and Headspace (excludes needle method).

If available water is insufficient to meet the sample volume requirements, it is acceptable to take a partial sample prioritizing tests in the order below. For sample prioritization specific to the needle method, see section B.5.3.4 Needle Method.

a. Field Measurements

b. H2O isotope (RD[14])

c. FIL

i. For low-volume situations, use a 250 or 500 mL bottle rather than sending a partially full 1 L bottle.

ii. A minimum viable sample consists of 100 mL FIL.

iii. When possible, DO NOT leave headspace in the FIL sample. If there is not enough volume to fill the 250 mL bottle, continue to collect the partial sample and indicate the presence of headspace in the data collection app to inform data users of suspect DIC and pH external lab values.

d. FIL.NUT

i. Leave headspace to allow for expansion during freezing.

e. ALK

i. Use the smallest bottle possible to obtain enough volume to perform the ALK titration while minimizing the risk of headspace.

ii. When possible, DO NOT leave headspace. If there is not enough volume to fill the smallest bottle, continue to collect the partial sample and indicate the presence of headspace in the data collection app to inform data users of suspect ALK external lab values.

f. RAW

i. Leave headspace.

g. RAW.NUT

i. Leave headspace to allow for expansion during freezing.

SOP C Sample Collection and Processing

C.1 Collect Unfiltered Water- RAW, RAW.NUT, and ANC Samples

1. Following triple rinsing of the collection bottles, collect raw samples (**Figure 6**):
    a. A 500 mL burned amber glass bottle for external lab (RAW)
        i. Leave headspace - fill to just below the neck to reduce potential for breakage if bottle freezes during shipment.
    b. A 125 mL wide mouth HDPE (RAW.NUT)
        i. Leave headspace - fill to just below the shoulder (100-120 mL) to reduce potential for bottle damage during freezing.
    c. [Surface water only] A 250 mL amber glass bottle with Phenolic lined cap – (ANC) ***to be analyzed at the Domain Support Facility.**
        i. Fill **COMPLETELY** to the rim and close cap tightly to minimize headspace.
            1) When possible, overflow each bottle from the bottom upwards and immediately cap leaving no headspace (**Figure 32**).
        ii. You may use a 125 mL amber glass bottle with Phenolic lined cap bottle if that is more appropriate for your system but collect enough water in case titrations must be re-done.
        iii. Note: ANC samples are only collected monthly.
2. If you collected the sample in a 4 L jug, make sure to shake the POM/RAW jug **for at least 15 seconds** before rinsing and or filling the unfiltered sample bottles.
    a. Do NOT shake the FIL, FIL.NUT, ALK jug prior to subsampling as that introduces air to the sample and can alter the analyte concentrations.
3. If collecting replicates, collect 2 additional sets of samples per sampling location at the same time and location as the primary samples.
4. Record data in the mobile app.
    a. Scan the barcode label with the tablet (**Figure 33**).
        i. Ensure barcode on tablet matches sample barcode, if not rescan barcode.
        ii. No barcodes are needed for ANC and ALK samples.
    b. Ensure that the human-readable sample ID matches the sample ID generated by the mobile app.
5. Immediately chill samples (4°C ± 2 °C). **<u>DO NOT FREEZE RAW and ANC samples. Freeze NUT samples as soon as possible.</u>**

Figure 33. Barcode label scanning.

C.2 Collect Filtered Water Samples – FIL, FIL.NUT, ALK

In wadeable streams sampling, you can filter directly from the stream, if possible, being sure not to have the tubing on the bottom of the stream (end of tubing should be ~ 10 cm under surface). For lakes and non-wadeable streams, you can filter directly out of the 4 L jug **after collecting the sample with a Kemmerer**. You may also use the 4 L jug for wadeable stream samples, as well. For most groundwater samples, filter directly into the sample bottle rather than the 4 L collection jug.

1. Set up the peristaltic pump (**Figure 34**):
   a. The peristaltic pump should be fitted with peristaltic tubing connected to ¼ in Inner Diameter (I.D.) C-Flex tubing on either end (**a**).
   b. Place a **CLEAN** end of the tubing into the stream (~ 10 cm below the surface of the water), if possible, the 4 L collection jug (**b**), or the 1L collection jug for some groundwater samples as described above. Rinse tubing with sample water or DI water before placing in jug, if necessary.
   c. Attach the other end of the tubing to a $^{3}/_{8}$ – ¼ in tubing connector, which is then attached to the peristaltic tubing and pump (**c**).
   d. The other end of the pump should connect to a $^{3}/_{8}$ – ¼ in tubing connector.
   e. Attach one end of ¼ in C-flex tubing (2 ft long) to the tubing adaptor (**d**).
   f. Using the drill peristaltic pump, rinse tubing with approximately 100 mL of sample water. The direction of the drill pump can be changed, if necessary.

g. When tubing has been rinsed and is mostly filled with water (i.e., no large air pockets), attach the end of the outflow tubing to an **<u>unused</u>** filter capsule fitted with a tubing connector (**e**).

   i. Make sure the tube is filled with water to reduce air being forced through the filter and potentially blowing a hole in the filter.

   ii. NOTE: Make sure to attach filter so that the direction of flow follows the FLOW arrow on the capsule filter. The flat end should be at the end (**Figure 36**).

h. Prime the filter by holding it upright. This allows the entire capsule to fill with water. Filter approximately 100 mL of sample water to rinse the filter and discard this rinse water.

Figure 34. Pump and filter setup, including a peristaltic sampling pump (modified from Woessner 2007), a 4 L sample bottle, tubing connectors to connect peristaltic and C-flex tubing, and a capsule filter. Image on right shows the correct way to prime the filter by holding it upright.

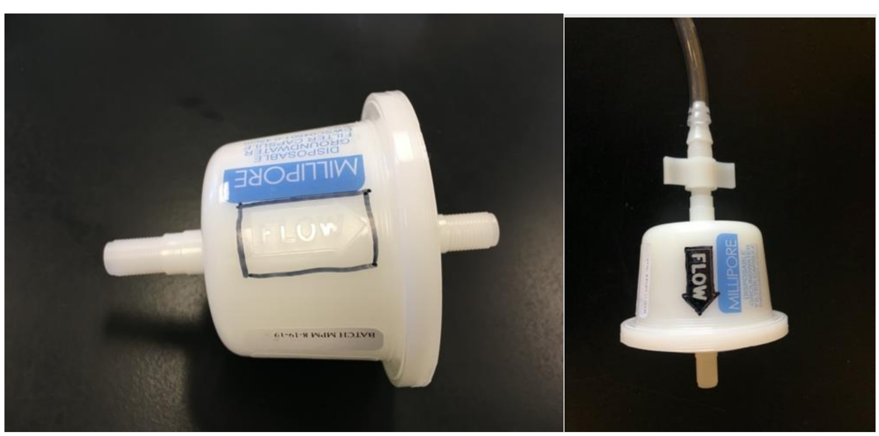


Figure 35. Pictures highlighting flow arrow on capsule filter. These have been highlighted for the purpose of the picture but will not be on your filter. They can be hard to see. Ensure you set up the filter so water flows through it correctly, with the flat end at the end of the setup.

2. Filter slowly. Do not pump too fast or you could blow out the filter, which will result in contaminating the filtered sample with particulates.
   a. Never filter faster than 1 L every 16 seconds (250 mL per 4 seconds).
   b. Use U-bold to secure drill trigger at desired speed.
3. When filtering, try to reduce oxygenation of the sample water as much as possible by:
   a. Filtering slowly.
   b. Using tubing to fill the sample from the bottom up (**Figure 32**), if possible, or running the filtered sample down the side of the bottle when filling.
   c. Take extra caution for GW samples as differences in pressure can exasperate oxygenation.
4. Rinse sample bottles and caps with filtered water. You may wish to secure the drill trigger at desired speed, thus freeing one hand while filtering.
   a. Filter approximately 25 mL into the 1 L glass bottle (FIL) and the 125-HDPE and 250-mL glass bottles (FIL.NUT and ALK, respectively). Cap and shake to rinse.
   b. Repeat rinsing 2 more times.
5. **Fill filtered glass sample bottle (FIL) and ALK bottle completely (NO HEADSPACE).**
   a. For low volume groundwater samples, use a 250 mL FIL bottle and the smallest ALK bottle possible to minimize chemical changes due to headspace.
   b. For the Needle Method the FIL sample is further subdivided between .FIL and .DIC because bubble-free sampling is time-intensive, and the active layer often consists of low-volume water pockets.
      i. Use a 47 mm GF/F syringe filter to filter a bubble-free. DIC sample (sampleType DIC) directly into a 60 mL sample bottle. Overflow the bottles from the bottom up. Leave no headspace and immediately cap. This will be used for lab analyses of pH and DIC analytes.
      ii. Use a 47 mm GF/F syringe filter to filter a separate non-bubble-free FIL sample (sampleType FIL) for the remaining analytes. Filter into a 250 mL sample bottle overflowing from the bottom up and immediately cap.
6. **Fill the FIL.NUT bottle, leaving headspace to allow for expansion of water during freezing. Fill to below the shoulder (100-120 mL of sample).**
7. **Inspect FIL bottle for evidence of cloudiness or larger particulates.** If these exist, you may have blown a hole in the filter. If evident, replace filter and repeat steps to refill bottle.
   a. **For groundwater**, the achievable level of clarity will differ dramatically between sites based on the depth of the water table and type of substrate.

i. Sites with very shallow groundwater may never reach full clarity. For these sites, pump slowly (max 15 psi) through two to three filters to improve clarity as much as possible.

ii. Murky water in groundwater wells may indicate the need for well redevelopment.

8. Record data in the mobile app.

    i. Scan the barcode label with the tablet (**Figure 33**). Ensure barcode on tablet matches sample barcode, if not rescan barcode.

    ii. Ensure that the human-readable sample ID matches the sample ID generated by the mobile app.

9. Place samples in cooler with ice to keep cool (4°C ±2°C) until returned to lab.

10. Group the NUT samples together so they can be frozen (-20°C) as soon as possible upon returning to lab.

11. Group ALK and ANC samples together and ensure they will not be accidentally shipped to the water chemistry analytical laboratory.

12. Dispose of the capsule filter after all samples have been filtered per site per bout. Capsule filters are single use.

    a. Lakes that stratify should use a different filter for each sampling station.

    b. Groundwater samples should use a different filter for each well.

    c. Exceptions:

        i. If collecting replicates (twice per year), you may re-use the capsule filter within a station.

        ii. If collecting lab and field blanks (once per year), you may reuse the filter after collecting the Filtered FB (Field Blank). The DI field blank MUST be collected before collecting sample water. Be sure to run at least 100 mL of sample water through the filter prior to collecting sample.

End the Sampling Day

Sample storage and shipping:

1. FIL and RAW samples should be shipped chilled to lab within 24 hours, if possible, preferably the same day as sample collection. Max hold time is 72 hours.

2. FIL.NUT AND RAW.NUT samples should be frozen immediately until shipping to external facility for nutrient analysis. It is best practice to use the Domain Inventory app for storage of samples with longer hold times, such as the nutrient samples, to reduce shipping errors.

3. ALK and ANC titrations should be completed within 24 hours, if possible. Max hold time is 72 hours.

Refreshing the sampling kit

1. Restock the sampling kit (shipping cooler) with new water chemistry sampling bottles with new labels attached, (alkalinity and ANC bottles can be rinsed with DI water and reused), filters, etc.
2. Discard any used capsule filters.

Equipment maintenance, cleaning and storage

1. Run clean water through the peristaltic pump to rinse tubing. Make sure to pump all water out of tubing before storage.
2. Charge drill pump batteries.
3. Ensure all bottles and equipment is rinsed with DI water. Ensure the field meter is thoroughly rinsed.

Ending groundwater sampling

1. Check that the cable is properly aligned with the docking ring.
2. Ensure that the sensor is connected and streaming before leaving the site.

SOP D Laboratory Analysis

Alkalinity and Acid Neutralizing Capacity

Alkalinity and Acid Neutralizing Capacity (ANC) are measures of the water's ability to buffer systems from changes in pH by neutralizing strong acids for filtered and non-filtered (i.e., whole-water samples), respectively. Thus, alkalinity and ANC are identical in systems without titratable particulates. Alkaline compounds include bicarbonate, carbonate, and hydroxides, each of which removes H^+ ions from the water, ultimately increasing the system pH. Lakes without these alkaline compounds are often unable to buffer against changes in acidity, and therefore, any acid added to the system, such as from acid rain or wastewater effluent, may result in an immediate decrease in lake water pH. Thus, alkalinity and ANC are important measures to understand and predict how a system will respond to acidic inputs.

To determine alkalinity and ANC concentrations, a known strength of acid is added until the three main forms (bicarbonate, carbonate, and hydroxide) are converted to carbonic acid. At pH 10, ~8.1, and ~5, hydroxide, if present, carbonate, and bicarbonates respectively are converted to carbonic acid (**Figure 36**). By a pH 4.5, all bicarbonate and carbonate species should be converted to carbonic acid. The pH at which the species are converted is the equivalence point. NEON will calculate total alkalinity and ANC, thus focusing on the bicarbonate equivalence point (~pH 5). The amount of acid needed to convert the species to carbonic acid is correlated with the amount of alkalinity and ANC in the sample. NEON expresses alkalinity as meq/L.

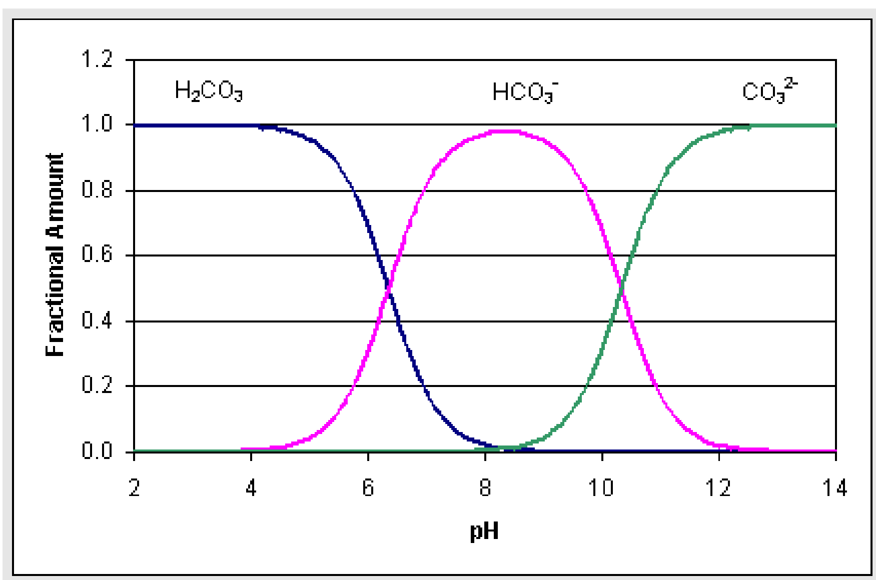


Figure 36. Fraction of carbonic acid(H_2CO_3), bicarbonate (HCO_3), and carbonate (CO_3^{2-}) as a function of pH (usu.edu).

NEON will largely follow the USGS procedures for the analysis of alkalinity and ANC using a digital titrator (Rounds 2012). Measurement will be determined at the Domain Support Facility following the Inflection Point Titration (IPT) Method for most of the NEON Aquatic sites. The IPT method is a titration method in which the sampler titrates on both sides of the expected equivalence points. The point at which the slope of the titration curve is the steepest is the inflection point. However, when alkalinity or ANC is extremely low (<0.4 meq/L or 20 mg/L) or conductivity is low (<100 µS/cm), the Gran function plot (Gran) method will be followed. This protocol focuses on the use of the IPT method, and briefly mentions the Gran method. For additional details on the IPT method or the Gran method, see the USGS protocol (Rounds 2012).

During Operations, NEON will verify the reproducibility of samples by completing a sample analysis on a replicate alkalinity sample or a reference sample, at a minimum of every 10 samples. Note: Only **one** additional ALK sample is collected for titrations completed in the Support Facility. Reproducibility should be ±5%. For low conductivity (<100 µS/cm), low alkalinity (<4 meq/L), reproducibility should be within 10%. For very low alkalinity samples (<1 meq/L), reproducibility requirements will be hard to meet due to rounding errors alone. For these very low alkalinity samples (<1 meq/L), we suggest increasing titration sample volumes to 150 mL.

Quality assurance will be performed on data collected via these procedures according to the NEON Science Performance QA/QC Plan (AD[04]).

For all sampling stations, ALK and ANC samples should be collected and analyzed in the domain, except:

- GW well stations- For domain collection and processing - only collect and process ALK.

D.1 Sample Processing Timing

Following sample collection, alkalinity and ANC samples should be kept on ice or refrigerated at 4°C ±2°C, unless they are processed immediately. Laboratory analysis should be completed as soon as possible after returning from the field. Alkalinity and ANC samples should be processed within 24 hours. Samples analyzed after the 24 hours window will be flagged. The maximum allowable time between sample collection and analysis is 72 hours.

D.2 Preparation

1. Turn on pH meter well in advance of sample analysis (approximately 30 minutes). Check the internal fluid levels and fill if necessary.
2. These pH probes can last 5 years but require regular maintenance.
   a. Each domain is responsible for reading the manual and following maintenance, storage, and cleaning instructions.
   b. Conduct monthly checks of 1) the pH internal electrode fluid level and 2) the storage solution fluid level. Refill if necessary.
   c. To avoid electrode solidification in the pH probe, the filling solution should be replaced with new and fresh KCl solution every 4-6 months.

d. Salt crystals on the probe from the KCl storage solution should be cleaned using DI water. Do not use ethanol.

e. Probe maintenance/filling solution should be recorded and tracked at each Domain.

f. If the probe exhibits slow or erratic behavior, the probe should be cleaned, and the internal fluid should be flushed and replaced with new pH electrode filling solution, **using a disposable pipette.**

   i. If fluid changes and cleanings do not fix erratic or slow response probes, you should order a new probe.

g. Where possible, include the pH probe in the annual lab equipment calibration/maintenance schedule.

3. If present, open the vent at the top of pH probe to open while performing titrations. Ensure the vent is closed when titrations are complete.

4. Ensure pH buffers and samples are at room temperature before calibrating and beginning titrations.

   a. Be sure to allow the sample bottle to sit on a lab bench until the temperature has equilibrated.

   b. Make sure buffer solution has not expired and is not reused.

      i. Discard all expired chemicals in accordance with Site Specific Chemical Hygiene Plan and Biosafety Manual or with Site Specific Chemical Disposal Procedures. Check Safety Data Sheets for more information or contact NEON Safety Department.

   c. Ensure the bottle has been capped during storage to reduce contamination.

5. Check the pH meter calibration at pH 4 and 7. DO NOT use Kimwipes on pH probe tip.

   a. pH 4 and 7 buffers are used for calibration because they are closest to the pH ranges, we are most interested in during the titration. If your sample water pH is >8, you should check, and recalibrate, if necessary, using the pH 10 buffer solution.

   b. If the pH meter is off by ≥0.1 pH units, calibrate pH meter following pH meter manual.

   c. After the entire calibration is complete:

      i. **If doing a 2-point calibration, record the slope after both buffers. If doing 3-point calibration, record after all three buffers.**

         1) **Record slope reported after calibration of pH 4 and pH 7 buffers and the slope between pH 7 and PH 10, if applicable.**

2) **The slope is given on the report screen immediately following calibration. This screen goes away after 5 seconds, but you can get it back by pressing the REPORT button at the bottom of the screen.**

6. Record the meter readings on the Water Chemistry Domain Lab Data Sheet (RD[05]). If the meter is re-calibrated, record the post-calibrated pH check values.
7. Ensure sulfuric acid titrant solutions have not expired.
   a. Discard all expired chemicals in accordance with Site Specific Chemical Hygiene Plan and Biosafety Manual or with Site Specific Chemical Disposal Procedures. Check Safety Data Sheets for more information or contact NEON Safety Department.
8. Allow samples to come to room temperature (20C +/- 5C) by letting the sample bottle(s) sit on the lab bench until the temperature has equilibrated.
   a. **Samples must remain in the closed bottle until they are measured to reduce exchange with oxygen**. This is important for all samples, but particularly important for GW samples.

D.3 Titration Workflow

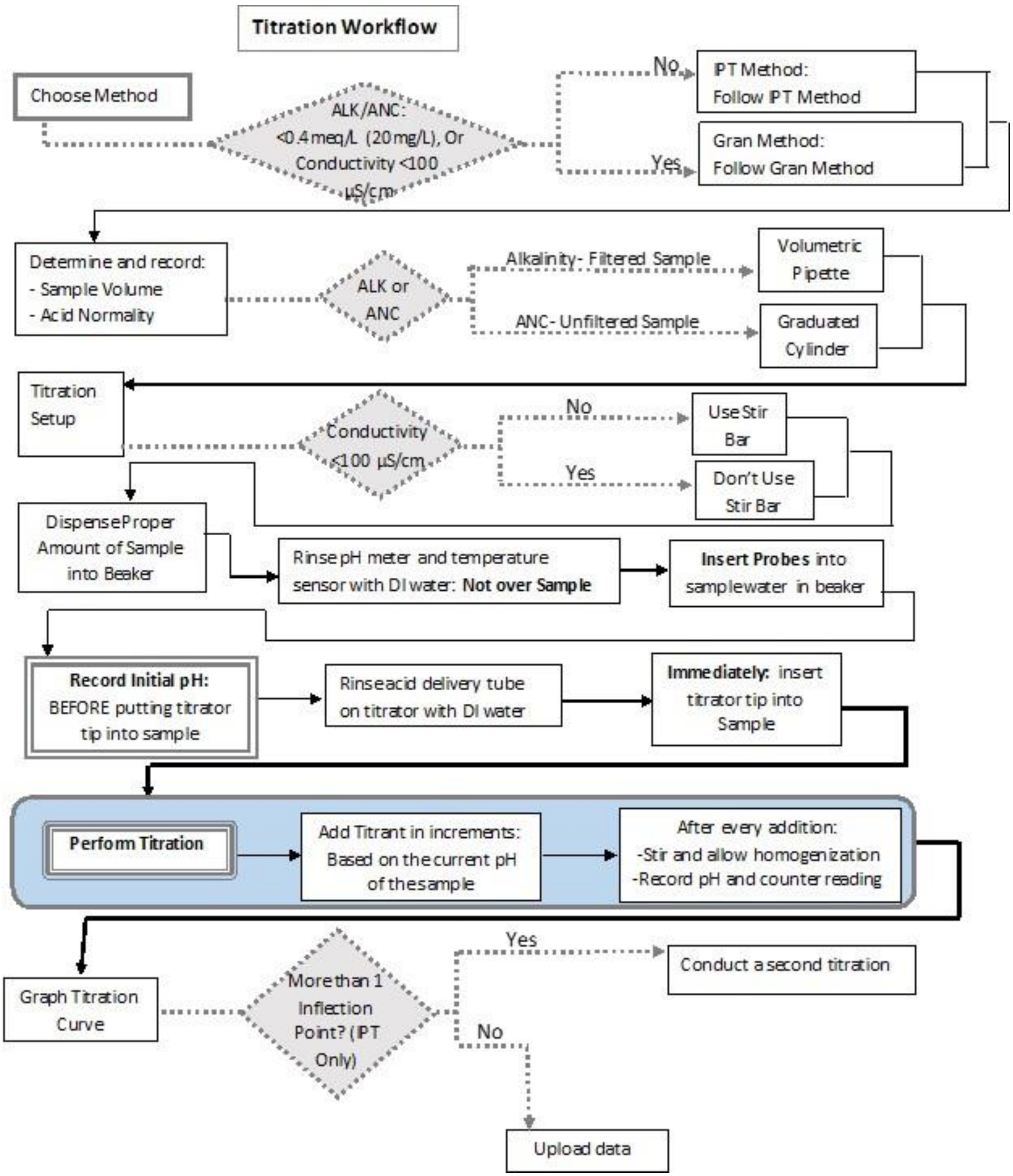


Figure 37. High Level titration workflow.

D.4 Titration Sample Processing

1. Determine the method (IPT or the Gran method) of measurement you will use by evaluating known conductivity or alkalinity measurements. Most waters will use the IPT method. However, when alkalinity or ANC is <0.4meq/L or 20mg/L or conductivity <100 µS/cm the Gran method should be followed. Record method type on the Water Chemistry Domain Laboratory Datasheet - Alkalinity/ANC Titrations (RD[05]). For additional details on the IPT or the Gran method, see the USGS protocol (Rounds 2012).

Note for Gran Method Users:

This protocol details the IPT Method, although the information in the steps is still useful to the Gran Method users. See USGS Gran method (Rounds 2012) for detailed instructions on using the Gran Method to calculate alkalinity. Contributing carbonate species will not be determined). In short, titrate **to change pH 0.2 – 0.3 pH units (**DO NOT GO TOO FAST). Titrate to pH of 3.5. Do NOT use a stir bar if conductivity is < 100 µS/cm, but swirl solution gently (20 seconds, do not create a vortex) between additions. Wait 15 seconds before recording data and adding more acid. NOTE: You do not need to wait for the pH meter to stabilize. It is better to be consistent with the wait time than to wait for the pH meter to stabilize, which might never happen.

2. Determine the sample volume and acid normality you will use (**Table 10**).
   - Most measurements will require a 50 mL volume with 0.16 *N* titrant. Thus, if you do not know the expected alkalinity or ANC values, start with a sample volume of 50 mL and 0.16*N* titrant, and adjust as necessary.
   - 1.6*N* will only be used when alkalinity or ANC is greater than 4.0 meq/L, although it may not be necessary. **Table 10** provides suggested sample volume and titrant normality but should be adjusted as necessary per site. Following initial data analysis, we suggest using 150 mL of sample if measured value is < 1.0 meq/L.
3. Record sample titration normality on the Datasheet (RD[05]).

Table 10. Suggested sample volume and titrant normality for alkalinity and ANC measurements based on approximate concentration ranges.

Alkalinity or ANC (meq/L)	Alkalinity or ANC (mg/L as $CaCO_3$)	Sample Volume (mL)	Titrant Normality (*N*)	Minimum Beaker Size (mL)
0-1.0	0-50	150	0.1600	200
1.0-4.0*	50-200	50	0.1600	100
4.0-20	200-1000	100	1.600	150
>20	>1000	25	1.600	50

* indicates the suggested volume and titrant solution if alkalinity or ANC is unknown. ANC is acid neutralizing capacity. Table modified from USGS TWRI Book 9, Alkalinity, Version 3.0 7/2006.

4. Attach the titrant cartridge to the digital titrator body. Chemical resistant gloves and safety glasses are needed when handling the cartridge and setting up the titrator.
   a. Do not remove the cartridge cap until after the cartridge is fully in place and plunged. Depress the plunger-release button and retract the plunger.

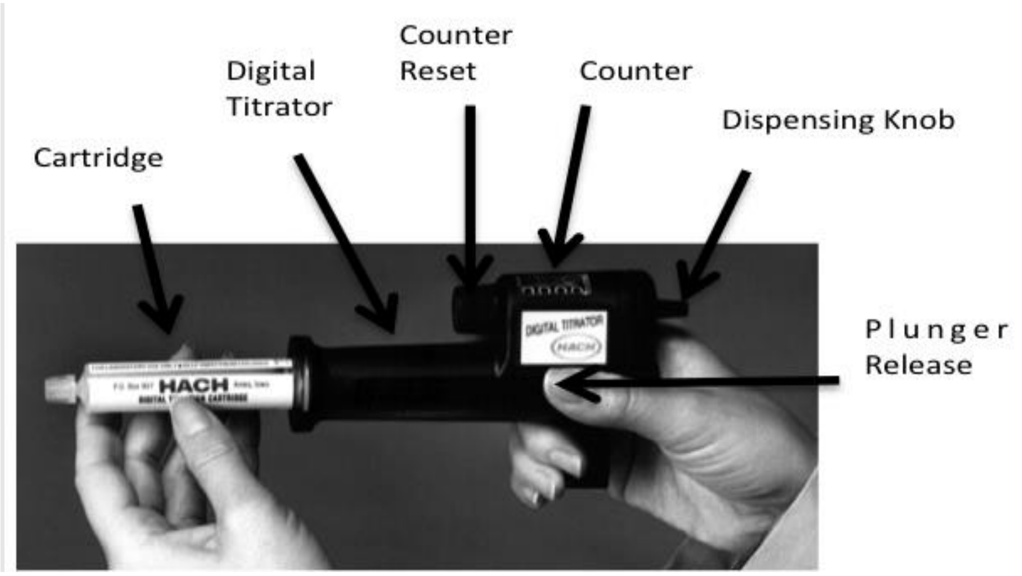


Figure 38. Inserting titrant cartridge into digital titrator. Photo from the Hach Digital titrator manual.

   b. Insert cartridge into the end slot of the titrator (**Figure 38**) and **rotate cartridge** one-quarter turn to lock into place
   c. Depress plunger-release button and push plunger forward until it is touching inside of cartridge. If plunger will not engage with the cartridge, ensure that the cartridge has been rotated one-quarter turn and is locked into place.
   d. Attach titrator set up to titrator bracket on the mounting bracket.
5. While wearing gloves and safety glasses, remove cap on titration cartridge and insert a clean titration tube into the cartridge tip. If tube is new, label tube with correct normality. You may need to turn the titrator upright, so the bubble comes to the tip. Store the cap in alkalinity test kit, so that you do not lose the cap. You will need to recap the cartridge when finished.
6. Turn the dispensing knob to expel a few drops of titrant into a discard/acid waste container (**Figure 39**). This should remove air bubbles from the tube.

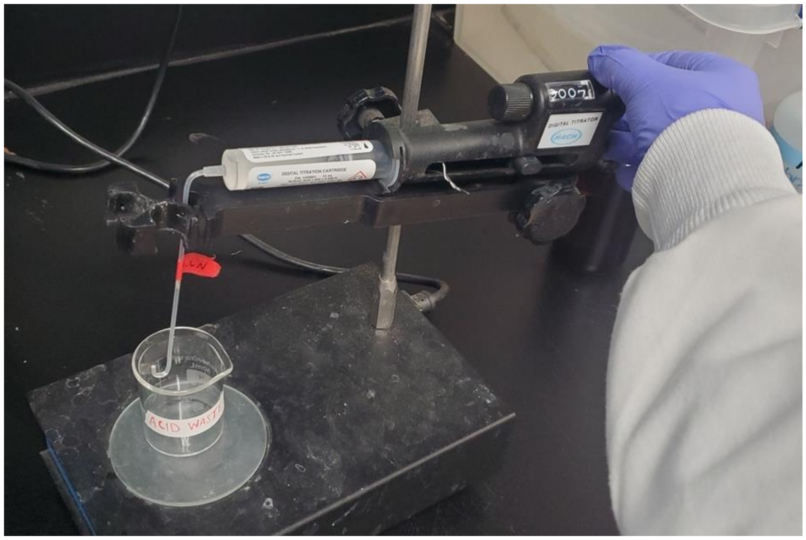


Figure 39. Expelling acid from digital titrator set-up into a temporary acid waste container.

7. **Reset the counter to zero** and rinse tip of tube with DI, if necessary.
8. Once the counter has been set to zero, do not turn the delivery knob.
9. If conductivity is greater than **100 µs/cm**, place a clean, small, magnetic stirrer into the appropriately sized beaker (**Table 10**). **Do not use a stir bar if conductivity is less than 100 µs/cm. Using a stir bar in low conductivity water will increase the diffusion of gases into the sample and alter the pH.**
10. If you have not already transferred your sample to beaker in section D.2, step 7, shake sample bottle for 15 s to homogenize. Invert the bottle at least 3 times since we are trying to suspend all particulates.
11. Using a clean **volumetric** pipette (for alkalinity, filtered sample) or a **graduated cylinder** (for ANC, unfiltered sample), measure out the appropriate volume of sample and transfer to appropriate glass beaker (**Table 10**).

    Note: a pipette is a more accurate measuring device and should be used on filtered alkalinity samples. Since particulates may get caught in the pipette tip, use a DI-rinsed graduated cylinders when measuring for non-filtered ANC samples.

12. Follow best practices for pipetting depending on the type of pipette you are using (i.e., TD - to dispense vs TC – to contain).
    a. For TD pipetting, release the liquid from the pipette. A small amount of liquid will remain in the tip of the pipette. This should not be blown out as this is accounted for in the TD measurement. If a drop of liquid remains on the outside of the pipette, this can be gently tapped against the side of the container to release it into solution.

   b. If using the TC line on pipettes, all liquid should be expelled from the pipette (no remaining liquid in the pipette).

13. Place the beaker on the stir plate and turn the power on. Stir should be slow and steady to avoid creating a vortex in the beaker. Reminder, do NOT use the stir bar and stir plate if conductivity is less than **100 µs/cm**.
    a. If sample splashes on wall of beaker, spray it down with DI water. Adding DI will not influence the titration reactions.
    b. If sample splashes out of beaker, start over.
14. **If conductivity is less than 100 µs/cm, do NOT use a stir bar. Using a stir bar in low conductivity water will increase the diffusion of gases into the sample and alter the pH.** If you have low conductivity water, after each titration, swirl the sample lightly for ~ 20 seconds by moving the beaker slowly in one circular motion, wait 15 seconds, then record the data and continue titrating. You do no need to wait for the pH meter to stabilize as long as your swirl time is consistent. Do not swirl so fast that you create bubbles or a vortex in the sample.
15. Rinse pH meter and temperature sensor with deionized water. Be cautious not to rinse probes over sample.
16. Insert pH meter and temperature sensor into sample water, making sure to not touch the stir bar or the sides and bottom of the beaker. DO NOT put the titrant tube in the solution yet.
    a. Sample solution must cover the sensor reference electrode on the pH bulb and temperature sensor (**Figure 40**). Increase volume, using pipettes or graduated cylinders, as necessary, or change beaker size, being sure to transfer the entire sample by rinsing beaker with DI into the smaller beaker. Volume of rinse DI should not be included as part of the sample volume.
    b. Only immerse the pH electrode enough to cover the glass pH bulb and the reference junction. The level of the pH fill solution in the outer cavity of the probe MUST be above the level of your sample.
    c. Stir sample briefly to ensure it is well-mixed.
17. **Record** on an electronic datasheet template that will be uploaded to SOM**:** Start time of titration, initial sample pH and temperature (**°**C), sample volume, titrant normality (0.16 or 1.60 *N*), and initial titrator count (should be reset to zero) (RD[05]). Make sure you record the initial pH **BEFORE** you put the titrant tip into the sample. Record field pH, if necessary (i.e., if multisonde is not operating properly)
18. Rinse the acid delivery tube with DI water to ensure no acid has accumulated on the tip before putting it into the sample. Immediately, insert the digital titrator tip into the sample in the beaker, without touching the stir bar. Tip should be immersed in the sample (**Figure 40**).

Figure 40. Image of titration set-up with digital titrator, stir bar, pH meter and temperature probe. Ensure nothing is touching the sides and bottom of the beaker or the stir bar.

19. **Add Titrant** (**Table 11**). After each addition of titrant:
    a. If using stir bar: Allow the stirrer to homogenize the sample for 15 s (wait 30 s for samples using 150 mL of sample water)
    b. If not using stir bar (conductivity < 100 micros/cm): gently, manually swirl the sample (~ 20 seconds followed by a 15 second rest) if you have a low conductivity sample.
    c. Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]). You do not need to fill out the grey-celled columns. They will be calculated later.

Near equivalence points (pH ~10, 8.1 and 5), pH can change rapidly (**Figure 41**).

This protocol focuses on total Alkalinity and ANC, thus focusing on the bicarbonate equivalence point at pH ~5. However, be sure to titrate slowly around **ALL** the above equivalence points if your system has a pH range including them. **If you add titrant too fast or in too great of increments, you will miss the inflection point completely!** Therefore, you must add titrant in smaller increments (~3) around these points, being sure to provide ample mixing time before the readings. After adding titrant, wait 15 s before recording and continuing the titration.

    d. pH ≥5.5:
        i. Titrate with larger increments to just above a pH 5.5. Do not add in increments that are so large that you skip this region completely.
        ii. **After each addition of titrant, allow the stirrer to homogenize the sample for 15 s.**

iii. **Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]).**

e. pH <5.5 - Bicarbonate equivalence point.:

i. Cautiously and slowly add titrant in small (but do **NOT** add less than **three counts** on the digital titrator) increments from pH 5.0 to ≤4.0. If using the Gran method, add acid in small (**BUT NO LESS THAN 3 COUNTS**) increments (to change pH 0.2 - 0.3 pH units) to pH ≤3.5.

ii. Titrate to pH ≤3.0 for samples with high organic acids or if sample range is unknown.

iii. **After each addition of titrant, allow the stirrer to homogenize the sample for 15 s.**

iv. **Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]) or an electronic datasheet template.**

Table 11. Guidelines for sulfuric acid titration for the IPT alkalinity and ANC sample analysis. pH numbers correspond to pH reading during the titration.

pH during titration	Titration addition guidelines for IPT method
≥8.1	Add in small increments, no less than 3 counts, until pH 8.0. Larger increments can be used for water with high carbonate concentrations.
<8.1 and ≥5.0	Add in larger increments, but do not skip region entirely
pH <5.5	Add in small increments, **no less than 3** counts

20. When possible, enter data into electronic datasheet template and graph the titration curve (change in pH divided by change in titrant volume (y-axis) by volume of titrant added (X-axis) (**Figure 41**).

a. If more than one inflection point occurs in proximity, the true inflection point has been missed, and a duplicate sample should be analyzed being sure to take precaution and add titrant in smaller increments around the inflection point.

b. If more than one titration inflection point occurs at 2 or more points near the equivalence point and you have used the minimum number of counts, you do not need to redo the analysis.

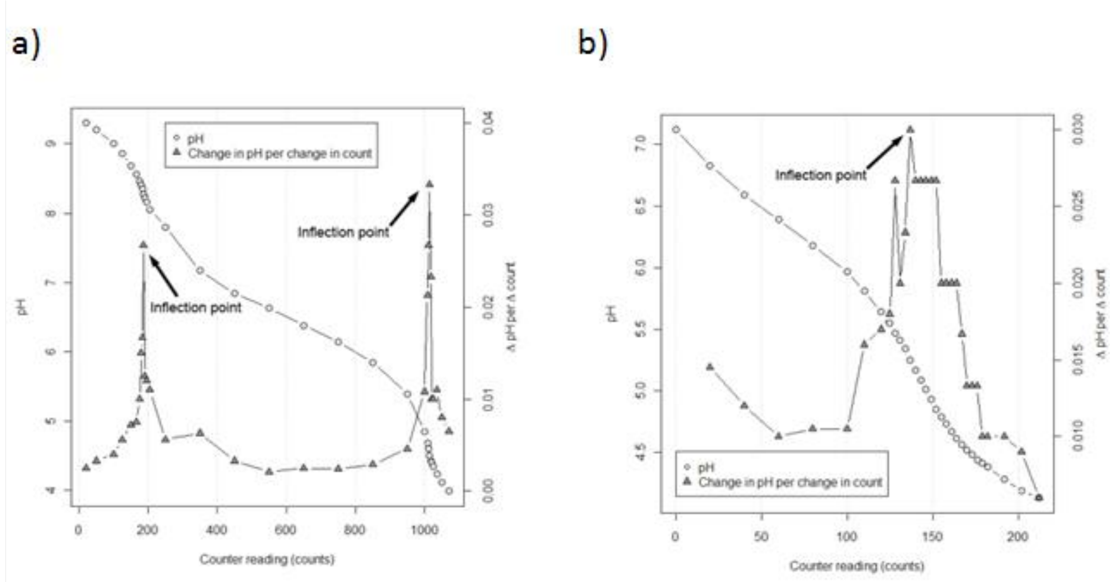


Figure 41. Example of inflection point titration using a digital titrator of a) a high alkalinity sample and b) a low alkalinity sample. Note difference in Y-axis scale. (Modified from USGS TWRI Book 9, Alkalinity, Version 3.0 7/2006).

21. When titration is finished, use soda ash or soda bicarbonate to return the sample pH to a pH 6 - 9. Use a pH meter to ensure the proper pH level.
22. Dispose of sample.
23. Repeat for all remaining samples at all stations.
24. Remove digital titrator from beaker. Depress plunger release and retract plunger to remove cartridge. Remove titrator tube. Cap cartridge tip.
25. Immediately double rinse titration tube and glassware with DI water and blot dry with lint-free soft paper tissue.
26. Place titration tubes in clean, sealable bag labeled with the titration normality (0.16 or 1.6 *N*).
27. Titration tubes can be reused if rinsed well but should be only used for the same titrant normality. Rinse tubes by attaching the tube to the end of a plastic squeeze pipette (tip cut off). Rinse with water followed by a rinse with air.
    a. When tubes begin to show wear (e.g., stretching at the end that attaches to titrant cartridge or leaking of acid out of tip), replace with a new one.
28. Store all glassware, titrator, titrator tubes, and chemicals appropriately.
29. Triple-rinse and re-use 250 mL alkalinity and ANC sample bottles.
30. pH probes should be stored with the storage bottle attached to the probe tip and immersed in the probe storage solution. Since Domains will have 2 probes (one for TOS and one for AOS),

but only one pH meter, the pH probe that is not connected to the meter should be stored in a cup or beaker to keep the probe upright.

SOP E Post-Field Sampling Tasks

E.1 Equipment Refresh and Maintenance

1. **Refreshing the laboratory supplies**
   a. Check expiration date of sulfuric acid titrant, pH filling and storage solutions, and pH buffer solutions. Order more if expiration has passed or will be passed within the next month.
   b. Ensure you have enough equipment for the next sampling event.
2. **Equipment maintenance, cleaning, and storage**
   a. Check the expiration date of pH buffers and acid cartridges. Order more if necessary.
   b. Double-rinse glassware and titrator tubes with DI water immediately after use. Glassware, titrator, titrator tubes and chemicals should be clean and dry before storage. Titrator tubes should be stored in resealable plastic bags and labeled with the titrant normality for which they were used. Store alkalinity kit parts in the blue field case. Store cartridges in a resealable plastic bag in the corrosive cabinet.
   c. Titrators do not require calibration. Hach titrators have a lifetime warranty. Please contact the manufacturer for trouble shooting.
   d. GW pH probe - Because the internal filling solution is a gel and cannot be replaced, the probe must be replaced at a minimum every 2 years. If probes exhibit signs of failure prior to 2 years, probes should be replaced ASAP. Signs of failure include long equilibration times when samples are at room temperature (minutes), errors on meter, or temperature values not in line with expected values.
   e. Domain Lab pH meter and probe – Follow pH meter manual maintenance guidelines. Additional information can be found in the pH Probe Meter Use and Maintenance in the NEON Training Center.
3. **Post visit groundwater sensor quality check**
   a. Check the quality of the data stream on DQ Blizzard after your visit.
      i. Ensure that Pressure, Temperature, and Conductivity are all streaming.
      ii. Look for similar values, trends, and behaviors in the data before and after the visit. Examples of issues could include:
         1) Missing data after sensor reconnected.
         2) A large jump in pressure values (**Figure 42**).
         3) Quiet data followed by noisy data (**Figure 43**).
         4) Unrealistic data values (e.g., a pressure of 0 would indicate that the sensor is dry and a pressure of 500 would suggest that the sensor is 50m under water).

b. Submit trouble tickets for any issues.

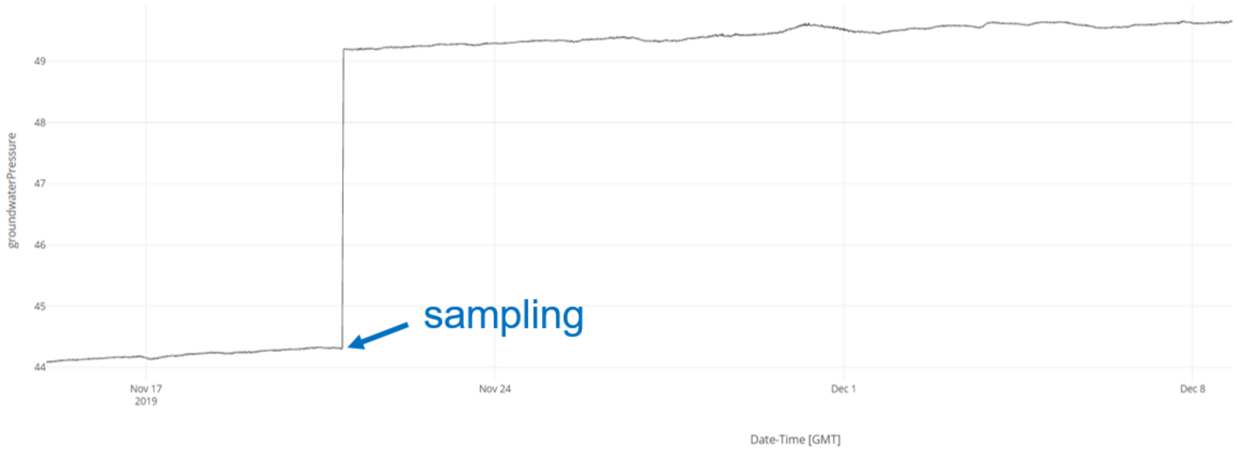


Figure 42. Example of a large jump in L0 pressure data after a sampling event.

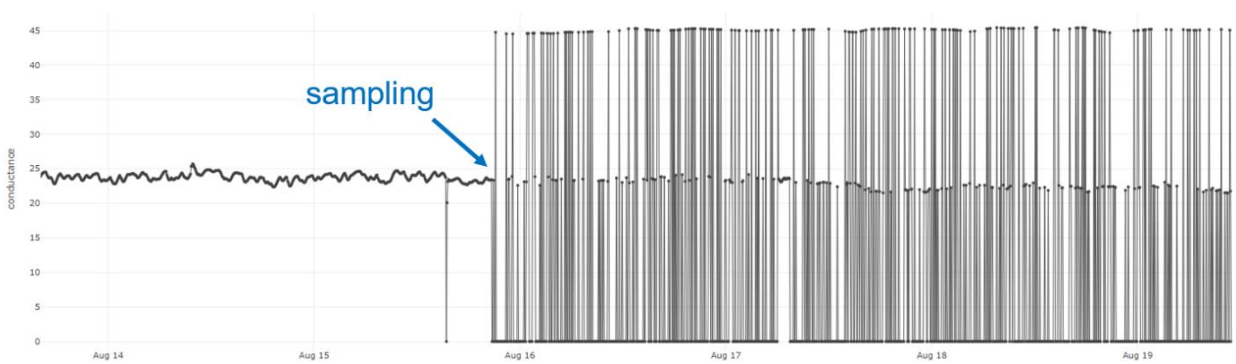


Figure 43. Example of noisy L0 conductivity data after a sampling event.

E.2 Document Incomplete Sampling Within a Site

The surface and ground water chemistry sampling is scheduled to occur at all prescribed sampling locations according to the frequency and timing described in Section 4 and Appendix C. Ideally, sampling will occur at these sampling locations for the lifetime of the Observatory (core sites) or the duration of the site's affiliation with the NEON project (gradient sites). However, sampling may be shifted from one location to another when sampling is compromised. In general, a sampling location is compromised when sampling becomes so limited that data quality is significantly reduced.

There are two main pathways by which sampling can be compromised. First, sampling locations can become inappropriately suited to answer meaningful biological questions – e.g., a terrestrial sampling plot is compromised after road-building activities, or a stream moves after a flood and the location is no longer within the stream channel). Second, sampling locations may be located in areas that are logistically impossible to sample on a schedule that that is biologically meaningful.

Example: For the ground water sampling program, a given well may go dry temporarily in which an alternative well is sample. If a designated sampling well has been dry for over 2 years, submit an incident.

***To document locations not sampled during the current bout*:**

1. Review the completed sampling effort and create **Sampling Impractical** records as described in Section 4.5 for plots at which sampling was scheduled but was not completed.
2. To document whether a location is compromised according to the criteria above:
   a. Review **Sampling Impractical** records from the *(AOS) Water Chemistry [PROD]* application and Portal data to identify locations where sampling was scheduled but was not completed due to environmental or site management factors.
3. Create an incident with the following naming convention to document the missed sampling and compromised location: 'AOS Sampling Incomplete: Water Chemistry – [Root Cause Description]'
   a. Example: 'AOS Sampling Location Compromised: GWW2 – Could not sample GWW 2 because well was dry.'

Staff scientists review incident tickets periodically to determine whether a sampling location is compromised.

SOP F Data Entry and Verification

Mobile applications are the preferred mechanism for data entry. Data should be entered into the protocol-specific application as they are being collected, whenever possible, to minimize data transcription and improve data quality. Mobile devices should be synced at the end of each field day, where possible; alternatively, devices should be synced immediately upon return to the Domain Support Facility.

However, given the potential for mobile devices to fail under field conditions, it is imperative that paper datasheets are always available to record data. Paper datasheets should be carried along with the mobile devices to sampling locations at all times. Data collected on paper data sheets must be transcribed within 14 days of collection or the end of a sampling bout (where applicable). See RD[04] for complete instructions regarding manual data transcription.

F.1 Entering Titration Data

1. Use the blank template in the water chemistry datasheet (RD[05]).
2. Save data as .csv file. The file should contain all the titration metadata (i.e., site, collectDate, sampleVolume) as well as the titration pairs.
3. Double check the ‘parentSampleID’ in the result file matches the sampleID in the water chemistry field data that has been entered into fulcrum.
4. If this is a replicate sample, double check the ‘domainSampleID’ has ‘.REP2’ at the end.
5. Upload the .csv file to the Shiny app (link to Shiny app can be found on the Water Chemistry SSL, ‘Domain Lab Titration Data’.
6. Download the result file.
7. Upload the result file to the CI spreadsheet uploader.

Quality Assurance

Data Quality Assurance (QA) is an important part of data collection and ensures that all data are accurate and complete. Certain QA checks can be conducted in the field (i.e., before a field team leaves a plot or site), while others can be conducted at a later date in the office (typically within a week of collection). Field QA procedures are designed to prevent the occurrence of invalid data values that cannot be corrected at a later time, and to ensure that data and/or sample sets are complete before the sampling window closes. Invalid metadata (e.g. collection dates, plotIDs) are difficult to correct when field crews are no longer at a sampling location.

Office QA procedures are meant to ensure that sampling activities are consistent across bouts, that sampling has been carried out to completion, and that activities are occurring in a timely manner. The

Office QA will also assess inadvertently duplicated data and transcription errors to maintain data validity and integrity. See the Data Management Protocol (RD[04]) for more discussion of QA measures.

Before samples ship to external facilities and/or their digital records load to the NEON database, the data must undergo thorough quality checks. The steps needed to accomplish this are outlined in the SWC QC Checklist, which is available on the NEON SSL.

Sample Identifiers & Barcodes

By default, each (sub)sample produced by this protocol receives a sample identifier, which contains information about the location, date, and sample type. Each (sub)sample will also be associated with a scannable barcode, which will not contain information about sample provenance, but will improve sample tracking and reduce transcription errors introduced by writing sample identifiers by hand.

Adhesive barcode labels should be applied to dry, room temperature containers in advance of their use in the field (at least 30 minutes prior but may be applied at the start of the season). Barcodes are unique, but are not initially associated with a particular sample, thus it is encouraged to apply these in advance. Use the appropriate barcode label type with each container (i.e., cryogenic Type II barcode labels only used for samples that are stored at -80°C, etc). Note that a barcode label is applied in addition to a sample identifier (hand-written or printed).

Barcodes are scanned into the data entry application when a sample is placed into a container; only one barcode may be associated with a particular sample. Do not reuse barcodes. If a barcode is associated with multiple samples, the data ingest system will throw an error and refuse to pull in entered data.

SOP G Sample Shipment

1. Follow sample shipping timelines in Section 4 to maintain appropriate sample hold times and storage conditions.
   a. Discrepancies between this protocol document and the Shipping Protocol should be communicated to Science.
2. Follow instructions in the NEON Protocol and Procedure: Shipping Ecological Samples, Sensors, and Equipment in order to ship samples to external laboratories or the biorepository (RD[16]).

8 REFERENCES

LTER Sampling protocols: http://ecosystems.mbl.edu/arc/streams/protocol2.html#WaterChemistry

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Soulsby, C., I. A. Malcolm, D. Tetzlaff, and A. F. Youngson. 2009. Seasonal and inter-annual variability in hyporheic water quality revealed by continuous monitoring in a salmon spawning stream. River Research and Applications 25:1304-1319.

U.S. EPA, 2004. Summary of Sample Depth Collected as part of the WQS for all Five Lakes. Appendix P.

U.S.G.S. 2006. National Field Manual for the Collection of Water-Quality Data. U.S. Geological Survey, Water Resources Office of Water Quality. Chapter A4. Collection of Water Samples. (Version 2.0). http://pubs.water.usgs.gov/twri9A/

Woessner, W.W., 2007. Building a Compact, Low-Cost, and Portable Peristaltic Sampling Pump. Ground Water 45(6): 795-797.

APPENDIX A QUICK REFERENCES

The following datasheets are associated with this protocol:

Table 12. Datasheets associated with this protocol.

NEON Doc. #	Title	Mobile Application
NEON.DOC.002906	Datasheets for AOS Protocol and Procedure: Water Chemistry Sampling in Surface Waters and Groundwater	(AOS) SWC [PROD]
NEON.DOC.001646	General AQU Field Metadata Sheet	(AOS) Field Metadata and Gauge Height [PROD]
NEON.DOC.002191	Datasheets for Secchi Depth and Depth Profile Sampling	(AOS) Secchi [PROD]
NEON.DOC.002494	Datasheets for AOS Sample Shipping Inventory	Shipping App [PROD]

These datasheets can be found in Agile or the NEON Document Warehouse, user guides for mobile applications may be found in NEON's internal sampling support library.

APPENDIX B REMINDERS

Before heading into the field: Make sure you…

- ☑ Collect and prepare all equipment including labels and filters.
- ☑ Type I barcodes used for FIL and RAW bottles. Type II barcodes used for Type II bottles.
- ☑ Pre-print labels on waterproof labels.
- ☑ Fill out the labels before they get wet.

Sample collection: Be sure to…

- ☑ Rinse sample bottles 3X with the appropriate sample water (i.e., use filtered water to rinse filtered sample bottles).
- ☑ Be sure capsule filter is attached correctly according to the flow arrow on the filter.
- ☑ Filter slowly through the capsule filter to reduce oxygenation (never filter faster than 1 L every 16 seconds or 250 mL in 4 seconds). Run filtered water down the side of bottle to further reduce oxygenation of the sample.
- ☑ Do not sample anywhere you or other field technicians have walked, or locations that appear recently disturbed. Wait for disturbance to pass.
- ☑ Fill FIL, ALK, and ANC bottles completely (no headspace). Leave headspace in FIL.NUT, RAW.NUT, AND RAW samples.

Sample titrations: Be sure to…

- ☑ Add titrant in smaller increments around equivalence points (pH~5).
- ☑ After each addition of titrant, allow the stirrer to homogenize the sample for 15-30 s. You must wait 30 s for larger volumes (150 mL samples) to stabilize. In low conductivity samples (100 µS/cm), stir manually for 20 s, then wait 15 s before recording.

Groundwater sampling: Be sure to…

- ☑ Check the cable position before and after sampling.
- ☑ Ensure that the sensor is connected and streaming before leaving the site.
- ☑ Check the quality of the data stream on DQ Blizzard after your visit.

APPENDIX C ESTIMATED DATES FOR ONSET AND CESSATION OF SAMPLING

The seasonal timing of groundwater sample collection is driven by the seasonal and cumulative hydrograph of the stream, river, or lake at the specific NEON aquatic site as surface water hydrology is often linked to groundwater hydrology and water quality (Soulsby et al. 2009). At river and stream sites, groundwater sample collection is temporally timed to capture seasonal variability around 25% and 75% (± 5%) of cumulative annual discharge. Groundwater chemistry sample timing will be reassessed once a minimum of three years of water table data are available to ensure that we are capturing seasonal variability in chemical and hydrologic conditions.

Table 13. Site-specific groundwater sampling windows and wells to samples.

Domain Number	Site ID	Bout 1 Window Start Date	Bout 1 Window End date	Bout 2 Window Start Date	Bout 2 Window End date	Wells to Sample
01	HOPB	3/5	3/24	6/16	10/7	1, 2, 3, 4
02	POSE	2/27	3/19	6/30	10/5	1, 3, 6, 8
02	LEWI	3/2	3/24	7/19	9/12	1, 2, 6, 8
03	SUGG	2/20	3/20	9/20	10/20	1, 5, 6, 8
03	BARC	2/20	3/20	9/20	10/20	4, 5, 6, 8
03	FLNT	2/14	3/6	7/14	9/27	1, 3, 6, 7
04	GUIL	5/4	6/1	10/2	10/25	1, 3, 5, 6
05	LIRO	4/15	5/15	10/10	11/10	1, 3, 5, 6
05	CRAM	4/15	5/15	10/10	11/10	1, 2, 4, 7
06	MCDI	4/8	4/24	6/26	7/17	2, 4, 5, 6
06	KING	4/8	4/24	6/26	7/17	1, 2, 4, 8
07	WALK	2/11	2/27	6/15	9/2	1, 2, 3
08	MAYF	2/18	3/11	8/6	10/9	1, 2, 7, 9
08	TOMB	2/11	3/2	5/29	8/15	1, 2, 3
08	BLWA	2/14	3/5	6/16	9/9	1, 2, 3
09	PRPO	4/15	5/15	10/15	11/15	1, 3, 5, 7
09	PRLA	4/15	5/15	10/15	11/15	1, 3, 7, 8
10	ARIK	4/2	4/26	7/25	8/19	1, 2, 4, 5
11	PRIN	3/24	4/28	7/25	9/17	1, 2, 4, 6
11	BLUE	4/2	5/8	7/24	10/13	2, 4, 7, 8
12	BLDE	5/18	6/12	7/13	8/10	1, 2, 7, 8
13	COMO	5/24	6/13	7/18	8/4	1, 2, 3, 4
13	WLOU	4/24	5/18	8/10	9/12	1, 2, 5, 8
14	SYCA	1/20	2/12	3/30	6/17	1, 2, 3, 4
15	REDB	4/7	4/23	8/17	9/26	2, 3, 4, 5
16	MART	2/15	3/11	10/14	11/19	1, 2, 5, 6
17	BIGC	3/31	4/16	5/31	6/13	1, 2, 5, 6
18	OKSR	7/1	7/28	8/1	9/1	3, 5, 7, 8
18	TOOK	7/1	7/28	8/1	9/1	1, 2, 7, 8
19	CARI	6/1	6/21	8/25	9/22	1, 5, 7, 8

APPENDIX D SITE-SPECIFIC INFORMATION

Each domain has site specific guidelines for timing of sample collection and can be found in Domain Specific Sampling Designs **(Table 14).** The dates in the Sampling Design documents are estimated from historical hydrologic data. Dates presented are only a guide and are derived according to the logic presented in Section 4.2. Because individual years may vary widely from the average dates provided below, it is essential that domain staff monitor real-time conditions to determine when to start (and stop) sampling per environmental conditions, as described in Section 4 of this protocol.

Table 14. Aquatic Site Sampling Design documents.

Domain Number	Document Number	Document Name
01	NEON.DOC.003600	Aquatic Site Sampling Design – NEON Domain 01
02	NEON.DOC.003601	Aquatic Site Sampling Design – NEON Domain 02
03	NEON.DOC.003602	Aquatic Site Sampling Design – NEON Domain 03
04	NEON.DOC.003603	Aquatic Site Sampling Design – NEON Domain 04
05	NEON.DOC.003604	Aquatic Site Sampling Design – NEON Domain 05
06	NEON.DOC.003605	Aquatic Site Sampling Design – NEON Domain 06
07	NEON.DOC.003606	Aquatic Site Sampling Design – NEON Domain 07
08	NEON.DOC.003607	Aquatic Site Sampling Design – NEON Domain 08
09	NEON.DOC.003608	Aquatic Site Sampling Design – NEON Domain 09
10	NEON.DOC.003609	Aquatic Site Sampling Design – NEON Domain 10
11	NEON.DOC.003610	Aquatic Site Sampling Design – NEON Domain 11
12	NEON.DOC.003611	Aquatic Site Sampling Design – NEON Domain 12
13	NEON.DOC.003612	Aquatic Site Sampling Design – NEON Domain 13
14	NEON.DOC.003613	Aquatic Site Sampling Design – NEON Domain 14
15	NEON.DOC.003614	Aquatic Site Sampling Design – NEON Domain 15
16	NEON.DOC.003615	Aquatic Site Sampling Design – NEON Domain 16
17	NEON.DOC.003616	Aquatic Site Sampling Design – NEON Domain 17
18	NEON.DOC.003617	Aquatic Site Sampling Design – NEON Domain 18
19	NEON.DOC.003618	Aquatic Site Sampling Design – NEON Domain 19

APPENDIX E EQUIPMENT

The following equipment is needed to implement the procedures in this document. Equipment lists are organized by task. They do not include standard field and laboratory supplies such as charging stations, first aid kits, drying ovens, ultra-low refrigerators, etc.

Table 15. Equipment list – Water chemistry sampling.

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
		Mobile data entry tablet, fully charged and synced before field work	Field data entry	1
	N	4 L jug	Collecting water	As needed, suggest 4 (GW and Lakes) and 2 (streams)
	N	Pieces of C-Flex® tubing, ¼" in I.D. and 3/8" outer O.D., 1.6 mm wall thickness, suggested 4ft and 2ft in length	Pumping water into sample containers	2
GB0727000	Y	Pump Assembly • Easy-load peristaltic pump head (e.g., Masterflex® L/S® Easy-Load® pump head) • 18-V drill pump (power source for pump head) • Tubing connectors	Pumping stream water into sample containers	 1 1 2
	N	18-V drill battery charger	Pumping water into sample containers	1
	N	U-bolt	Keeping the drill in the "on" position to pump stream water continuously	1
	N	Squirt bottle (125 mL)	Creating a flat surface for filtering water samples	1
	N	Non-porous flat surface	Creating a flat surface for filtering water samples	1

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
YSI 6052030	Y	Meter, dissolved oxygen and conductivity, handheld, backlit LCD display; YSI Pro 2030 or equivalent- cable and probes sold separately	Temperature and conductivity meter- must order probes and cable separately	1
YSI 6052030-4 or longer as needed	Y	Cable for YSI Pro 2030 or equivalent, including conductivity and temperature sensors: • Stream and groundwater: 4m length • Lake and river sites: as needed	Cable for handheld with conductivity and temperature sensors	1
YSI 605202	Y	DO probe, galvanic, item includes DO probe and 1 set of 6 replacement tips for conductivity/temperature handheld meter Polarographic is acceptable to use instead of galvanic but there is a 15 min warm up time before probe can be used.	DO galvanic probe and replacement tips- must order separately	1
Consumable items				
	N	Pall Supor capsule filter (0.45 µm Supor Membrane for high flow rates) or equivalent. Groundwater sampling capsule – Must meet EPA filtration requirements for dissolved metal analysis. 1 per sample	Collecting water for filtered samples	1
	N	Waterproof labels (1” x 2 $^{5}/_{8}$”), pre-printed adhesive labels	Labeling sample bottles with barcode-readable	As needed
	N	Adhesive barcode labels (Type I and Type II)	Labeling sample bottles with barcode-readable	1 sheet
	N	Permanent marker	Labeling samples	2
	N	1L jug of DI	Rinsing tubing before placing in 4 L jug	1
	N	Conductivity calibration solutions	Calibrating hand-held conductivity meter	1
YSI 605913	Y	Replacement DO sensor tips for MX110375	Replacement part for DO sensor tips- order when appropriate	As needed

Table 16. Equipment list – Water chemistry bottles for dissolved and totals (see Figure 5).

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
	N	Amber Glass bottles with Phenolic Lined Cap • Alkalinity • Acid Neutralizing Capacity (ANC)	ALK and ANC sample containers, per site	2 per station*
	N	Ice chisel	Creating hole in ice	1
	N	Ice auger, 10" diameter	To be used with ice auger	1
	N	Gas-powered auger	To be used with ice blade	1
Consumable items				
Use SSL link to order from external lab.	Y	1L amber bottle- acid rinsed (A/R) and cleaned and burnt (C/B)- HQ Field Support will order	Prepared bottle for filtered water sample (FIL)	1 per station
Use SSL link to order from external lab.	Y	500 mL amber bottle- A/R and C/B- HQ Field Support will order	Prepared bottle for unfiltered water sample (RAW) and for filtered water sample (FIL) for low volume locations	1 per station
Use SSL link to order from external lab.	Y	60 mL amber bottle- A/R and C/B - HQ Field Support will order	Prepared bottle for D18/19 DIC subsample	1 per station in D18/19
Thermo Fisher (2189-0004 or 312189-0004)	N	125 mL HDPE wide mouth economy bottles	Bottles for nutrient samples (FIL.NUT and RAW.NUT)	2 per station
	N	4 L jug	Collecting samples, if needed	1

*Take extras in field

Table 17. Additional equipment list – Sampling lakes and rivers for water chemistry.

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
	N	Boat	Accessing the sampling location	1
	N	Anchor with rope	Keep boat in place while sampling	2
	N	Oars	Backup control of boat movement	2
	N	Trolling electric motor	Moving and controlling boat	1
	N	Marine deep cycle battery	Powering trolling boat motor	1
	N	Safety kit for boat (e.g., flares, bailer, float with rope)	Safety	1
	N	First aid kit	Safety	1
	N	Personal flotation devices (PFDs)	Safety	1 per person
Cole-Parmer 05485-10	Y	Kemmerer sampler with rope and messenger	Collecting samples	1
Fisher Scientific BME224250	Y	Horizontal Van Dorn sampler with rope and messenger	Sample collection in rivers with fast flow	1
	N	GPS (Accuracy <4m)	Navigating to sampling locations	1
	N	Secchi Disk	Determining the depth of the euphotic zone	1

R/S=Required/Suggested

Table 18. Equipment list – Sampling groundwater for water chemistry.

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
	N	Clean 5-gallon bucket	Storing the groundwater well sensor and cable during sampling	1
318830003	Y	QED sample pro pump	Pumping groundwater from the well	1
318830001	Y	QED MP-50 compressor/ controller	Pumping groundwater from the well	1
	N	Battery (12V, minimum of 3.6Ah)	Pumping groundwater from the well	8
318830002	N	Bucket of ¼” x ¼” dual bonded tubing (250ft of tubing in each bucket). Tubing is dedicated per each well for the duration of the sampling events	Pumping groundwater from the wells	1 per site, require for 1st sampling event
Cut tubing from 0318830002	N	Dedicated tubing for wells (in large plastic bags). Make sure to get the tubing identified for the well that is sampled. The sealable bags shall be labeled with the Well ID.	Measuring water height	1
	N	Water level tape (metric) with battery	Measuring water height	1
	N	Collection cell, such as a 250 mL graduated cylinder	Monitoring groundwater well chemistry	1
	Y	pH 3110 & SENTIX41 Probe with battery	Probe for analyzing field pH	1
	N	For minimum purge wells only: 1/8″ ID tubing and 1/8” to ¼” tubing connector	[Minimum-purge Method Only] Pumping groundwater using the minimum purge method	1 dedicated tube per minimum
	N	3-way male slip stopcocks	[Needle Method Only] For bubble-free syringe sampling at D18/D19 sites	2 per well
	N	140 mL Luer lock sterile syringe	[Needle Method Only] For bubble-free syringe sampling at D18/D19 sites	1 per well

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
	N	Groundwater sampling needle	[Needle Method Only] Specially made needle for sampling D18/19 sites	1 at 50cm length and 1 at 70cm
	N	3/16" ID tygon tubing	[Needle Method Only] Tubing for sampling D18/19 sites with the syringe and needle	Dedicated section for each sampling well
	N	EMD Millipore 47mm syringe filter holder	[Needle Method Only] Filtering the pH and FIL subsamples in D18/19	1 for D18, 1 for D19
Consumable items				
	N	Whatman GF/F glass fiber filter 47mm - ashed	[Needle Method Only] Filtering the pH and FIL subsamples in D18/19	1 for D18, 1 for D19
	N	pH calibration solution	Calibrating hand-held pH meter	1

Table 19. Equipment list – Sample field storage and shipping. See RD[16] Shipping Ecological Samples, Sensors and Equipment.

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
	N	Shipping cooler	Shipping samples	1
Consumable items				
	N	Packing material	Filling up extra space and adding absorbent material	As needed
	N	Resealable plastic bags (gallon and quart size)	Separately enclosing the shipping labels, ice packs, and samples	As needed
	N	Ice or ice packs (< or = 0°C packs)	Keeping the samples cool (water ice is preferable if logistically feasible)	As needed
	N	Clear packing tape, roll	Labeling shipment	1

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
	N	shipping labels	Labeling shipment and cooler return	2

Table 20. Equipment list – Laboratory processing: Materials and supplies for the alkalinity and ANC laboratory measurement procedure.

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
Durable items				
Fisherbrand ™ 13-620-183A (preferred) or Thermo-scientific 8172BNWP	N	pH meter, with automatic temperature compensator • pH electrode, calibrated • Thermometer, calibrated	Reading pH of the samples	1
	N	Magnetic stirrer	Mixing the sample with the titrant solution	1
	N	Stir bars, Teflon® coated, smallest size	Mixing the sample with the titrant solution	2
	N	Volumetric pipets, class A "TD" [a] - 25 mL - 50 mL - 100 mL	Measuring volume and transferring sample to glass beaker for ALK samples	1
	N	Graduated cylinders, class A "TD" [b] - 25 mL - 50 mL - 100 mL	Measuring volume and transferring sample to glass beaker for ANC samples	1
	N	Pipette squeeze bulb	Used with volumetric pipet	1
	N	Glass beakers - 50 mL - 100 mL - 150 mL (or larger as needed)	Sample container for pH readings-sized appropriately for titration volume needed to allow for submerged pH and thermometer probe tip	1

Supplier/ Item No.	Exact Brand	Description	Purpose	Quantity
	N	Squeeze bottle with DI water	Rinsing pH probe	1
Hach 1690001	Y	Hach Digital titrator and mounting assembly	Adding titration solution to sample	1
Hach 4157800	Y	Delivery tubes, 90° angle, transparent	Adding titrant solution to sample, 1 per titrant solution	2
	N	Plastic squeeze bulb pipette (3mL)	Rising acid deliver tube after use	1
	N	Safety- gloves, glasses, acid spill kit, lab coat	Safety	1
	N	Stopwatch	Titration stir timing	1
	N	Acid waste container		1
Consumable items				
	N	DI water (max conductivity of 1 µs/cm)	Rinsing pH probe	1
	N	Parafilm	Covering sample to reduce air exchange	As needed
Lovibond DT011-02 and DT011-01	Y	Titrant solution - Sulfuric acid (H_2SO_4) 0.16*N* - Sulfuric acid (H_2SO_4) 1.6*N*	Added to samples in order to measure ANC and ALK	1
	N	Baking soda	Acid disposal	1