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<i>Title:</i> AOS/TOS Protocol and Procedure: Water Chemistry Sampling in Surface Waters and Groundwater	<i>Date:</i> 10/07/2019
<i>NEON Doc. #:</i> NEON.DOC.002905 <i>Author:</i> K. Goodman	<i>Revision:</i> G

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

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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 PCN, 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	11/07/2019	ECO-06280	Update to new format. ANC only collected monthly. Updated titration cartridges



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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 the 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. This can impart a large influence on the biotic assemblage and its tolerance to shifts in chemistry. 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 and helps understand 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 regarding 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 are tolerant of small changes in chemistry; however, large shifts in chemistry can have dramatic effect on the biotic community structure and function through processes such as nutrient uptake and retention. Long-term



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observations provide an effective means of keeping track of possible 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.001155	NEON Training Plan
AD[05]	NEON.DOC.050005	Field Operations Job Instruction Training Plan
AD[06]	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 Level 1, Level 2 and Level 3 Data Products Catalog
RD[04]	NEON.DOC.001271	NEON Protocol and Procedure: Manual Data Transcription
RD[05]	NEON.DOC. 002906	Datasheets for AOS Protocol and Procedure: Water Chemistry Sampling in Surface Waters and Groundwater
RD[06]	NEON.DOC.003282	NEON Protocol and Procedure: Site Management and Disturbance Data Collection
RD[07]	NEON.DOC.002792	AOS Protocol and Procedure: 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	All Systems Standard Operating Procedure: Decontamination of Sensors, Field Equipment, and Field Vehicles
RD[11]	NEON.DOC.001197	AOS Protocol and Procedure: 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	Shipping Ecological Samples, Sensors and Equipment



2.3 Acronyms

Acronym	Definition
A/R	Acid-rinsed
ALK	Alkalinity
ANC	Acid Neutralizing Capacity
ASR	Analytical Services Request
C/B	Cleaned and burned
°C	Degrees Celsius
DI	Deionized
DO	Dissolved Oxygen
FIL	Filtered Chilled
GF/F	Grade F Glass Fiber Filter
GW	Groundwater
H ₂ SO 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
PCN	Total Particulate Carbon and Nitrogen
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



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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 in the water and increase the pH 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 PVC to water.

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

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 (m³) 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.

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). This protocol describes the collection, field processing, preservation (if applicable) and shipping of total, dissolved, and particulate 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 CO₂.

The sampling strategy for surface water is specific to the type of waterbody. The strategies for sampling wadeable streams, non-wadeable streams, 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 main 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. The water chemistry sampling location should be located, when possible, within 1 meter downstream of the main stream sensor set (sensor set 2) so that the sensor measurements can be validated with stream water chemistry samples (**Error! Reference source not found.**).

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 (Kemmerer should be placed with top at 0.25 m and bottom at 0.75 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 location (4 total sampling stations). In lakes and rivers with a **very** shallow hypolimnion (hypolimnion thickness < 2 m) do not collect a hypolimnion sample. However, you should still be calling the epilimnion c1 even if c2 hypolimnion depth (i.e. thickness) is too shallow to sample. This allows users to quickly identify a stratification was present. In lakes and rivers with a shallow hypolimnion (hypolimnion thickness 2-4 m), the sample is collected from the mid-point of the hypolimnion. In lakes with a deep hypolimnion (hypolimnion thickness >4 m) an integrated sample is collected (Figure 12). Note that if lake inlet and outlet streams are present, samples are collected just downstream of the inlet and outlet 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



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sampling. For **groundwater** sampling, samples are budgeted on a basis of an average of one sample per well per year at each site, or 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 groundwater wells (Table 12).** For rivers and wadeable streams, the four sampling wells are selected in attempt to cover all of 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 inlet side and two on the outlet 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 during the life of the Observatory and are guided by various parameters. For example, 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 reporting system.

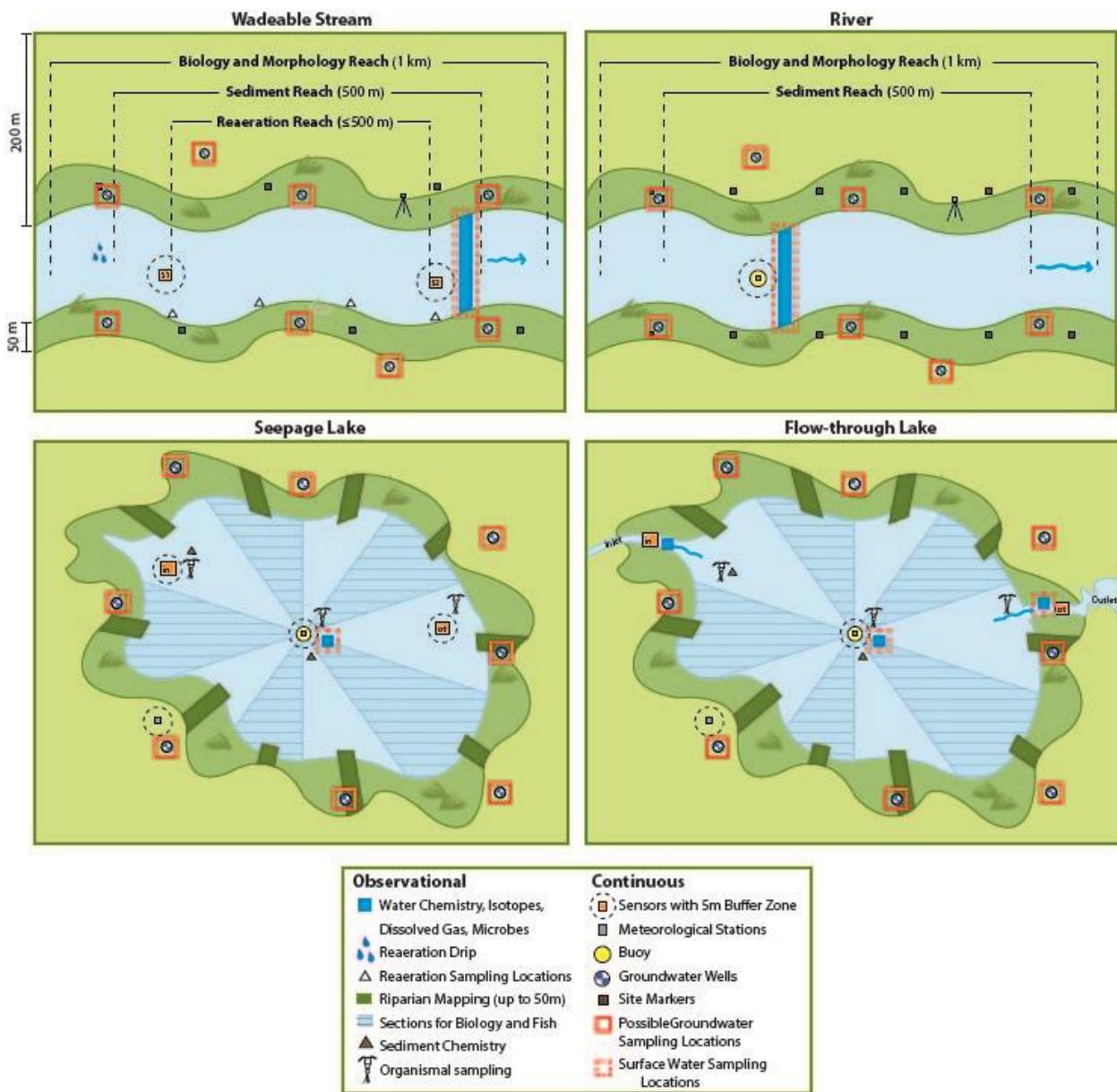


Figure 1. Generic site layouts for wadeable streams, rivers, and lakes surface water and groundwater sampling locations. Seepage lakes are lakes with no true inlet and outlet, while flow-through lakes have a true inlet and outlet.



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4 SAMPLING SCHEDULE

4.1 Sampling Frequency and Timing

When applicable, chemistry samples should be collected on Tuesday to coincide with NEON atmospheric wet chemistry sampling, as well as other National chemistry sampling efforts. Sample timing should follow site-specific timing guidelines found in the Domain Specific Sampling Design documents (Table 12).

Wadeable stream and river water chemistry sampling occurs up to 26 times per year at each NEON location. **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 12).

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 Surface Water Dissolved Gas and Aquatic Stable Isotope protocols. See Domain Specific Sampling Design documents for site-specific sampling dates (<i>Table 12</i>).
	Lake	1 day	12	Sampling dates are synchronized with the Surface Water Dissolved Gas and Aquatic Stable Isotope protocols. See Domain Specific Sampling Design documents for site-specific sampling dates (<i>Table 12</i>).
SOP B.5	All - GW	2 days	2	Sampling dates are synchronized with Aquatic Stable Isotope protocols. See Domain Specific Sampling Design documents for site-specific sampling dates (<i>Table 12</i>).

Scheduling Considerations

1. 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



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events surface, water microbes will also be collected. Ensure there is enough time to process all samples within the appropriate time frame.

2. It is advised to not collect field samples on Friday given shipping and support facility laboratory processing requirements.
3. **Replicates for external analysis:** Three times per year, NEON will quantify measurement uncertainty and environmental variability by collecting two additional surface water samples for external analysis. Remember to account for these replicates when ordering consumable supplies.
 - a. Replicate sample collection should be spread throughout the sampling season to capture different hydrological and biological conditions.
 - b. 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.
 - c. In stratified lakes, at least two of the three replicate sampling events should occur during periods when the lake is stratified during the summer.
 - d. No replicates are collected from groundwater wells.
4. **Replicates for alkalinity laboratory processing:** One additional titration will be completed, at a minimum, of every 10 samples per site.
5. **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:
 - a. Keep samples cold until they are processed in the laboratory.
 - b. Process titration samples in the laboratory as soon as possible.
 - 1) (Ideally) Process titration samples within 24 h of collection.
 - 2) (Required) Process titration samples within 72 h of collection.
6. ANC is only collected monthly.

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 that have a



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snowmelt-dominated or storm-dominated flow regime are sampled more intensively during time periods of high flow, when the majority of the nutrients are moving through the system and sampled sporadically during times of base flow. Stream systems that are 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 just following turnover in both the spring and autumn season. 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 window of time with which to align a groundwater chemistry sampling event 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.

4.3 Timing for Laboratory Processing and Analysis

For external laboratory analysis, surface water samples should be 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.

For internal laboratory analysis, samples for alkalinity and ANC should be kept on ice or refrigerated at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Laboratory analysis should be processed within 24 hours, when possible. Samples analyzed after the 24 hours window will be flagged. The maximum allowable time period 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 protocol sampling date or within 5 days of the scheduled sampling date, proceed with the reschedule and no additional action is necessary.
- 2) Rescheduled > 14 days from the protocol sampling date or > 5 days of the scheduled sampling date, submit a 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 11) 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 a 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 2. Contingency decisions for Water Chemistry Sampling in Surface Waters and Groundwater.

Delay/ Situation	Action	Outcome for Data Products
Minutes - Days/ Unsafe weather conditions	<p>If weather conditions deteriorate and conditions become unsafe:</p> <ul style="list-style-type: none">• 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 (>1 m) to hold the boat stationary over a sampling point), <p>Action:</p> <ol style="list-style-type: none">1. Return to shore and wait in a safe location for 30 min2. If conditions improve, resume sampling3. If not, return to the Domain Support Facility and sample at another time.	No adverse outcome.
Hours/ Wadeable stream, Unsafe for wading	<p>If stream conditions are too high to safely wade into the thalweg:</p> <ol style="list-style-type: none">1. Sample from stream side, only if the following are true:<ul style="list-style-type: none">• the stream is well mixed due to the high flows,• AND you are not sampling in a dead zone or back eddy	No adverse outcome.



Delay/ Situation	Action	Outcome for Data Products
	2. If you cannot sample, reschedule.	
Hours/ Wadeable stream, ice-covered	<p>If wadeable stream is:</p> <ul style="list-style-type: none">• <u>ice-covered but still flowing</u>: if safe, break ice and sample• <u>has thick ice that is hard to break</u>: bring a shovel, ice-chisel, or other tool• <u>unsafe to break ice</u>: 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 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.): <ul style="list-style-type: none">• make a hole in the ice and proceed with sampling.	No adverse outcome.
Hours/ Lake inlet and outlet in winter sampling	During winter, lake sites with inlet and outlet 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: <ul style="list-style-type: none">• Wait 5-10 minutes to allow the water to clear and disturbance to pass.	No adverse outcome.
Hours/ Not able to process water samples on site	If water samples cannot be processed ion site (due to field conditions, time limits, etc.), collect water samples in two 4 L jug, keep on ice, process as soon as possible.	No adverse outcome.
	Requirements: <ul style="list-style-type: none">• The filtration should be completed within <u>4 hours</u> and no more than 6 hours. Data processed after 4 hours will be flagged.• <u>Samples must be kept cold (~4°C)</u> and dark to reduce nutrient transformation.• <u>Water jugs must be shaken before sampling or filtration</u> to re-suspend particulates and homogenize water.	
Hours/Sampling location shallow	If sampling location is too shallow to obtain a clean sample: <ul style="list-style-type: none">• 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.



Delay/ Situation	Action	Outcome for Data Products
Hours/ Low water	<p>Low Water Situation Examples:</p> <ul style="list-style-type: none">• 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 <p>Actions:</p> <ol style="list-style-type: none">1. Continue sampling in the water chemistry sampling locations <u>provided the sample bottle can be filled without disturbing sediments.</u>2. Be sure to note state of water level in the data collection app.	No adverse outcome.
Hours/ Wells dry during low flow	<p>When sampling a groundwater well following the low flow method, if the well goes dry at the lowest flow rates:</p> <p><u>Contact Science about the possibility of implementing an alternative sampling method.</u></p>	No adverse outcome.
Hours/ on site filtration not possible	<p>If temperatures are below freezing and filtration equipment is not functional on site:</p> <p><u>Collect sample and filter in a sheltered area</u>, such as the field vehicle or return to the Domain Support Facility for filtration.</p>	No adverse outcome.
Days-Months/ Water body entirely dry or frozen	<p>If the water body is entirely dry or frozen solid so there is no water to sample:</p> <ol style="list-style-type: none">1. Complete Sampling Impractical Record.2. Reschedule sampling until water is available for sampling.	No adverse outcome.
Days-Months/ Groundwater when steam sampling not possible	<p>If site conditions dictate that <u>stream</u> sampling is not possible due to the stream being dry:</p> <p>Then <u>postpone the groundwater-sampling</u> event until flow returns in the stream.</p>	No adverse outcome.
Days-Months/ Groundwater pump freezing	<p>If temperatures are below freezing and water in the <u>groundwater</u> pump discharge line is freezing:</p> <ol style="list-style-type: none">1. Stop sampling. Complete Sampling Impractical.2. Reschedule the sampling bout for a time when ambient temperatures are above freezing and in conjunction with surface water sampling. <p><u>Since GW sampling occurs at most twice a year, the events should be timed with above freezing weather conditions.</u></p>	No adverse outcome.



Delay/ Situation	Action	Outcome for Data Products
Days-Months/ Groundwater level below bottom of well	<p>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.</p> <p><u>Under these conditions sampling of groundwater is not possible and timing of the sampling bout or wells to be sampled should be reevaluated by Science.</u></p>	No adverse outcome.
Days-Months/ Standing water surrounding groundwater well	<p>Though groundwater wells are generally sited for slightly elevated locations, times will occur when standing water surrounds the base of the well.</p> <p><u>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.</u></p>	No adverse outcome.
Days-Months/ Groundwater with seasonal permafrost thawing	<p>For sites that have the “generation” of groundwater resulting from seasonal thawing of permafrost,</p> <p><u>Sampling is targeted for times when the permafrost is sufficiently thawed to allow for collection of groundwater samples.</u></p>	No adverse outcome.
Damaged groundwater well	<p>If a groundwater well is damaged (i.e. casing is broken internally) or bent:</p> <p>Do not try to sample this well.</p> <p>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 <u>submit a trouble ticket for a new well to be selected for sampling.</u></p>	No adverse outcome.
Days- Weeks/Surface sampling reschedule	If surface water sampling must be rescheduled and can be rescheduled within 14 days of protocol sampling dates or within 5 days of the scheduled sampling date, 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 protocol sampling dates or within 5 days of the scheduled sampling date, 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 rescheduled within the sampling window specified in the site-specific sample strategy document as well as within 2	No adverse outcome.



Delay/ Situation	Action	Outcome for Data Products
	days of a surface water chemistry bout, proceed with the reschedule. No additional action is necessary.	
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 12*).
- **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.



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The documentation that must accompany missed sampling depends on the timing, subsequent action, and the audience appropriate for numerous scenarios ([Figure 2](#)).

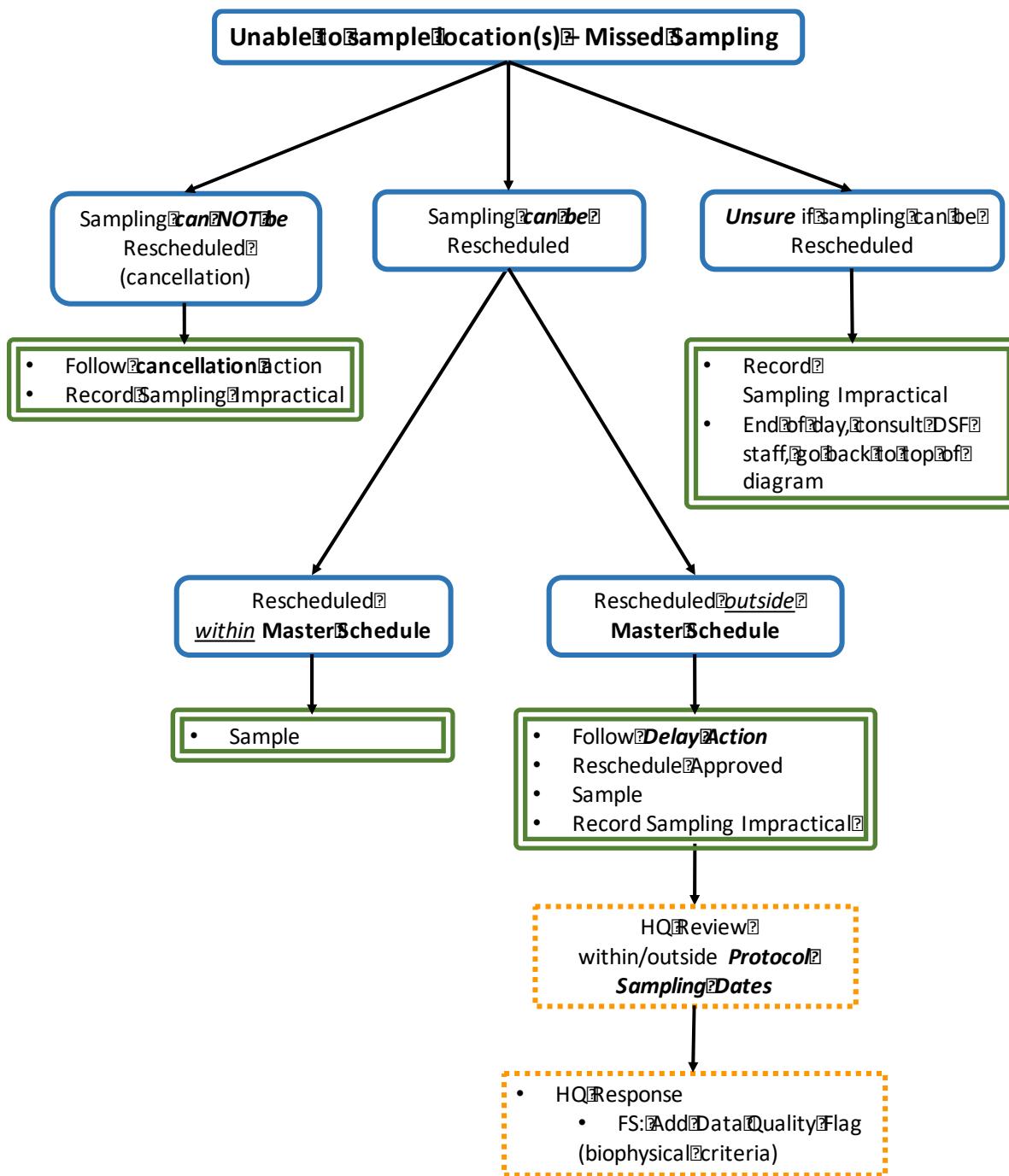


Figure 2. The documentation to account for a Missed Sampling event depends on the situation for each plot of each bout that is not sampled. Blue rounded boxes represent contingencies, green double line boxes describe the required actions, Orange dotted boxes indicate HQ actions. Missed Sampling events may also require a Data Quality flag and/or creation of a Site Management record.



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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 proposed date (Table 12) or within 5 days of the scheduled sampling date.
 - 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. Create a Fulcrum record for each Missed Sampling event in the field.
4. For each Missed Sampling record, the **Sampling Impractical** field must be populated in the mobile collection device (**Table 3**).

Table 3. Protocol-specific Sampling Impractical reasons entered in the Fulcrum application. In the event that 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	Low yield groundwater well
Shallow groundwater	Shallow groundwater; depth of groundwater column less than 0.1 m
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 12. 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 (relocatable 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 2**). If 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



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submitted. Please note that if sampling at particular locations requires significantly more time than expected, Science may propose to move these sampling locations.

Table 4. 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 Operations Field Safety and Security Plan (AD[02]) and EHS Safety Policy and Program Manual (AD[01]). Additional safety issues associated with this field procedure are outlined below. The Field Operations Manager and the Lead Field Technician have primary authority to stop work activities based on unsafe field conditions; however, all employees have the responsibility and right to stop their work in unsafe conditions.

Activities in streams should only be performed when flow conditions are safe. Do not attempt to wade a stream where velocity x depth is $\geq 10 \text{ ft}^2/\text{s}$ ($0.93 \text{ m}^2/\text{s}$). 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



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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 to the waters of that particular location (i.e., current status, tidal charts, 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 required safety training as defined in the NEON Training Plan (AD[04]). Additionally, technicians must complete protocol-specific training for safety and implementation of this protocol as required in Field Operations Job Instruction Training Plan (AD[05]).

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 technicians 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

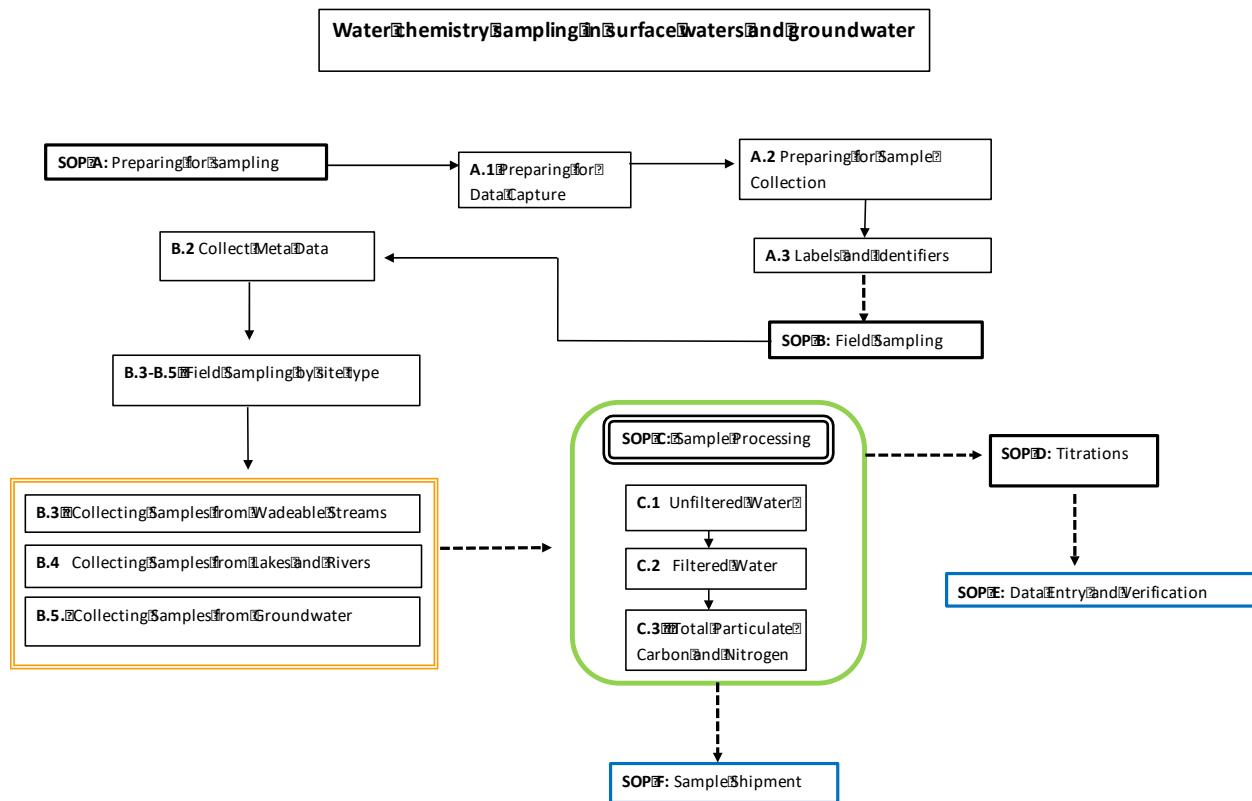


Figure 3. High level workflow diagram that visually shows how the Water Chemistry Sampling in Surface Waters and Groundwater SOPs are sequentially connected.

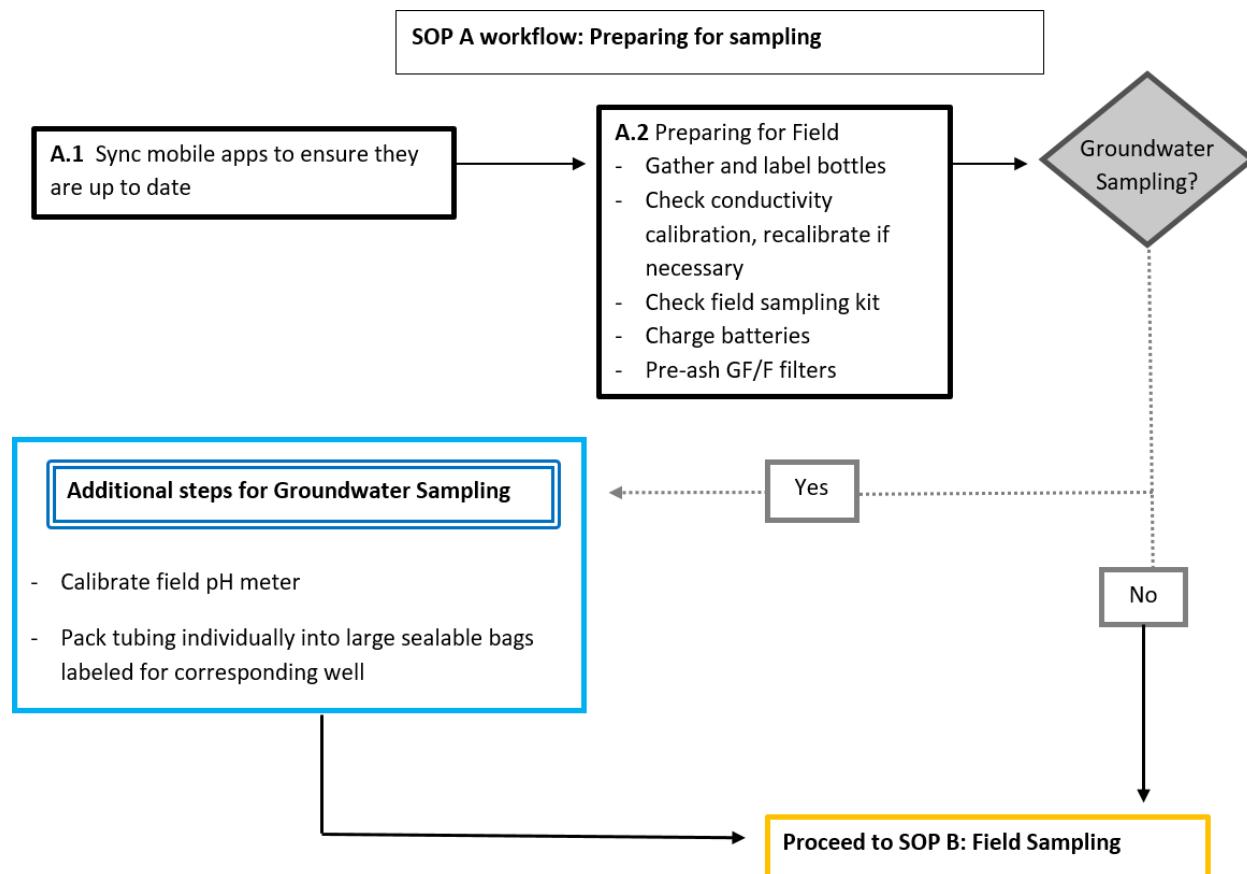
SOP A Preparing for Sampling

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 and synced at the beginning of each field day, whenever possible. For detailed instructions on protocol specific data entry into mobile devices, see the NEON Internal Sampling Support Library (SSL).

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. As a best practice, field data collected on paper datasheets should be digitally transcribed within 7 days of collection or the end of a sampling bout (where applicable). However, given logistical constraints, the maximum timeline for entering data is within 14 days of collection or the end of a sampling bout (where applicable). See RD[04] for complete instructions regarding manual data transcription.



A.2 Preparing for Sample Collection

All Sampling Location Types

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 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 senor 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 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 250mL bottle.
4. Pre-ash GF/F filters:
 - a. Place layers of 25 mm GF/F filters on aluminum foil. Use multiple layers of foil if needed, filters can be touching and placed on top of one another but should not be stacked more than 3 filters deep between foil layers to ensure air flow is not restricted and all filters get ashed.
 - b. Place in muffle furnace (500°C) for a minimum of 6 hours.



WARNING: Use designated safety equipment when working near or in the muffle furnace. DO NOT touch hot surfaces.

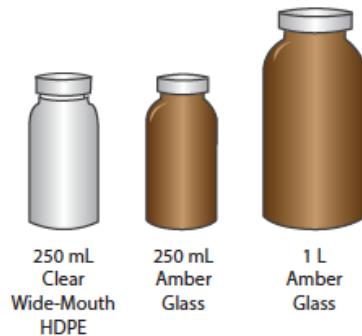
- After furnace has cooled, remove from the furnace and stack filters using filter forceps, and place in original box or an ashed, glass beaker covered with foil. CAUTION: Ashed filters may be hot. Use designated safety equipment at all times.
- Label box/beaker with permanent marker to read "ASHED, Your Name, Date".
- Place box in sealed zip-top bag.
- Ashed filter may be stored indefinitely, as long as they remain in the box and stay dry.



NOTE: 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.

**Additional Steps for Groundwater sampling only:**

5. Calibrate pH prior to each sampling bout
 - a. 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.
 - b. Calibrate the sensor according 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. Make sure buffer solution has not expired and is not reused.
 - c. If the pH meter is off by ≥ 0.1 pH units, recalibrate pH meter following pH meter manual.
 - d. Remove batteries from the pH meter between uses.
 - e. Between pH measurements, immerse the combination electrode in reference electrolyte (KCl 3 mol/L).
 - f. Prior to the next measurement, shortly rinse the combination electrode with the test sample or deionized water.
 - g. 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 Collecting Samples from Groundwater).

**Figure 5.** Water chemistry bottle types.

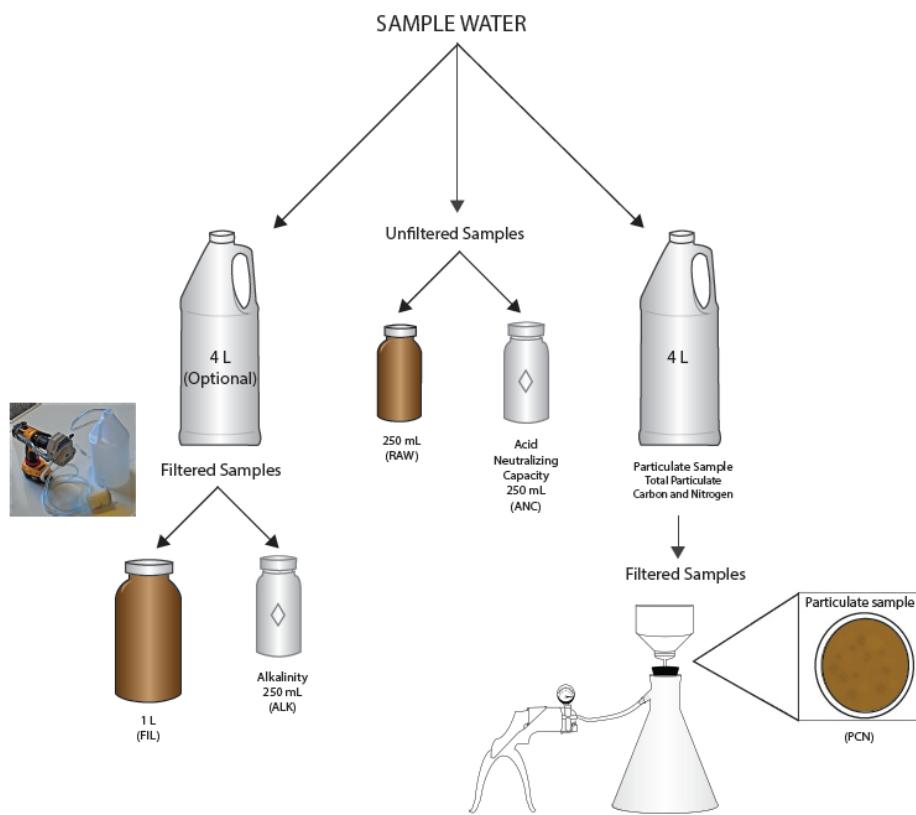


Figure 6. Flowchart of Water Chemistry Sample Collection and Filtration. ♦ Indicates 250mL, wide-mouth sample bottles that remain at the Domain Support Facility for analysis. ANC is only collected monthly. Letters in parenthesis indicate the sample type that correspond to the chemistry labels (see Figure 8).

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 6 provides a quick reference to the types of sample that require barcodes. The rule of thumb is that the primary field sample will **ALWAYS** need a barcode due to its importance in generating future samples. Likewise, the final disposition of all vial samples must have a barcode affixed to assist in the shipping and receipt of samples destined for the Biorepository or an external laboratory.

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 4C to 105C and still scan. Labels are waterproof but should be filled out before getting wet to ensure ink is dry.



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1. Prepare final sample containers by affixing one Type I adhesive barcode label to each bottle or whirl pack bag 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. If vials are used, 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.



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

2. Attach pre-printed labels (Figure 8. a and b) to bottles (Figure 5).

a) **SampleID :** _____
(siteID.stationID.YYYYMMDD.sampleType)
Sample Type: **FIL** **RAW**
NEON PCN Filter vol.(mL) _____

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

Determine the sampleID based on the sampling location, stationID, date, type of sample (

3. 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).



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4. **Table 5)** . If replicates are taken then a value will be added to replicates coming after the original sample.

- If sampled cannot be collected at the defined spot = 're'. This indicates that the sample was collected somewhere else within the reach, must record in app why (e.g., the normal sampling location is dry).
- Replicate sampleID convention: Use for occasions when additional replicates are collected (3 times per year). There is no need to add the number '1' to the first sample of the replicate set's sampleID.

2nd collected sample = site.station.YYYYMMDD.sampleType.2

3rd collected sample = site.station.YYYYMMDD.sampleType.3

5. 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 5.** SampleID format.

SampleID format: siteID.StationID.date.sampleType						
Part of sampleID	Location	Location Specifics		ID		
siteID	4-letter site code					
stationID	Stream	All		ss		
	River	Not Stratified		c0		
		Stratified	Top layer below surface	c1		
			Bottom layer below surface	c2		
	Lake	Not Stratified		c0		
		Stratified	Top-layer: Epilimnion	c1		
			Middle: Thermocline	c2		
			Bottom-layer: Hypolimnion	c3		
	Groundwater	Well number		w1- w8		
	Sample collected elsewhere from the normal location			re		
Date	YYYYMMDD					
sampleType	Filtered			FIL		
	Raw/Unfiltered			RAW		
	Particulate carbon and nitrogen			PCN		
	Alkalinity			ALK		
	Acid neutralizing capacity			ANC		
	Dissolved inorganic carbon and pH (D18/19 only)			DIC		
	If replicates of sample taken then add value onto end of sampleID for 2 nd and 3 rd replicate	First Replicate of Sample (primary)		Leave as is		
		Second Replicate of Sample		Add .2		
		Third Replicate of Sample		Add .3		

**Table 6.** 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	1L amber glass bottle	Barcode I & Pre-printed label	External Lab
Raw Sample	Unfiltered water	PRIN.ss.20170712.RAW	SWC: Water Chemistry	250mL amber glass bottle	Barcode I & Pre-printed label	External Lab
Particulate Sample	Particulate matter collected on filter paper	PRIN.ss.20170712.PNC	SWC: Water Chemistry	GF/F Filter wrapped in foil	Barcode I & Pre-printed label	External Lab
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	250mL clear wide mouth bottle	Barcode I & Pre-printed label	Domain Lab
ANC Sample	Unfiltered water	PRIN.ss.20170712.ANC	SWC: Water Chemistry	250mL clear wide mouth bottle	Barcode I & Pre-printed label	Domain Lab

SOP B Field Sampling

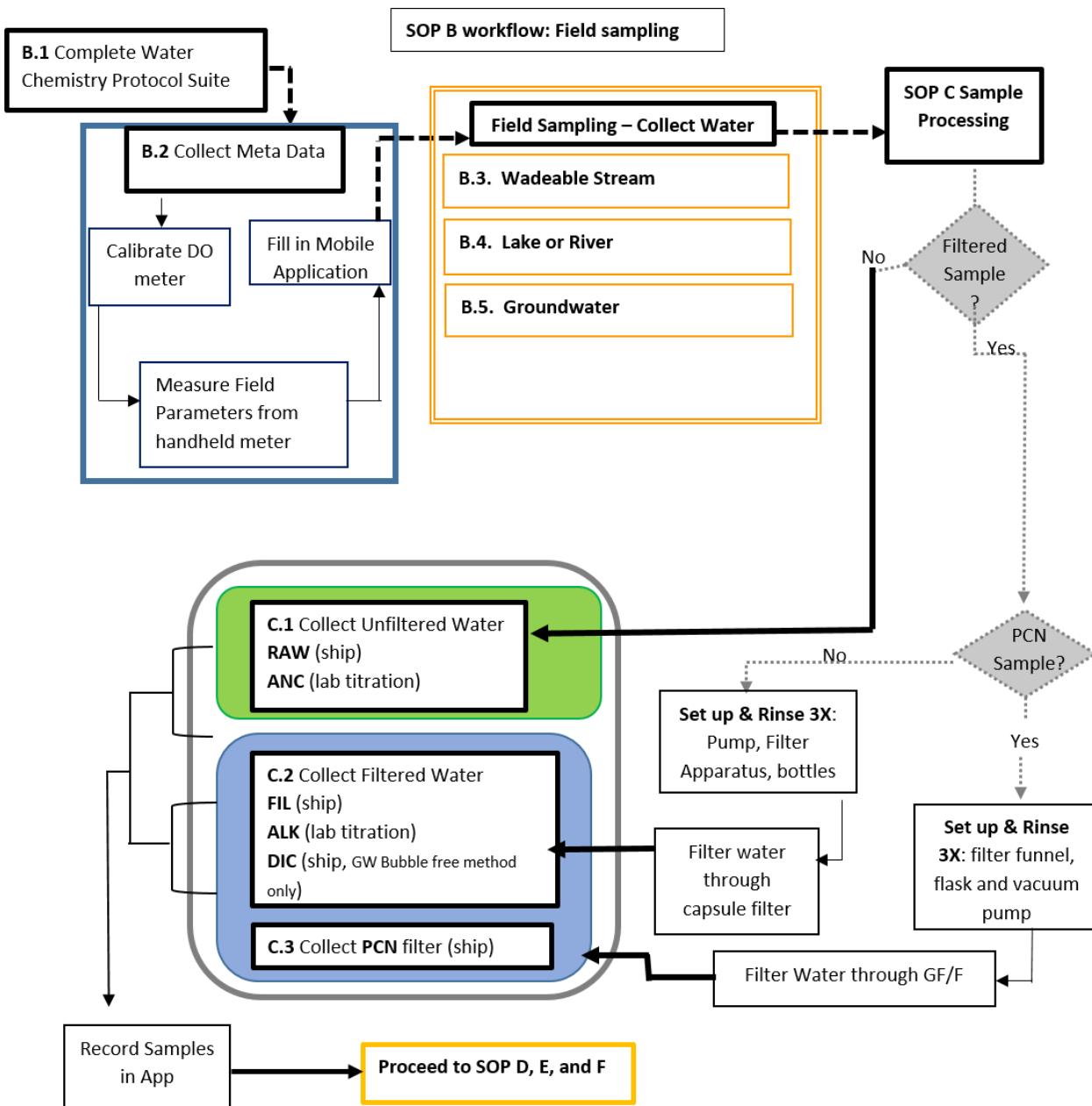


Figure 9. Breakout workflow diagram of SOP B: Field Sampling



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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 water chemistry suite during monthly sampling events in streams and every other month in lakes and rivers.

B.2 Meta Data for All Water Chemistry Samples

In the field, fill out the General AQU Field Metadata Mobile App or Fieldsheet (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 must 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]).
3. For surface water, measure and record water temperature, Specific Conductivity, DO, and DO percent saturation 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.
 - i. Conductivity 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, uS/cm).
 - ii. 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 (**Error! Reference source not found.**).

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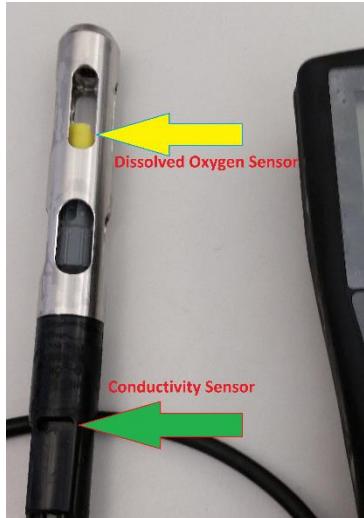


Figure 10. Picture of handheld meter showing location of sensors on probe.

B.3 Collecting Samples from Wadeable Streams



Be cautious when sampling. Items can easily fall into stream while bending to sample.

1. ALWAYS sample in the THALWEG with the bottle opening pointed upstream and into the main flow of water (Figure 11) and ~ 10 centimeters below the surface (to avoid sampling floating material or surface film).
 - a. You may step into the stream, but minimize bed disruption as little as possible as you walk.
Take samples UPSTREAM from where you are standing.

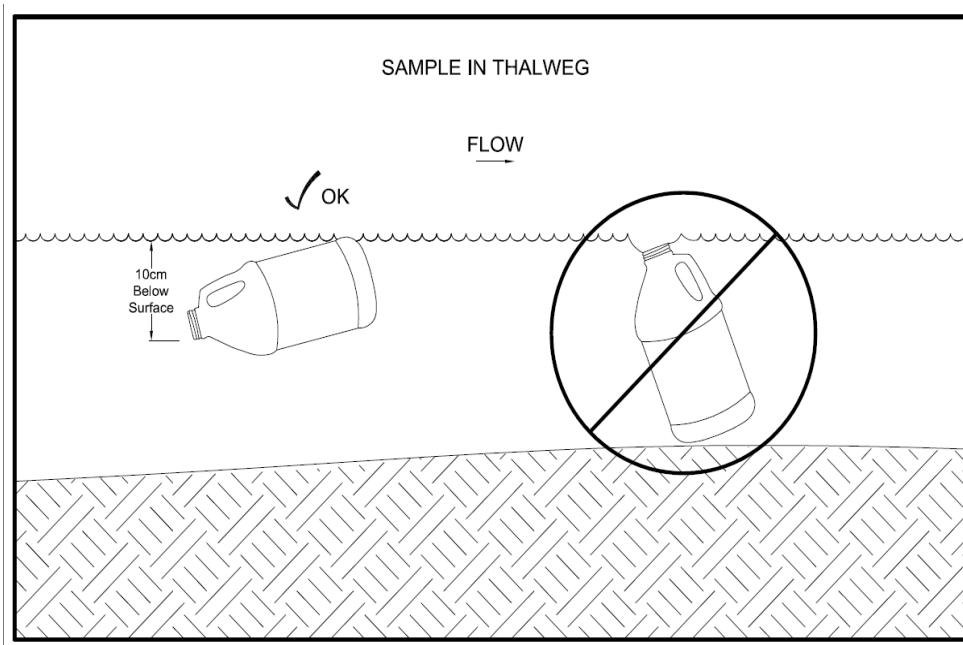


Figure 11. Diagram of proper and poor placement of a water sample bottle

2. Rinse the collection and sample bottles and caps with the appropriate sample water (i.e., use filtered water to rinse filtered samples):
 - a. Bottles to be rinsed with stream water:
 - 1) 4 L jug (can be used for filtered samples and/or PCN, see below)
 - 2) 250 mL burned amber glass bottle for external lab
 - 3) ANC - 250 mL wide-mouth, HDPE – ***to be analyzed at the Domain Support Facility.**
 - b. To rinse: Hold the cap in your hand when the cap is not on the bottle (setting the cap down increases risk of contamination).
 - 1) 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. Remove the cap, and allow stream water to fill approximately $\frac{1}{5}$ of the collection bottle. Remove bottle from stream, cap and shake. Discard water downstream. Repeat 2 more times.
 - 2) NOTE: You may also use the field pump to pump water out of the stream (from just below the surface) and into your bottles for rinsing.
3. Fill the 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.
 - 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.



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- c. Recap bottle under stream.
4. If collecting replicates, collect 2 additional sets of samples at same time and location as the primary samples.
5. Proceed to B.6 B.5.1 Determine Best Sample Method

For non-permafrost sites, the appropriate groundwater sampling method is determined by evaluating the recharge rate and water column height of a given well (Figure 14). Tundra and Taiga sites will use a **needle method** described in section



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B.5.3.5 Needle Method.

Wells that recharge at a rate greater than 100 mL/min are considered high yield wells and are sampled via the **low-flow method** for water column heights greater than 0.5 m, or the **bailer method** for water column heights of less than 0.5 m. In the absence of contradictory knowledge, all sites will start with the assumption of high yield wells and attempt the low-flow method (or bailer method for shallow water). The majority of NEON sites will use the low-flow sampling method.

During low-flow or bailer method sampling technicians will discover the recharge rate of a given well. Some wells may be classified as low yield wells (wells with recharge rates lower than 100 mL/min). Pumping low yield wells using the traditional low-flow method will cause enough drawdown that the well will run dry over the course of sampling. In this case, contact Science for help determining the appropriate alternative method which may include the **minimum purge method** or **purge dry method** followed by sampling once replenished.

Decision Workflow:

If the site is located in a tundra or taiga ecosystem, proceed to section



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1. B.5.3.5 Needle Method. Otherwise, proceed to step 2.
2. Prior to the field
 - a. If the well has never been sampled, plan to use the low-flow method for thick water columns (> 0.5 m) or the bailer method for water columns < 0.5 m.
 - i. If water column height is unknown, bring materials for both potential methods.
 - b. If the well has been sampled before and recharge behavior is known, plan to sample using the previously established method.
 - i. Bring both the low-flow sample pro pump setup and bailers to the site if you suspect that well conditions have changed since the last sample bout.
3. In the field
 - a. Determine water column height as described in section B.5.2 Locate well and assess water depth
 - b. Calculate recharge rate as described in section B.5.2 Locate well and assess water depth .
 - i. For recharge rates > 100 mL/min:
 - a) Use low-flow sampling (B.5.3.1 Low-flow Pump Method) for water column heights > 0.5 m

Use the bailer method (



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- b) B.5.3.3 Bailer Tube Method) for water column heights < 0.5 m.
- ii. For recharge rates < 100 mL/min:
- a) If this well has been previously sampled under similar recharge and depth conditions, sample using the previously established method.
 - b) If this is the first time sampling this well:
 - (1) Select “sampling impractical, low yield well”.
 - (2) Write a trouble ticket to Science detailing the issue and include depth to water table for the well. There are 2 possible remediations:
 - Change in sampled wells. Science may reconsider the wells chosen for sampling in the site sampling strategy if other non-sampled wells show higher yield.

Change in sampling method. Science will help determine if the minimum purge method (

- B.5.3.2 Minimum Purge Method) or purging to dryness (B.5.3.4 Purge Dry Method) are appropriate.

Because the elevation of the water table can change throughout the season, it should also be noted that some sites might need to use multiple sampling methods. For example, a site might have enough water to use the preferable low-flow method in the spring, but require the bailer method in the fall. Sampling method may also vary between wells with differing water levels or recharge rates at a single site. The following sections provide specific details for each groundwater extraction method.

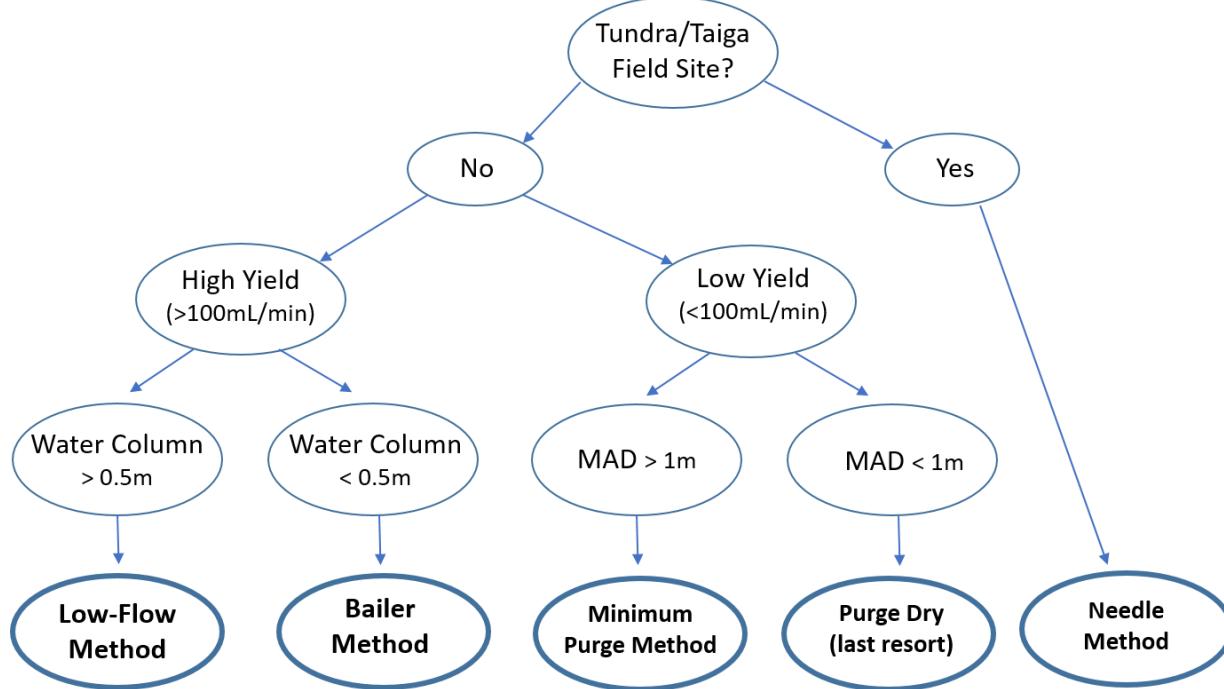


Figure 14. Decision tree for determining appropriate groundwater sampling method.

B.5.2 LOCATE WELL AND ASSESS WATER DEPTH

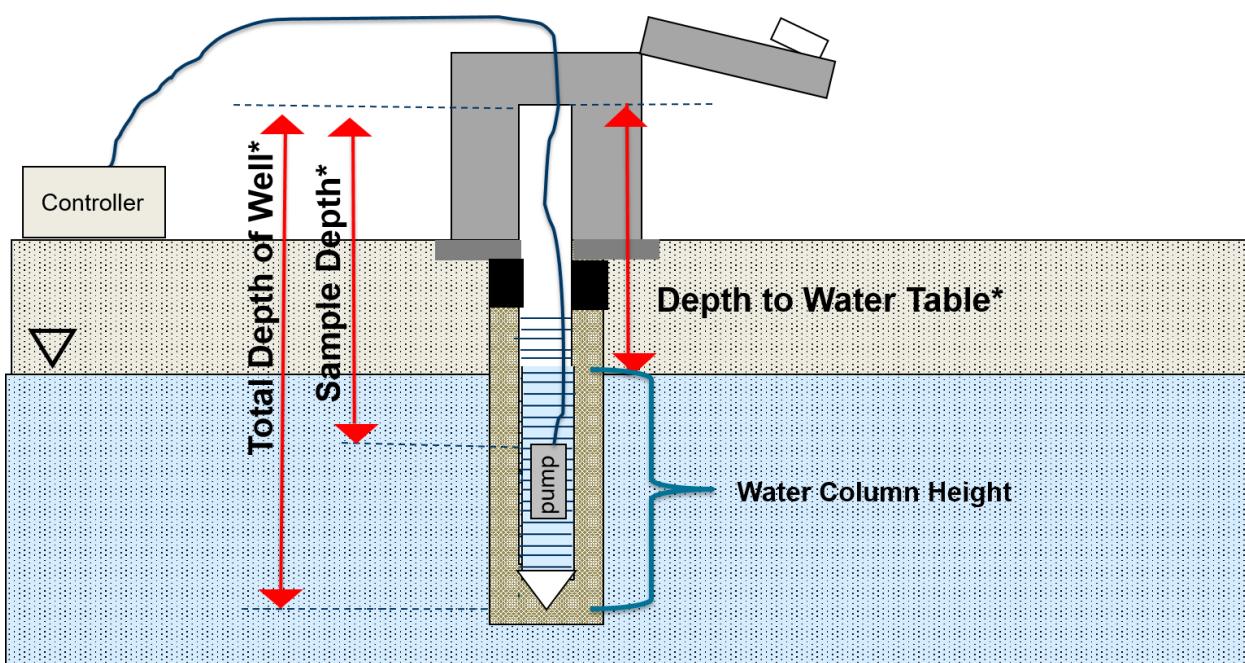
1. Shut down wells by disconnecting trolls from the circuit board in the power box as described in the Groundwater Preventive Maintenance document [RD 12]. Remember to reconnect the trolls and reset the grape after finishing work on a well. Disconnecting the sensor from the cable should be avoided as this can cause damage to the connection over time.
2. 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.



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3. Unlock the Well. Open the lock and flip open the protective well lid, then remove the white PVC cap from the well.
4. Remove the AquaTroll sensor from the well.
 - a. Pull the sensor cable and mounting cable out of the well gently so as 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. The other end of the sensor cable will be attached directly to the telemetry unit. Leave this connected.
5. Take key groundwater measurements prior to starting the groundwater extraction process (**Figure 15**).
 - 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 16b**). 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 16c**. 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 16c**). For wells fitted with snorkel caps, unscrew the cap at the coupler and measure on the PVC lip as shown in **Figure 16d**.
 - iii. Wipe down water meter tape with bleach wipes between wells. (Make sure the wipes contain bleach. Note that normal Clorox wipes do not contain bleach).
 - 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 and record in the data collection app. (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.



Drawing is not to scale

* Measure from top of PVC casing
Record to 0.01 m

Figure 15. Key groundwater measurements

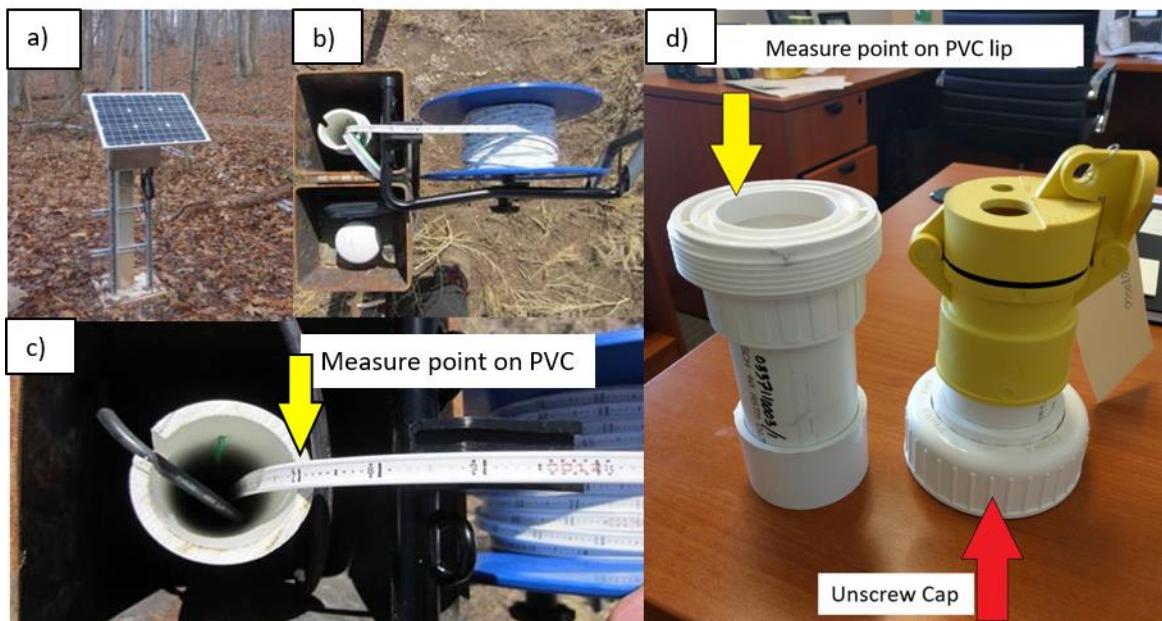


Figure 16. (a) Standard groundwater well at a NEON site (b) Water-level tape attached to outer well casing. (c) Reading the depth to water from the water-level tape on standard well. The tapes are marked in "meters" with each foot increment marked in red. Readings are taken at the top of the inner PVC 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 Pump Method

This method is used for high yield wells (recharge rates greater than 100 mL/min) with water column heights of greater than 0.5 m.

1. Calculate water column height (**Figure 15**) as shown in section B.5.2 Locate well and assess water depth.
2. Calculate the depth to set the sampling pump as follows:

Water Column Height (m)	Sample Depth (Pump Inlet)
≥ 1.5 m	(Well Water Depth) + (1 m)
0.5-1.5 m	(Depth of Well) – (0.5 m)
< 0.5 m	Bailer Tube Method

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 = $(15.55 - 5.55) = 10.00 \text{ m}$

Sample Depth: $(5.55 \text{ m} + 1 \text{ m}) = 6.55 \text{ m}$

Example 2:

Total Depth of Well = 7.25 m

Depth to Water Table = 5.85 m

Water Column Height = $(7.25 - 5.85) = 1.4 \text{ m}$

Sample Depth: $(7.25 \text{ m} - 0.5 \text{ m}) = 6.75 \text{ m}$

3. Cut Tubing to Correct Length. (NOTE: Use tubing cutters provided in the well kit to cut tubing, NOT scissors). The tubing used to sample the groundwater wells is dual bonded tubing with one line for air delivery to the pump and one line for water discharge from the pump. 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 pump, up the PVC well casing, and then back to the ground to reach the controller and collection cell. 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 ends you have to trim in the future.

4. Set-up the Sample 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 17(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.)

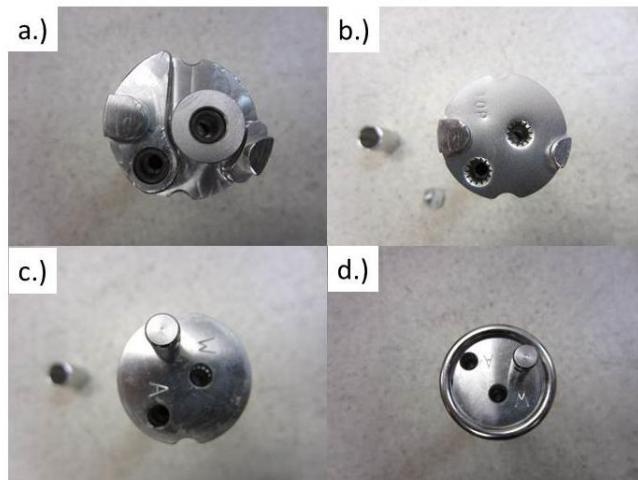


Figure 17. Assembly of the fitting plate at the top of the pump for holding the air and water lines. (a) Bare top of pump. (b) Fitting/grab plate added (“TOP” must face upwards). (c) Top plate added. (d) Collar added to lock parts (a-c) together.

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 18** shows the components of the pump including the bladder.

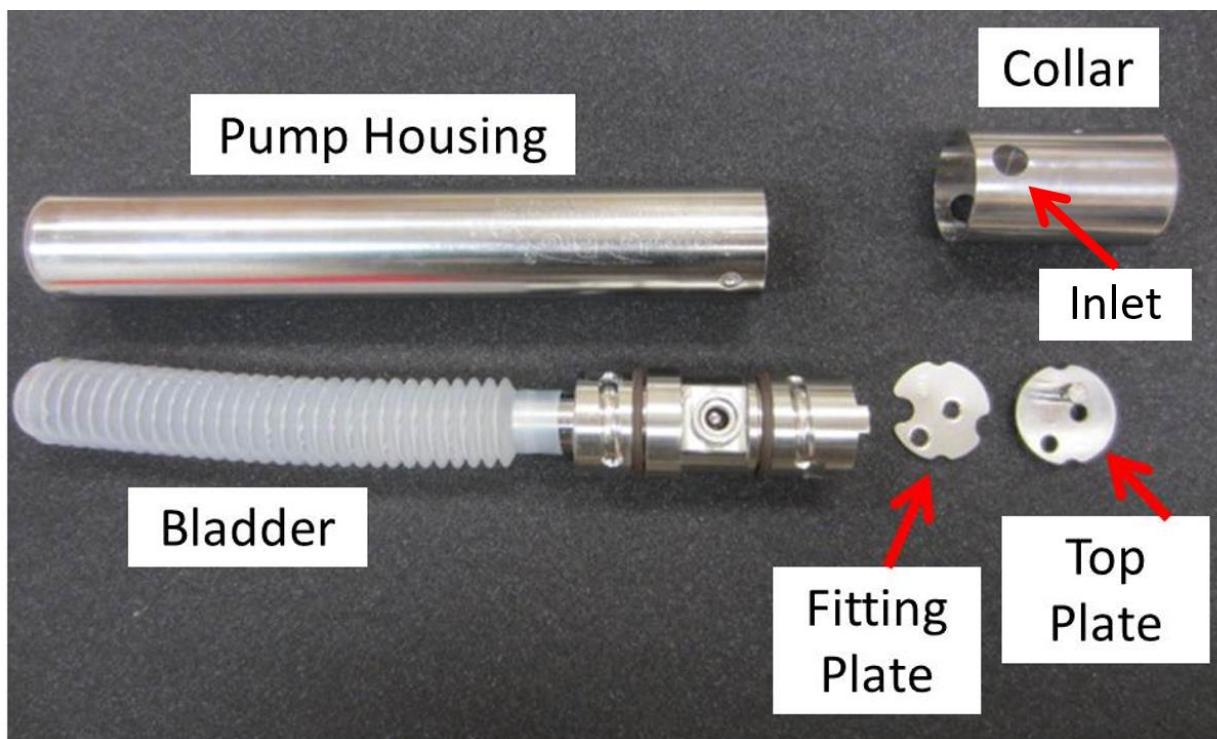


Figure 18. Components of the sampling pump.

6. Attach Tubing Lines and Cable
 - a. 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 19**. (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 push into the pump top by about 1 cm. A little water dabbed on the ends of the tubing help 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.
 - b. Attach the post (thread into threaded port) and cable to the pump as shown in **Figure 20**.



Figure 19. Attaching grey air-line and white water-lines to pump
(top-right photo shows lines pushed through top plate and “teeth” of grab plate)

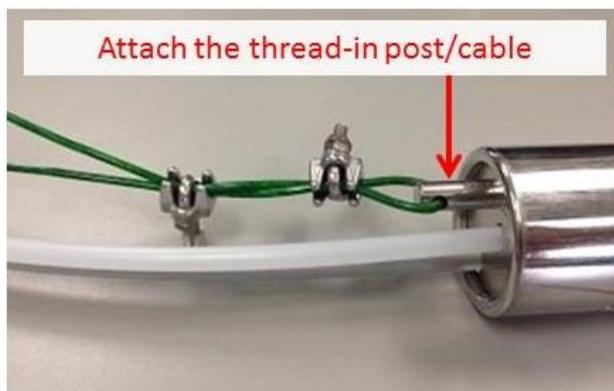


Figure 20. Attach post and cable to the pump via the top plate.

7. 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.**
8. 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 21**), 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 22**).

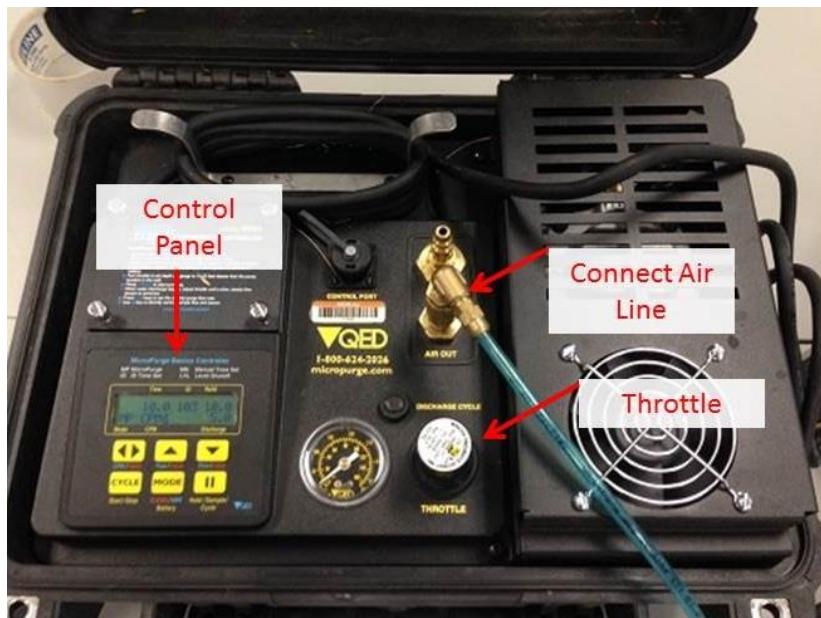


Figure 21. Attach blue air-line to controller.



Figure 22. 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 23**).

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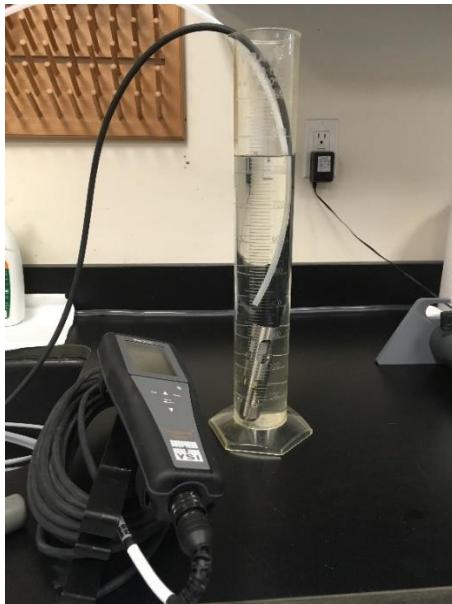


Figure 23. Groundwater Chemistry Collection cell using a 1000 mL graduated cylinder.

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 into 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 24**). 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). 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.

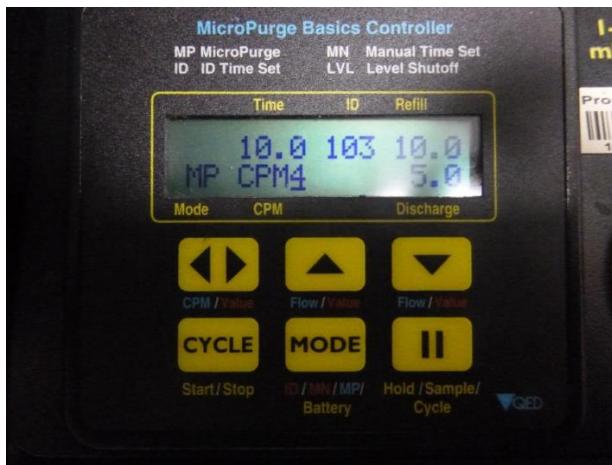


Figure 24. Groundwater pump control panel screen. Note the Refill and Discharge times on the right.

9. Monitor water level and determine recharge rate: Water-level within the well should be monitored every few minutes using the water-level tape in the procedure detailed earlier. 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). If the water depth declines more than the 10% threshold, then select a decreased discharge rate by either choosing a shorter discharge time on the controller or turning the throttle counter-clockwise 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.
Recharge rate is the rate at which the well water is replenished during pumping. Once the water reaches a relatively constant level during pumping, the recharge rate is equal to the discharge rate. If a steady water level cannot be achieved with flow rates below 100 mL/min, the well is low yield and technicians should write a trouble ticket.



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10. Monitor water quality: While the pump is discharging water from the well, monitor the water quality parameters Specific Conductance (uS/cm) and Water Temperature (°C) using the YSI hand-held meter to provide a metric to determine when the water is ready to be collected for sampling.
- 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, uS/cm).
 - Once you start removing water, take readings from the hand-held meter approximately every 3-5 minutes during the pumping event and noted on the sampling sheet in addition to the time.
 - 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.
 - 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.
=
- e. *Total Well Depth – Depth to Water x π (well radius)²*
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.
- f. **Record** pH at the time of sampling using the hand-held pH meter in the data collection app.

11. 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. Record sampling method in the data collection application.

FILTER THE SAMPLES MINIMIZING THE EXPOSURE TO AIR AS DESCRIBED IN SECTION

12. B.5.4 Groundwater Field Filtering and Prioritization.
13. Decontaminate between wells.
 - 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
 - Shake container and soak for 10 minutes
 - Remove pump components and squirt down with DI
 - Reassemble pump with new or dedicated bladder for each well
 - Wipe down water meter tape with bleach wipes and squirt with DI between wells.
 - For each well use dedicated tubing for the section that goes into the well



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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.

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, ALK, RAW, PCN filter. However, it is necessary to discontinue the sampling once maximum allowable drawdown (described in the following section) is reached. If maximum allowable drawdown is less than 1 m do not use this method.

b. Timing

This method requires that the pump 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 placement. Due to the timing requirements and the desire for minimal mixing of the water column, this method would require techs to know that their wells qualify as low yield wells prior to the sampling event. Ideally, pumps will be placed in low yield wells in the week prior to scheduled sampling. Thus, if it is discovered during sampling that a well is low yield, sampling of that well will have to be postponed and a trouble ticket should be submitted.

2. Methodology

- a. Calculate the amount of tubing needed to place the pump 0.3m from the bottom of the well, plus and extra 1 – 2 m of tubing for ease of reaching the pump. Secure the tubing in place by attaching it to the AquaTROLL cable with a zip tie at a minimum of 48 hours prior to sampling(**Figure 25**). Tubing with 1/8"ID will fit in the same slot as the cable.

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- i. The AquaTroll can be removed for pump placement and then replaced immediately afterwards and left in place during sampling as long as the sensor and the pump do not obstruct each other.
- ii. Care should be taken to cause minimal disturbance to the water column.



Figure 25. Pump tubing secured in place with zip tie.

- b. Place pump at correct depth. **The inlet for the pump is near the top of the pump noted by the hole in the side of the pump body (Figure 26). This is the specific point on the pump to set to the specified depth. When placing the pump, measure from this point.**
- c. 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.
 - i. If water table is above the screened interval of the well:
$$\text{MAD} = \text{depth to pump placement} - \text{depth to top of screen} - 0.5\text{m}$$
Example 1:
Depth to pump placement = 5 m
Depth to top of screened interval = 2 m
Depth to water table = 1 m



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$$\text{Maximum Allowable Drawdown} = 5 \text{ m} - 2 \text{ m} - 0.5 \text{ m} = 2.5 \text{ m}$$

- ii. If water table is within the screened interval of the well:

$$\text{MAD} = \text{depth to pump placement} - \text{depth to water table} - 0.5\text{m}$$

Example 2:

$$\text{Depth to pump placement} = 5 \text{ m}$$

$$\text{Depth to top of screened interval} = 2 \text{ m}$$

$$\text{Depth to water table} = 2.5 \text{ m}$$

$$\text{Maximum Allowable Drawdown} = 5 \text{ m} - 2.5 \text{ m} - 0.5 \text{ m} = 2 \text{ m}$$

Note: If the calculated MAD is less than 1m, do not use this method and move on to the Purge Dry method.

- d. Prior to sampling, remove a set volume based on tube length (**Table 7**). Measure and record water temperature, temperature-corrected conductivity, DO percent saturation, and pH for the discharged water. Divide the volume removed into thirds and use it to rinse the 4L jug 3 times.

SAMPLES CAN BE COLLECTED IMMEDIATELY FOLLOWING THE SMALL VOLUME REMOVAL. IN ORDER TO MINIMIZE TURBIDITY AND DISTURBANCE TO THE WATER COLUMN, SAMPLES SHOULD BE REMOVED AT A RATE AT OR BELOW 100 ML/MIN. MEASURE DRAWDOWN WITH THE WATER TAPE AS THE SAMPLE IS BEING COLLECTED AND DISCONTINUE COLLECTION IF THE MAD IS REACHED. IF MAXIMUM DRAWDOWN IS MET PRIOR TO OBTAINING THE FULL VOLUME NEEDED FOR THE GROUNDWATER CHEMISTRY SUITE, PRIORITIZE SAMPLES AS DETAILED IN SECTION

- e. B.5.4 Groundwater Field Filtering and Prioritization.

Table 7. 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

- f. If a site has more than one low yield well, additional tubing and bladders may be required to ensure that sampling can occur in the desired time frame. Tubing and bladders for all low yield wells will need to be placed in the wells during the week prior to sample collection to allow for the effect of pump placement to dissipate.
- g. Alternatively, a peristaltic pump with dedicated tubing could be used as long as the well is sampled at a flow rate around or below 100 mL/min. Deeper wells may require 1/8" inner diameter tubing to appropriately lift the water sample. Use dedicated tubing for each well.



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- i. Weight the end of the peristaltic pump tubing with stainless steel nuts as shown in **Figure 26**. Then firmly insert a 2-way luer-lock and remove its handle to secure nuts. Alternatively, the optional Quick Bullet weight can be used to weight down tubing.
- ii. Lower the tubing to desired depth of 0.3 m from the well bottom at least 48 hours prior to sampling and secure to the AquaTroll cable with zip tie.
- iii. Proceed to collect samples as described above.

Note: 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 26. Nuts added to peristaltic pump tubing for weight.

B.5.3.3 Bailer Tube Method

Domains with wells that are high yield but have shallow groundwater less than 0.5 m will require the bailer tube method. This method is much simpler than the Low-Flow method and is performed by evacuating the water in the well using a “bailer tube” which is a small diameter hollow tube that has check ball in the bottom of it (**Figure 27**). Note: you may also use the peristaltic pump instead of the bailer tube to remove the three well volumes, as indicated below.



Figure 27. Image of a bailer tube.

1. Use a dedicated bailer and rope for each sampling well.
2. Lower the tube into the well on the end of a rope below the static water level filling-up the bailer tube with water.
3. Pull the tube out of the well and pour contents into a bucket (pour out of the top of the bailer tube). This process repeats until three “well-volumes” are removed from the well. A well-volume is defined as the volume of water contained within the well and is calculated as:

$$\text{Well Volume} = (\text{Total Well Depth} - \text{Depth to Water}) \times \pi r^2 h$$

Where the “Total Well Depth” and “Depth to Water” are measured from the top of the PVC well casing and “r” is the radius of the well (3.2cm diameter, 1.6cm radius, $\pi r^2 = 8.03 \text{ cm}^2$). **Each meter of water in the well is equivalent to approximately 0.8L. For ease of calculation, multiply the height of water in the well by 0.8 to get the approximated volume in Liters.** For example, if the depth to water in a well is measured as 1.32m and the total depth is measured as 1.98m, then the height of water in the well is 0.66m and one “well volume” is $(0.66\text{m}) \times (0.8\text{L/m of water}) = 0.53\text{L}$ of water. The three well volumes are equivalent to 1.59L of water.

4. After three well volumes are removed from the well, extract additional water with the bailer to triple rinse the 4 L jug. Each rinse volume should fill roughly 1/5 of the jug. The collect sample water by again using the bailer tubes to pull water from the well and pouring the water directly into the clean 4 L jugs.
5. **Record** water quality parameters (SPC, DO, Temp, and pH) at the end of the three well volumes by filling a small bucket or bottle with well water and using the hand-held meter to measure the parameters in the data collection app.



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6. Record the sampling method and approximate volume of water discharged/removed from the well prior to collecting water for samples.

IF AVAILABLE WATER IS INSUFFICIENT TO MEET THE SAMPLE VOLUME REQUIREMENTS, PRIORITIZE SAMPLES AS DETAILED IN SECTION

7. B.5.4 Groundwater Field Filtering and Prioritization

B.5.3.4 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). Thus, this data will be flagged for users.

1. Use bailers or a peristaltic pump at a high rate 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 (uS/cm), and Water Temperature (°C) in the data collection app.
2. Use dedicated bailers and ropes or, if using the pump, use dedicated tubing for each well. 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).
3. Return within 24 to 48 hours to directly sample the volume that has return to the well.
 - a. Remove a minimum of 50 mL from well. Record pre-sampling field measurements on this volume and use it to rinse the 4L jug.

SAMPLE WELL. WHEN OBTAINING THE FULL SAMPLE VOLUME IS NOT POSSIBLE, PRIORITIZE SAMPLES AS DETAILED IN SECTION

- b. B.5.4 Groundwater Field Filtering and Prioritization.

B.5.3.5 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 28**). Use individual dedicated syringes and tubing for each well location.



Figure 28. 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.



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5. Collect sample

- a. Insert the needle at an angle next to the well infrastructure and sample slightly above the frozen interface (**Figure 28**). 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. Fill a 140 mL syringe using a bubble-free technique.
 - i. **Bubble-free** technique: Bubble-free sampling will minimize contact between the anoxic sample and the atmosphere which can impact pH, Alkalinity, and DIC.
 - a) 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.
 - b) 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 air tight so that no atmospheric gases are drawn into the syringe.
 - c) Close the stopcock attached to the tygon tubing to maintain a bubble-free connection to the groundwater and disconnect the two stopcocks.
 - d) Expel air from syringe (**Figure 29**)
 - 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 of the plunger.
 - e) 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.

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Figure 29. Expel air bubbles from the syringe during bubble-free sampling.

- f) Re-attach the stopcocks to one another. Make sure that the connection is tight so that air is not introduced.
- g) 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 30**). Expel all but ~5 mL of water from the syringe.



Figure 30. Stopcock position for expelling water during bubble-free sampling.



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- h) 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.
 - i) Indicate instances in the data collection app to inform data users when water table conditions render bubble-free sampling impossible.
 - ii. Once you have collected 140mL 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.
 - iii. Remove the syringe plunger and immediately insert the calibrated pH probe into the remaining water. Record pH in the data collection app.
 - iv. Discard water.
- c. Fill the syringe again with 140mL using the bubble-free technique.
 - i. Filter 15 mL through the syringe filter into the 60mL DIC bottle three times to triple rinse.
 - ii. 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.
 - d. 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 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. **RAW**
 1. LEAVE headspace to prevent freezing
 - iv. **PCN**
 - v. **Remaining Field Measurements**
 1. Pour syringe water into a 250mL graduated cylinder and insert the YSI probe.
 2. Record Dissolved Oxygen Saturation (%), Specific Conductance (uS/cm), and Water Temperature (°C) in the data collection app.



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B.5.4 GROUNDWATER FIELD FILTERING AND PRIORITIZATION

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.

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)

- a. 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 sections above.

2. Field Filtering

For groundwater samples, filter the FIL and ALK samples in the field as close as possible to the time of collection. See Collect Filtered Water Samples (FIL) for specifics of filtering using the peristaltic drill pump.

a. Field Filtering for Minimum Purge method:

- i. For these wells, it may be possible to directly filter the water as it is being pumped out of the well. Connect the groundwater pump outflow tubing directly to the peristaltic pump intake. Connect one end of a capsule filter to the outflow of the peristaltic pump and one end to additional tubing that can reach the bottom of the sample bottle.
- ii. A series of multiple filters in line can be used for dirtier water.
- iii. Filter directly into the FIL and ALK sample bottles. Overflowing each bottle from the bottom upwards and immediately cap leaving no headspace.

b. Field Filtering for Low-Flow method

- i. Slower recharge here, refers to any wells where the sample cannot be directly pumped from the water table through the filter without introducing air between them.
- ii. Insert the outflow end of the groundwater sample tubing through an appropriately sized hole drilled into a 1L Nalgene cap (**Figure 31**). 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 (*or optional Swagelok design detailed below) to create an airtight seal between the tubes and cap.

- iii. Pump directly from well into the 1L Nalgene container, filling from the bottom up.
- iv. Allow container to overflow, then seal the cap onto the container.
- v. Start the drill pump. Simultaneously run both pumps so that the water line remains at or close to the top of the Nalgene.
- vi. Pump the outflow of the drill pump through the capsule filter and through a final tube to fill the FIL and ALK containers from the bottom up. Make sure to rinse this tube with DI between wells.
- vii. Overflow the containers then immediately cap.

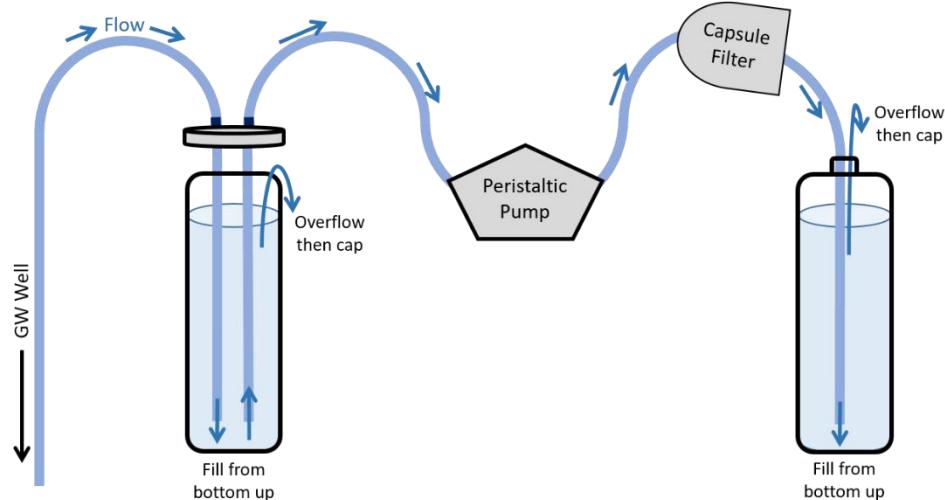


Figure 31. Filtering setup to minimize sample aeration during filtration for low-flow and minimum purge groundwater samples.



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- c. Field Filtering for the Bailer and Purge Dry methods:
 - i. Some aeration is unavoidable with the bailer method so we collect an unfiltered water sample in a 4L jug and directly filter from the jug. Fill the 4 L jug (or more if necessary) directly from the bailer.
 - ii. Filter the FIL and ALK samples in the field directly from the 4 L jug through the capsule filter into the sample jars.
 - iii. Cap the jug with the remaining sample and set aside for Sample Processing. Set the jug in a cooler with ice.
- d. Field Filtering for the Needle Method
 - i. The needle method will utilize a 47 mm GF/F syringe filter the .DIC, .FIL, 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



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B.5.3.5 Needle Method.

- a. Field Measurements
- b. H₂O isotope (RD[14])
- c. FIL
 - i. For low-volume situations, use a 250 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 250mL 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. 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.
- e. RAW
 - i. Leave headspace
- f. PCN filter

B.4 Rinsing

1. Rinse the collection and sample bottles and caps with the appropriate sample water (i.e., use filtered water to rinse filtered samples, and unfiltered water to rinse unfiltered bottles (Figure 6)).
2. Hold the cap in your hand when the cap is not on the bottle (setting the cap down increases risk of contamination).
3. Rinsing is location type specific and covered under the field sampling SOPs above.
 - a. Bottles to be rinsed with Unfiltered water:
 - 1) 4 L jug (can be used for filtered samples and/or PCN, see below)
 - 2) 250 mL burned amber glass bottle for external lab



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- 3) ANC - 250 mL wide-mouth, HDPE – ***to be analyzed at the Domain Support Facility.**
- b. To rinse bottles for filtered samples (FIL and ALK) rinse with filtered water. See below.



6. Sample Processing

B.5 Collecting Samples from Lakes and Rivers

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:
 - a. If NO, do not take any more samples.
 - b. 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.
 - c. Is there a true (i.e. flow-through) inlet and outlet to the lake?
 - 1) If No, do not take any more samples
 - 2) If Yes, collect samples sampled just downstream of the inlet and outlet infrastructure, following the wadeable stream sampling protocol.
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.

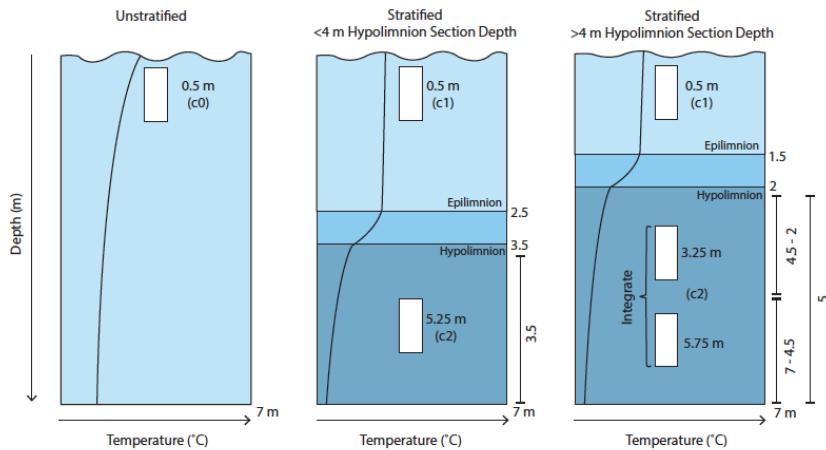


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- a. A minimum of 0.5 m of water below the ice is required to sample.
- b. If < 0.5 m of water depth is available in the central (buoy) location, then move to a location that is within 10 m of the original location and note the new GPS location.

a)



b)

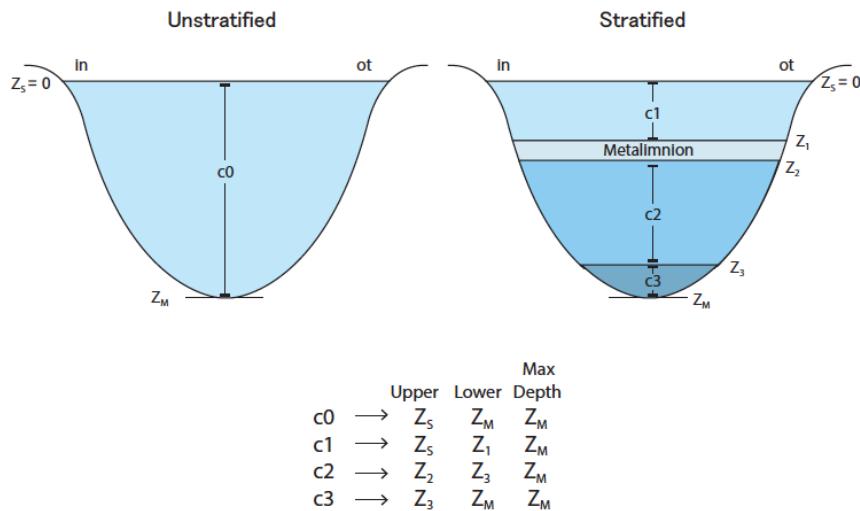


Figure 12. Example of an unstratified and stratified lake water column a) sampling depths with placement of thermocline and b) identification of upper and lower section depths. In deep lakes, 2 thermal stratifications may occur, creating 3 sections. Note, hypolimnion sampling is determined by the hypolimnion 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.



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Field Sampling – Lakes and Rivers

1. Take your 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.
2. Record the date and the time of day (use local, military time; ex. 13:46) that samples were collected in the Surface Water Chemistry Field Sampling Datasheet (RD[05])
3. Record DO, water temperature and specific conductivity. 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 sampler 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.
 - a. 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 definite 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.
7. Ensure the spout is CLOSED.
8. 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.
9. 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.
10. Retrieve the sampler from the water column. Water is dispensed into the appropriate containers/sample bottles through the spout (Figure 13a).
11. Repeat steps 1 through 10 for each sample.

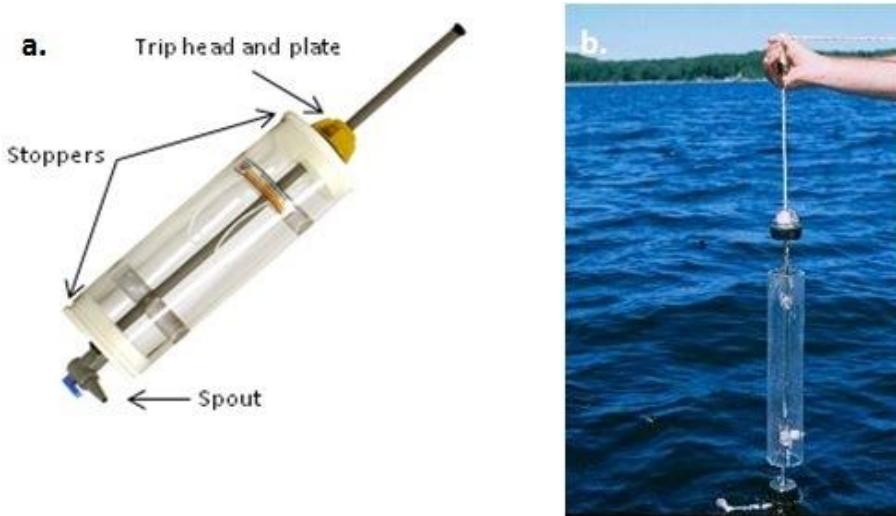


Figure 13. Illustration of Kemmerer sampler for water sampling (a). Illustration of how the Kemmerer is lowered into the water by holding the rope and messenger (b)

12. 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 just fill two 4 L jugs to be used for all raw and filtered water in SOP C):
 - a. Bottles that can be rinsed with raw sample water:
 - 1) 4 L jug(s) (can be used for filtered samples and/or PCN, see below)
 - 2) 250 mL burned amber glass bottle for external lab (code RAW)
 - 3) ANC - 250 mL wide-mouth, HDPE – ***to be analyzed at the Domain Support Facility.**

To rinse: Hold the cap in your hand (setting the cap down increases risk of contamination). Empty part of the Kemmerer sampler into the collection bottle. Fill approximately $\frac{1}{5}$ of the collection bottle with water. Cap bottle and shake. Discard water away from the area you are sampling (other side of the boat or downstream of any current). Repeat 2 more times.
13. If collecting replicates, collect 2 additional sets of samples per sampling location at same time and location as the primary samples.
 - a. Lake:
 - 1) Non-Stratified: collect two replicate sample sets per each sample type (.FIL, .RAW, and .PCN) at the buoy station (c0 if non-stratified).
 - 2) Stratified, collect c1 and c2 samples as normal, and collect two replicate sets at each sampling location (i.e. 2 additional sets at c1 and two additional sets at c2), for an additional 6 samples per sample type per sampling location.
 - b. River: Collect 2 additional sets of samples at 0.5 m.
14. Proceed to B.6



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B.6 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 below (Figure 14) and discussions with NEON Science. The low-flow method is the preferred and most common method used by NEON domains. When the low-flow method is not practical for given site conditions, alternative methods may be used, including minimum purge sampling, the bailer method, and purging to dryness methods. 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.

For all sites: Decontaminate all materials (or use dedicated materials) between wells. Decontamination procedures are described in the following sections. Always work on wells with known or suspected contamination issues last. This will minimize the chances of cross-contamination.

NOTE: Groundwater domain ANC samples are not collected, **only domain ALK samples are collected.**

B.5.1 DETERMINE BEST SAMPLE METHOD

For non-permafrost sites, the appropriate groundwater sampling method is determined by evaluating the recharge rate and water column height of a given well (Figure 14). Tundra and Taiga sites will use a **needle method** described in section



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B.5.3.5 Needle Method.

Wells that recharge at a rate greater than 100 mL/min are considered high yield wells and are sampled via the **low-flow method** for water column heights greater than 0.5 m, or the **bailer method** for water column heights of less than 0.5 m. In the absence of contradictory knowledge, all sites will start with the assumption of high yield wells and attempt the low-flow method (or bailer method for shallow water). The majority of NEON sites will use the low-flow sampling method.

During low-flow or bailer method sampling technicians will discover the recharge rate of a given well. Some wells may be classified as low yield wells (wells with recharge rates lower than 100 mL/min). Pumping low yield wells using the traditional low-flow method will cause enough drawdown that the well will run dry over the course of sampling. In this case, contact Science for help determining the appropriate alternative method which may include the **minimum purge method** or **purge dry method** followed by sampling once replenished.

Decision Workflow:

If the site is located in a tundra or taiga ecosystem, proceed to section



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4. B.5.3.5 Needle Method. Otherwise, proceed to step 2.
5. Prior to the field
 - a. If the well has never been sampled, plan to use the low-flow method for thick water columns (> 0.5 m) or the bailer method for water columns < 0.5 m.
 - i. If water column height is unknown, bring materials for both potential methods.
 - b. If the well has been sampled before and recharge behavior is known, plan to sample using the previously established method.
 - i. Bring both the low-flow sample pro pump setup and bailers to the site if you suspect that well conditions have changed since the last sample bout.
6. In the field
 - a. Determine water column height as described in section B.5.2 Locate well and assess water depth
 - b. Calculate recharge rate as described in section B.5.2 Locate well and assess water depth .
 - i. For recharge rates > 100 mL/min:
 - a) Use low-flow sampling (B.5.3.1 Low-flow Pump Method) for water column heights > 0.5 m

Use the bailer method (



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- b) B.5.3.3 Bailer Tube Method) for water column heights < 0.5 m.
- ii. For recharge rates < 100 mL/min:
- a) If this well has been previously sampled under similar recharge and depth conditions, sample using the previously established method.
 - b) If this is the first time sampling this well:
 - (1) Select “sampling impractical, low yield well”.
 - (2) Write a trouble ticket to Science detailing the issue and include depth to water table for the well. There are 2 possible remediations:
 - Change in sampled wells. Science may reconsider the wells chosen for sampling in the site sampling strategy if other non-sampled wells show higher yield.

Change in sampling method. Science will help determine if the minimum purge method (

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- B.5.3.2 Minimum Purge Method) or purging to dryness (B.5.3.4 Purge Dry Method) are appropriate.

Because the elevation of the water table can change throughout the season, it should also be noted that some sites might need to use multiple sampling methods. For example, a site might have enough water to use the preferable low-flow method in the spring, but require the bailer method in the fall. Sampling method may also vary between wells with differing water levels or recharge rates at a single site. The following sections provide specific details for each groundwater extraction method.

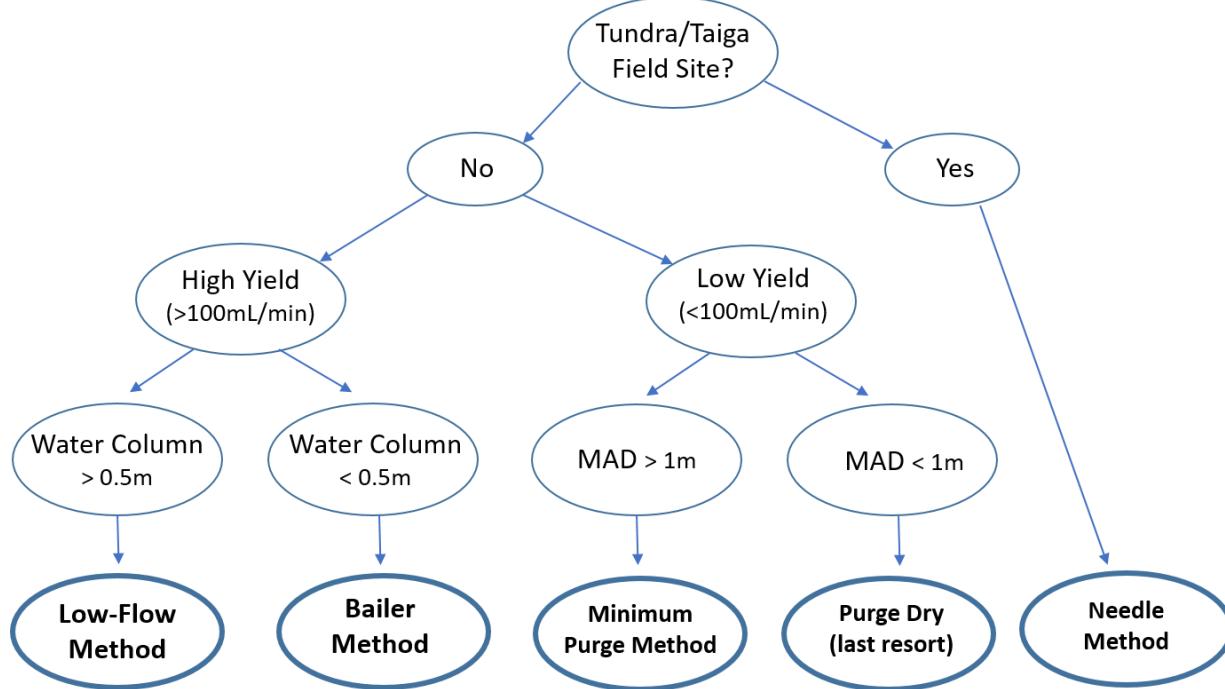


Figure 14. Decision tree for determining appropriate groundwater sampling method.

B.5.2 LOCATE WELL AND ASSESS WATER DEPTH

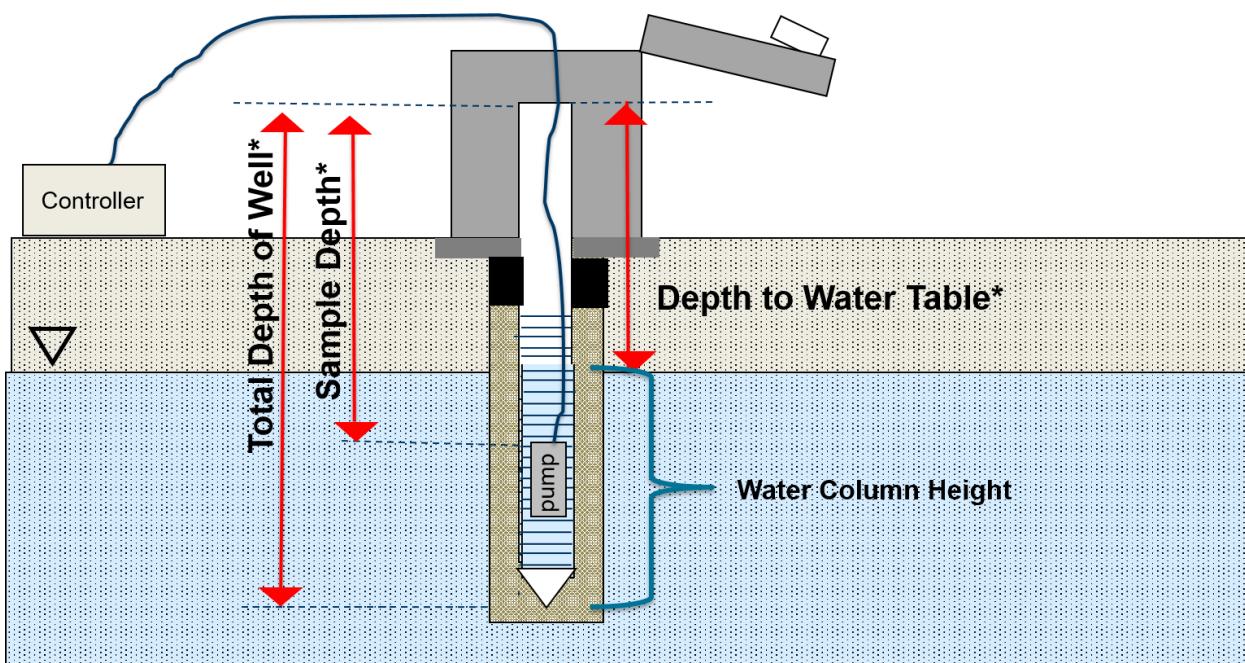
- Shut down wells by disconnecting trolls from the circuit board in the power box as described in the Groundwater Preventive Maintenance document [RD 12]. Remember to reconnect the trolls and reset the grape after finishing work on a well. Disconnecting the sensor from the cable should be avoided as this can cause damage to the connection over time.
- 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.



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8. Unlock the Well. Open the lock and flip open the protective well lid, then remove the white PVC cap from the well.
9. Remove the AquaTroll sensor from the well.
 - a. Pull the sensor cable and mounting cable out of the well gently so as 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. The other end of the sensor cable will be attached directly to the telemetry unit. Leave this connected.
10. Take key groundwater measurements prior to starting the groundwater extraction process (**Figure 15**).
 - 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 16b**). 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 16c**. 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 16c**). For wells fitted with snorkel caps, unscrew the cap at the coupler and measure on the PVC lip as shown in **Figure 16d**.
 - iii. Wipe down water meter tape with bleach wipes between wells. (Make sure the wipes contain bleach. Note that normal Clorox wipes do not contain bleach).
 - 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 and record in the data collection app. (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.



Drawing is not to scale

* Measure from top of PVC casing
Record to 0.01 m

Figure 15. Key groundwater measurements

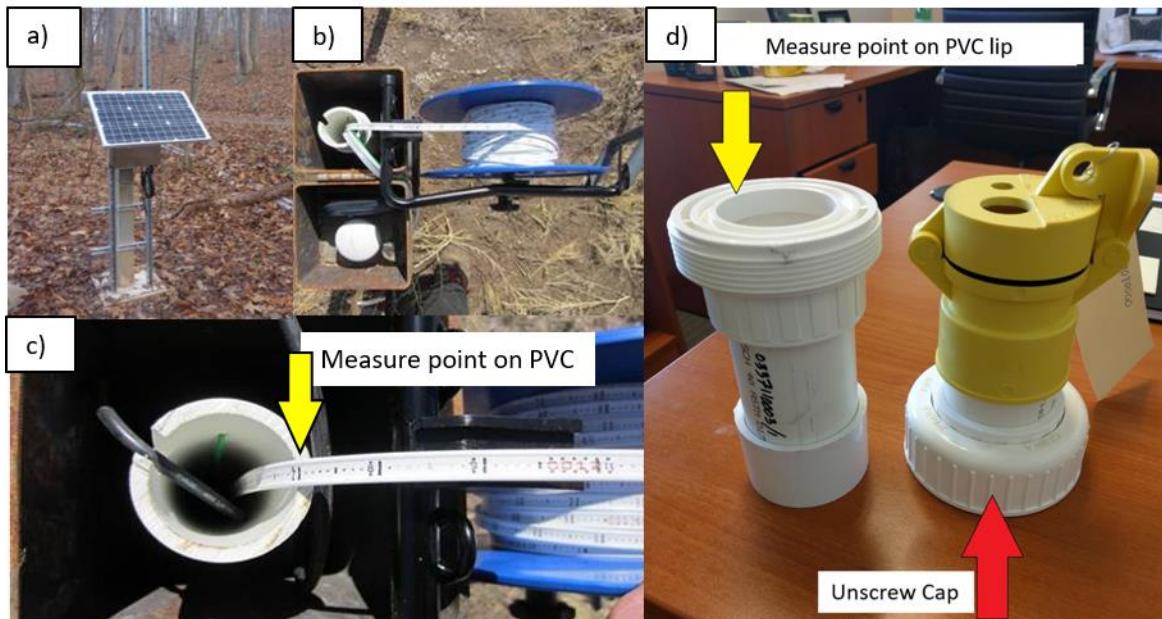


Figure 16. (a) Standard groundwater well at a NEON site (b) Water-level tape attached to outer well casing. (c) Reading the depth to water from the water-level tape on standard well. The tapes are marked in "meters" with each foot increment marked in red. Readings are taken at the top of the inner PVC 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 Pump Method



This method is used for high yield wells (recharge rates greater than 100 mL/min) with water column heights of greater than 0.5 m.

14. Calculate water column height (**Figure 15**) as shown in section B.5.2 Locate well and assess water depth.
15. Calculate the depth to set the sampling pump as follows:

Water Column Height (m)	Sample Depth (Pump Inlet)
≥ 1.5 m	(Well Water Depth) + (1 m)
0.5-1.5 m	(Depth of Well) – (0.5 m)
< 0.5 m	Bailer Tube Method

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 = $(15.55 - 5.55) = 10.00 \text{ m}$

Sample Depth: $(5.55 \text{ m} + 1 \text{ m}) = 6.55 \text{ m}$

Example 2:

Total Depth of Well = 7.25 m

Depth to Water Table = 5.85 m

Water Column Height = $(7.25 - 5.85) = 1.4 \text{ m}$

Sample Depth: $(7.25 \text{ m} - 0.5 \text{ m}) = 6.75 \text{ m}$



16. Cut Tubing to Correct Length. (NOTE: Use tubing cutters provided in the well kit to cut tubing, NOT scissors). The tubing used to sample the groundwater wells is dual bonded tubing with one line for air delivery to the pump and one line for water discharge from the pump. 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 pump, up the PVC well casing, and then back to the ground to reach the controller and collection cell. 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 ends you have to trim in the future.

17. Set-up the Sample 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).
- 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 17(a-d)** illustrates this for each step.
 - 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.)

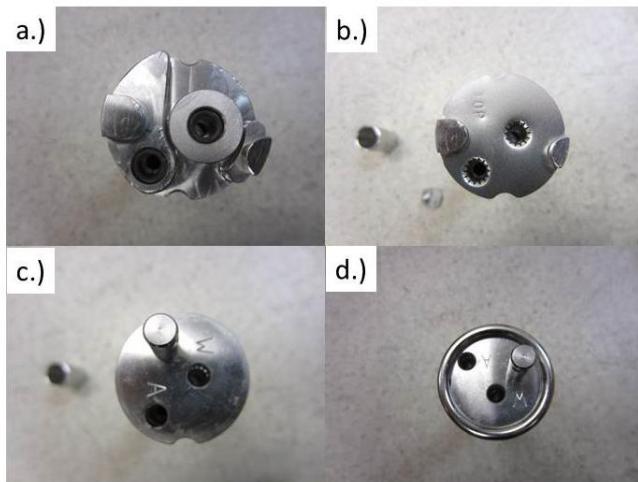


Figure 17. Assembly of the fitting plate at the top of the pump for holding the air and water lines. (a) Bare top of pump. (b) Fitting/grab plate added (“TOP” must face upwards). (c) Top plate added. (d) Collar added to lock parts (a-c) together.

18. 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 18** shows the components of the pump including the bladder.

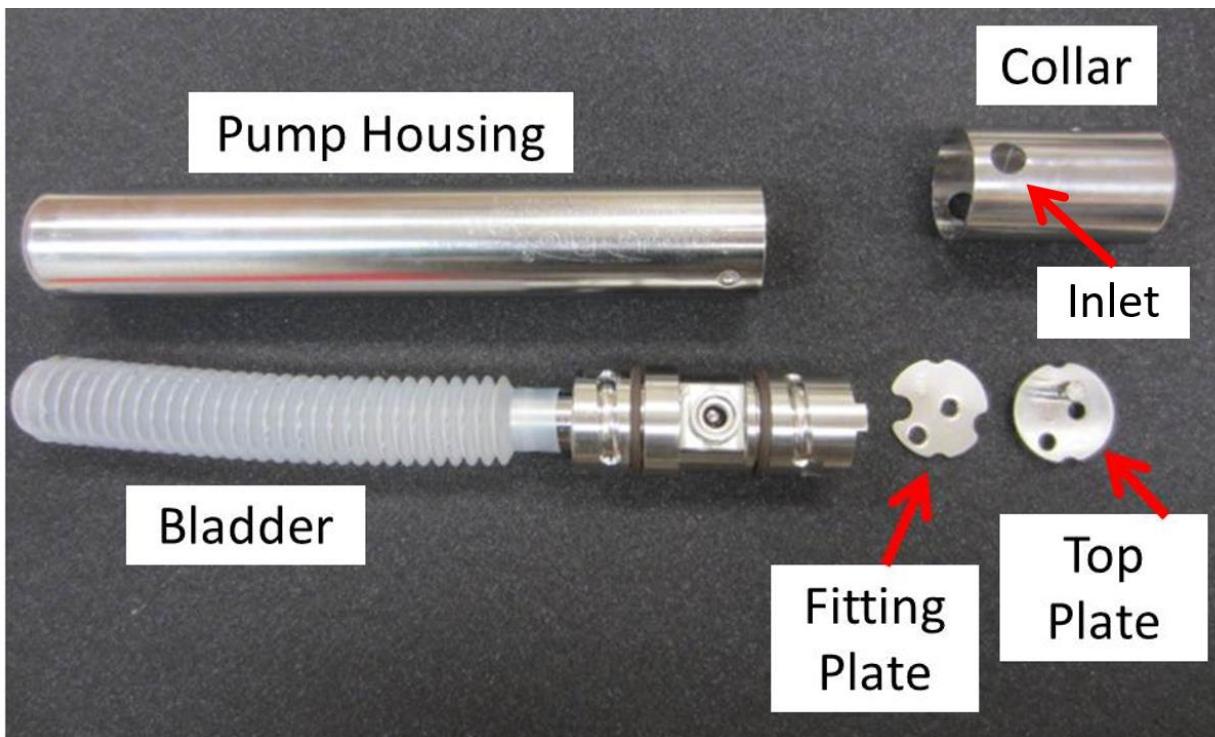


Figure 18. Components of the sampling pump.

19. Attach Tubing Lines and Cable

- a. 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 19**. (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 push into the pump top by about 1 cm. A little water dabbed on the ends of the tubing help 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.
- b. Attach the post (thread into threaded port) and cable to the pump as shown in **Figure 20**.



Figure 19. Attaching grey air-line and white water-lines to pump
(top-right photo shows lines pushed through top plate and “teeth” of grab plate)

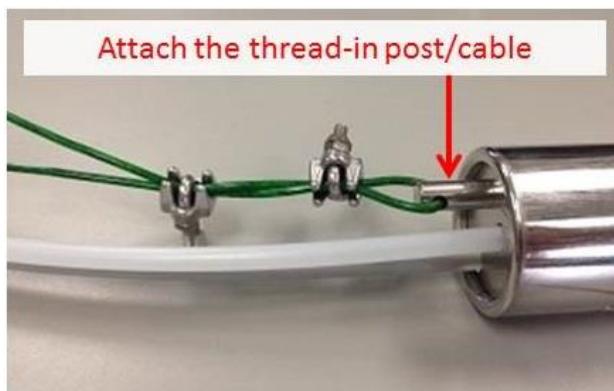


Figure 20. Attach post and cable to the pump via the top plate.

20. 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.**

21. Set-up the Controller / Compressor / Collection Cell

- Connect the blue air-line tubing contained in the controller kit to the AIR OUT port on the controller compressor (**Figure 21**), 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 22**).

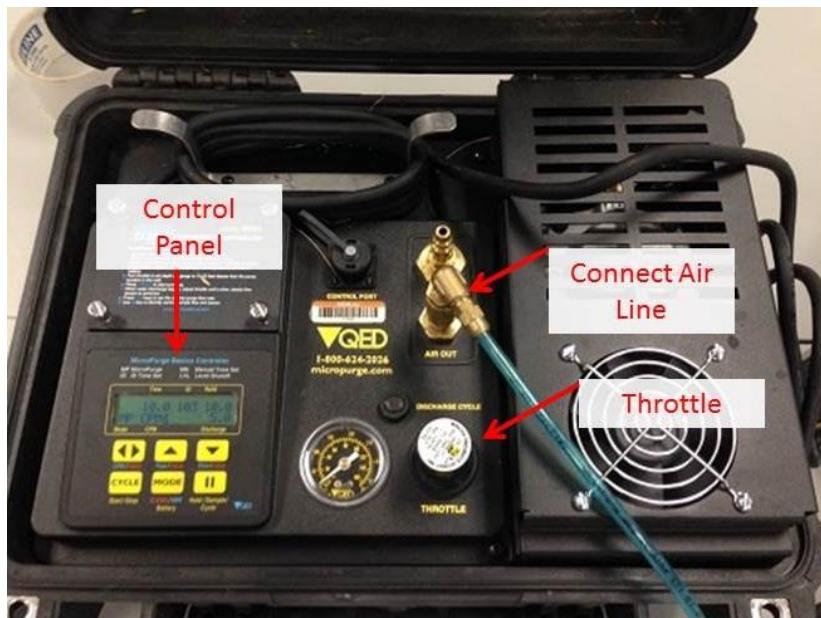


Figure 21. Attach blue air-line to controller.



Figure 22. 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 23**).

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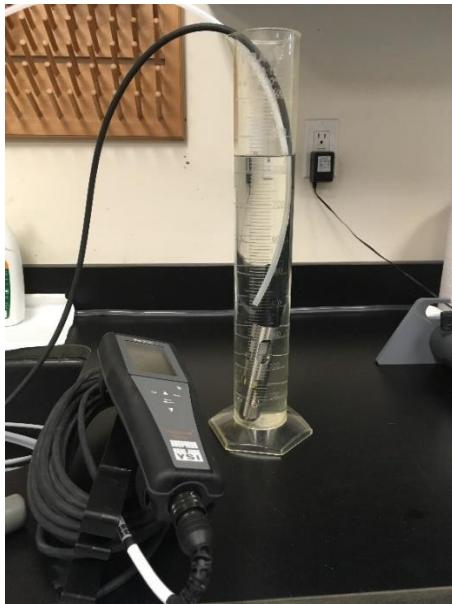


Figure 23. Groundwater Chemistry Collection cell using a 1000 mL graduated cylinder.

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 into 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 24**). 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). 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 24. Groundwater pump control panel screen. Note the Refill and Discharge times on the right.

22. Monitor water level and determine recharge rate: Water-level within the well should be monitored every few minutes using the water-level tape in the procedure detailed earlier. 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). If the water depth declines more than the 10% threshold, then select a decreased discharge rate by either choosing a shorter discharge time on the controller or turning the throttle counter-clockwise 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. **Recharge rate** is the rate at which the well water is replenished during pumping. Once the water reaches a relatively constant level during pumping, the recharge rate is equal to the discharge rate. If a steady water level cannot be achieved with flow rates below 100 mL/min, the well is low yield and technicians should write a trouble ticket.



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23. Monitor water quality: While the pump is discharging water from the well, monitor the water quality parameters Specific Conductance ($\mu\text{S}/\text{cm}$) and Water Temperature ($^{\circ}\text{C}$) using the YSI hand-held meter to provide a metric to determine when the water is ready to be collected for sampling.
- 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, $\mu\text{S}/\text{cm}$).
 - Once you start removing water, take readings from the hand-held meter approximately every 3-5 minutes during the pumping event and noted on the sampling sheet in addition to the time.
 - 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.
 - 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 = ($\text{Total Well Depth} - \text{Depth to Water}$) $\times \pi (\text{well radius})^2$*
- 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.
 - Record** pH at the time of sampling using the hand-held pH meter in the data collection app.
24. 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. Record sampling method in the data collection application.

FILTER THE SAMPLES MINIMIZING THE EXPOSURE TO AIR AS DESCRIBED IN SECTION

25. B.5.4 Groundwater Field Filtering and Prioritization.
26. Decontaminate between wells.
 - 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
 - Shake container and soak for 10 minutes
 - Remove pump components and squirt down with DI
 - Reassemble pump with new or dedicated bladder for each well
 - Wipe down water meter tape with bleach wipes and squirt with DI between wells.
 - For each well use dedicated tubing for the section that goes into the well



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<i>NEON Doc. #:</i> NEON.DOC.002905 <i>Author:</i> K. Goodman	<i>Revision:</i> G



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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.

3. 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, ALK, RAW, PCN filter. However, it is necessary to discontinue the sampling once maximum allowable drawdown (described in the following section) is reached. If maximum allowable drawdown is less than 1 m do not use this method.

b. Timing

This method requires that the pump 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 placement. Due to the timing requirements and the desire for minimal mixing of the water column, this method would require techs to know that their wells qualify as low yield wells prior to the sampling event. Ideally, pumps will be placed in low yield wells in the week prior to scheduled sampling. Thus, if it is discovered during sampling that a well is low yield, sampling of that well will have to be postponed and a trouble ticket should be submitted.

4. Methodology

- a. Calculate the amount of tubing needed to place the pump 0.3m from the bottom of the well, plus and extra 1 – 2 m of tubing for ease of reaching the pump. Secure the tubing in place by attaching it to the AquaTROLL cable with a zip tie at a minimum of 48 hours prior to sampling(**Figure 25**). Tubing with 1/8"ID will fit in the same slot as the cable.

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- i. The AquaTroll can be removed for pump placement and then replaced immediately afterwards and left in place during sampling as long as the sensor and the pump do not obstruct each other.
- ii. Care should be taken to cause minimal disturbance to the water column.



Figure 25. Pump tubing secured in place with zip tie.

- b. Place pump at correct depth. **The inlet for the pump is near the top of the pump noted by the hole in the side of the pump body (Figure 26). This is the specific point on the pump to set to the specified depth. When placing the pump, measure from this point.**
- c. 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.
 - i. If water table is above the screened interval of the well:
$$\text{MAD} = \text{depth to pump placement} - \text{depth to top of screen} - 0.5\text{m}$$
Example 1:
Depth to pump placement = 5 m
Depth to top of screened interval = 2 m
Depth to water table = 1 m



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$$\text{Maximum Allowable Drawdown} = 5 \text{ m} - 2 \text{ m} - 0.5 \text{ m} = 2.5 \text{ m}$$

- ii. If water table is within the screened interval of the well:

$$\text{MAD} = \text{depth to pump placement} - \text{depth to water table} - 0.5\text{m}$$

Example 2:

$$\text{Depth to pump placement} = 5 \text{ m}$$

$$\text{Depth to top of screened interval} = 2 \text{ m}$$

$$\text{Depth to water table} = 2.5 \text{ m}$$

$$\text{Maximum Allowable Drawdown} = 5 \text{ m} - 2.5 \text{ m} - 0.5 \text{ m} = 2 \text{ m}$$

Note: If the calculated MAD is less than 1m, do not use this method and move on to the Purge Dry method.

- d. Prior to sampling, remove a set volume based on tube length (**Table 7**). Measure and record water temperature, temperature-corrected conductivity, DO percent saturation, and pH for the discharged water. Divide the volume removed into thirds and use it to rinse the 4L jug 3 times.

SAMPLES CAN BE COLLECTED IMMEDIATELY FOLLOWING THE SMALL VOLUME REMOVAL. IN ORDER TO MINIMIZE TURBIDITY AND DISTURBANCE TO THE WATER COLUMN, SAMPLES SHOULD BE REMOVED AT A RATE AT OR BELOW 100 ML/MIN. MEASURE DRAWDOWN WITH THE WATER TAPE AS THE SAMPLE IS BEING COLLECTED AND DISCONTINUE COLLECTION IF THE MAD IS REACHED. IF MAXIMUM DRAWDOWN IS MET PRIOR TO OBTAINING THE FULL VOLUME NEEDED FOR THE GROUNDWATER CHEMISTRY SUITE, PRIORITIZE SAMPLES AS DETAILED IN SECTION

- e. B.5.4 Groundwater Field Filtering and Prioritization.

Table 7. 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

- f. If a site has more than one low yield well, additional tubing and bladders may be required to ensure that sampling can occur in the desired time frame. Tubing and bladders for all low yield wells will need to be placed in the wells during the week prior to sample collection to allow for the effect of pump placement to dissipate.
- g. Alternatively, a peristaltic pump with dedicated tubing could be used as long as the well is sampled at a flow rate around or below 100 mL/min. Deeper wells may require 1/8" inner diameter tubing to appropriately lift the water sample. Use dedicated tubing for each well.



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- i. Weight the end of the peristaltic pump tubing with stainless steel nuts as shown in **Figure 26**. Then firmly insert a 2-way luer-lock and remove its handle to secure nuts. Alternatively, the optional Quick Bullet weight can be used to weight down tubing.
- ii. Lower the tubing to desired depth of 0.3 m from the well bottom at least 48 hours prior to sampling and secure to the AquaTroll cable with zip tie.
- iii. Proceed to collect samples as described above.

Note: 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 26. Nuts added to peristaltic pump tubing for weight.

B.5.3.3 Bailer Tube Method



Domains with wells that are high yield but have shallow groundwater less than 0.5 m will require the bailer tube method. This method is much simpler than the Low-Flow method and is performed by evacuating the water in the well using a “bailer tube” which is a small diameter hollow tube that has check ball in the bottom of it (**Figure 27**). Note: you may also use the peristaltic pump instead of the bailer tube to remove the three well volumes, as indicated below.



Figure 27. Image of a bailer tube.

8. Use a dedicated bailer and rope for each sampling well.
9. Lower the tube into the well on the end of a rope below the static water level filling-up the bailer tube with water.
10. Pull the tube out of the well and pour contents into a bucket (pour out of the top of the bailer tube). This process repeats until **three** “well-volumes” are removed from the well. A well-volume is defined as the volume of water contained within the well and is calculated as:

$$\text{Well Volume} = (\text{Total Well Depth} - \text{Depth to Water}) \times \pi r^2$$

Where the “Total Well Depth” and “Depth to Water” are measured from the top of the PVC well casing and “r” is the radius of the well (3.2cm diameter, 1.6cm radius, $\pi r^2 = 8.03 \text{ cm}^2$). **Each meter of water in the well is equivalent to approximately 0.8L. For ease of calculation, multiply the height of water in the well by 0.8 to get the approximated volume in Liters.** For example, if the depth to water in a well is measured as 1.32m and the total depth is measured as 1.98m, then the height of water in the well is 0.66m and one “well volume” is $(0.66\text{m}) \times (0.8\text{L/m of water}) = 0.53\text{L}$ of water. The three well volumes are equivalent to 1.59L of water.

11. After three well volumes are removed from the well, extract additional water with the bailer to triple rinse the 4 L jug. Each rinse volume should fill roughly 1/5 of the jug. The collect sample water by again using the bailer tubes to pull water from the well and pouring the water directly into the clean 4 L jugs.
12. **Record** water quality parameters (SPC, DO, Temp, and pH) at the end of the three well volumes by filling a small bucket or bottle with well water and using the hand-held meter to measure the parameters in the data collection app.



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13. Record the sampling method and approximate volume of water discharged/removed from the well prior to collecting water for samples.

IF AVAILABLE WATER IS INSUFFICIENT TO MEET THE SAMPLE VOLUME REQUIREMENTS, PRIORITIZE SAMPLES AS DETAILED IN SECTION

14. B.5.4 Groundwater Field Filtering and Prioritization

B.5.3.4 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). Thus, this data will be flagged for users.

4. Use bailers or a peristaltic pump at a high rate 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 (uS/cm), and Water Temperature (°C) in the data collection app.
5. Use dedicated bailers and ropes or, if using the pump, use dedicated tubing for each well. 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).
6. Return within 24 to 48 hours to directly sample the volume that has return to the well.
 - a. Remove a minimum of 50 mL from well. Record pre-sampling field measurements on this volume and use it to rinse the 4L jug.

SAMPLE WELL. WHEN OBTAINING THE FULL SAMPLE VOLUME IS NOT POSSIBLE, PRIORITIZE SAMPLES AS DETAILED IN SECTION

- b. B.5.4 Groundwater Field Filtering and Prioritization.

B.5.3.5 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.

6. In the domain, pre-assemble the 47mm GF/F glass fiber filters in the syringe filter holders.
7. 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.
8. Assemble the needle, tubing, two three-way stopcocks, and syringe (**Figure 28**). Use individual dedicated syringes and tubing for each well location.



Figure 28. Sampling needle and syringe setup.

9. Take precautions to avoid disturbing the ground surrounding the sample location.
 - c. Use the boardwalks and stand downhill of the location when possible.
 - d. If taking physical well measurements on the same day, complete the water chemistry sample prior to working on the well.



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10. Collect sample

- e. Insert the needle at an angle next to the well infrastructure and sample slightly above the frozen interface (**Figure 28**). 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.
- f. Fill a 140 mL syringe using a bubble-free technique.
 - i. **Bubble-free** technique: Bubble-free sampling will minimize contact between the anoxic sample and the atmosphere which can impact pH, Alkalinity, and DIC.
 - a) 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.
 - b) 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 air tight so that no atmospheric gases are drawn into the syringe.
 - c) Close the stopcock attached to the tygon tubing to maintain a bubble-free connection to the groundwater and disconnect the two stopcocks.
 - d) Expel air from syringe (**Figure 29**)
 - 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 of the plunger.
 - c. 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.

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Figure 29. Expel air bubbles from the syringe during bubble-free sampling.

- f) Re-attach the stopcocks to one another. Make sure that the connection is tight so that air is not introduced.
- g) 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 30**). Expel all but ~5 mL of water from the syringe.



Figure 30. Stopcock position for expelling water during bubble-free sampling.



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- h) 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.
- i) Indicate instances in the data collection app to inform data users when water table conditions render bubble-free sampling impossible.
- ii. Once you have collected 140mL 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.
- iii. Remove the syringe plunger and immediately insert the calibrated pH probe into the remaining water. Record pH in the data collection app.
- iv. Discard water.
- g. Fill the syringe again with 140mL using the bubble-free technique.
 - i. Filter 15 mL through the syringe filter into the 60mL DIC bottle three times to triple rinse.
 - ii. 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.
- h. 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.
 - vi. **H₂O Isotope (RD[14])**
 - vii. **FIL**
 5. Use a 250 mL bottle for low-volume situations rather than sending a partially full 1 L bottle.
 6. If using a 250 mL bottle, LEAVE headspace to prevent freezing.
 7. A minimum FIL sample is 100 mL.
 8. Filter the FIL sample in field directly after sample collection.
 - viii. **RAW**
 2. LEAVE headspace to prevent freezing
 - ix. **PCN**
 - x. **Remaining Field Measurements**
 1. Pour syringe water into a 250mL graduated cylinder and insert the YSI probe.
 2. Record Dissolved Oxygen Saturation (%), Specific Conductance (uS/cm), and Water Temperature (°C) in the data collection app.



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B.5.4 GROUNDWATER FIELD FILTERING AND PRIORITIZATION

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.

4. 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)

- a. 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 sections above.

5. Field Filtering

For groundwater samples, filter the FIL and ALK samples in the field as close as possible to the time of collection. See Collect Filtered Water Samples (FIL) for specifics of filtering using the peristaltic drill pump.

a. Field Filtering for Minimum Purge method:

- i. For these wells, it may be possible to directly filter the water as it is being pumped out of the well. Connect the groundwater pump outflow tubing directly to the peristaltic pump intake. Connect one end of a capsule filter to the outflow of the peristaltic pump and one end to additional tubing that can reach the bottom of the sample bottle.
- ii. A series of multiple filters in line can be used for dirtier water.
- iii. Filter directly into the FIL and ALK sample bottles. Overflowing each bottle from the bottom upwards and immediately cap leaving no headspace.

b. Field Filtering for Low-Flow method

- viii. Slower recharge here, refers to any wells where the sample cannot be directly pumped from the water table through the filter without introducing air between them.
- ix. Insert the outflow end of the groundwater sample tubing through an appropriately sized hole drilled into a 1L Nalgene cap (**Figure 31**). 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

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when closed. Use parafilm (*or optional Swagelok design detailed below) to create an airtight seal between the tubes and cap.

- x. Pump directly from well into the 1L Nalgene container, filling from the bottom up.
- xi. Allow container to overflow, then seal the cap onto the container.
- xii. Start the drill pump. Simultaneously run both pumps so that the water line remains at or close to the top of the Nalgene.
- xiii. Pump the outflow of the drill pump through the capsule filter and through a final tube to fill the FIL and ALK containers from the bottom up. Make sure to rinse this tube with DI between wells.
- xiv. Overflow the containers then immediately cap.

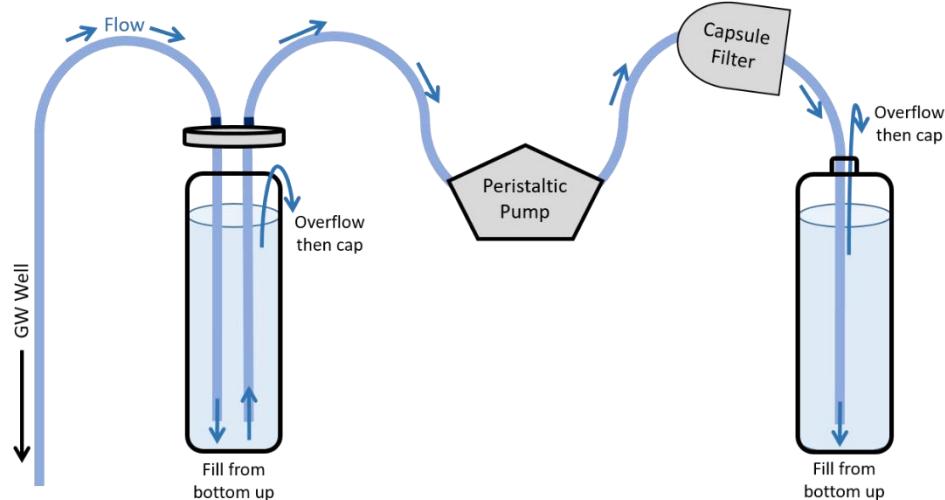


Figure 31. Filtering setup to minimize sample aeration during filtration for low-flow and minimum purge groundwater samples.

***Optional Swagelock Design for Groundwater Filtering**

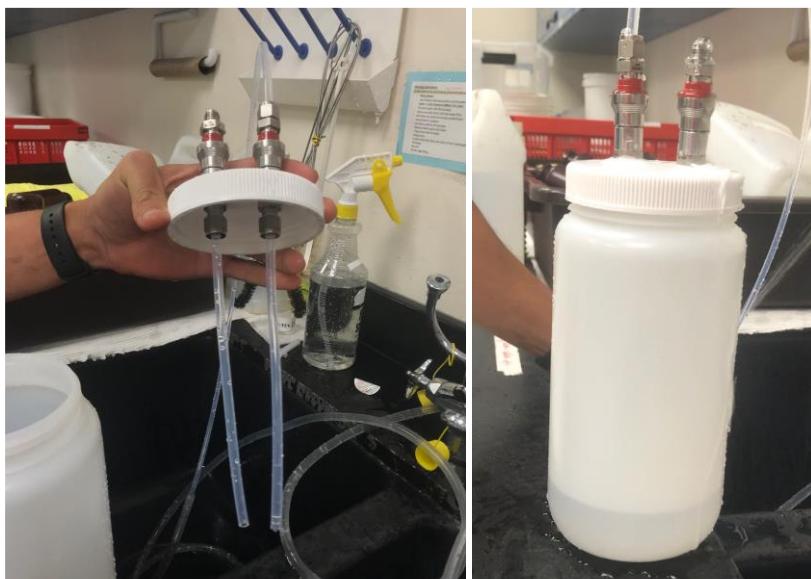
The following optional Swagelok design may be used in place of parafilm for the Nalgene tube fittings.

Materials:

- 2L Nalgene container
- 2 x SS-QC4-B-400 - Stainless Steel Instrumentation Quick Connect Body, 0.2 Cv, 1/4 in. Swagelok Tube Fitting
- 2 x SS-QC4-D-400 - Stainless Steel Instrumentation Quick Connect Stem with Valve, 0.2 Cv, 1/4 in. Swagelok Tube Fitting

Assembly:

- Drill two $\frac{1}{4}$ inch holes on the cap of the 2L Nalgene bottle.
- Screw in female bulkhead (SS-QC4-B-400) onto the cap
- Attach male Quick Disconnect fitting (SS-QC4-D-400)
- Cut tubing to measure from the bottom of bulkhead to $\sim \frac{1}{2}$ inch above the bottom of the Nalgene bottle.
- Attach Swagelock tubing fittings.

**c. Field Filtering for the Bailer and Purge Dry methods:**

- i. Some aeration is unavoidable with the bailer method so we collect an unfiltered water sample in a 4L jug and directly filter from the jug. Fill the 4 L jug (or more if necessary) directly from the bailer.



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- ii. Filter the FIL and ALK samples in the field directly from the 4 L jug through the capsule filter into the sample jars.
 - iii. Cap the jug with the remaining sample and set aside for Sample Processing. Set the jug in a cooler with ice.
- d. Field Filtering for the Needle Method
- i. The needle method will utilize a 47 mm GF/F syringe filter the .DIC, .FIL, and .ALK samples directly into the sample bottles.
 - ii. Overflow the bottles from the bottom up. Leave no headspace and immediately cap.

6. 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



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B.5.3.5 Needle Method.

- a. Field Measurements
- b. H₂O isotope (RD[14])
- c. FIL
 - iv. For low-volume situations, use a 250 mL bottle rather than sending a partially full 1 L bottle.
 - v. A minimum viable sample consists of 100 mL FIL.
 - vi. When possible, DO NOT leave headspace in the FIL sample. If there is not enough volume to fill the 250mL 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. 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.
- e. RAW
 - i. Leave headspace
- f. PCN filter

B.7 Rinsing

4. Rinse the collection and sample bottles and caps with the appropriate sample water (i.e., use filtered water to rinse filtered samples, and unfiltered water to rinse unfiltered bottles (Figure 6)).
5. Hold the cap in your hand when the cap is not on the bottle (setting the cap down increases risk of contamination).
6. Rinsing is location type specific and covered under the field sampling SOPs above.
 - a. Bottles to be rinsed with Unfiltered water:
 - 1) 4 L jug (can be used for filtered samples and/or PCN, see below)
 - 2) 250 mL burned amber glass bottle for external lab



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- 3) ANC - 250 mL wide-mouth, HDPE – ***to be analyzed at the Domain Support Facility.**
- b. To rinse bottles for filtered samples (FIL and ALK) rinse with filtered water. See below.



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SOP C Sample Processing**C.1 Collect Unfiltered Water- RAW and ANC Samples**

1. Following sampling and triple rinsing the collection bottles, collect unfiltered samples (Figure 6):
 - a. A 250 mL burned amber glass bottle for external lab (sampleType RAW)
 - fill with headspace, filled to just below the neck to reduce potential for breakage if bottle freezes during shipment.
 - b. A 250 mL wide mouth HDPE – FILLED/NO HEADSPACE (sampleType ANC) *to be analyzed at the Domain Support Facility.
 - Fill the ANC collection bottle **COMPLETELY** to the rim and close cap tightly to minimize headspace.
 - You may use a 125 mL HDPE bottle if that is more appropriate for your system, but collect enough water in case titrations must be re-done.
 - ANC samples are only collected monthly.
 - c. Collect a 4 L Jug (or two, if necessary) to be filtered for Total Particulate Carbon and Nitrogen (sampleType PCN) analysis.
 - NOTE: the **filter** is your sample and will be analyzed for PCN; SOP C.3. You may need less than 4 L. This is site specific.
2. If you collected the sample in a 4 L jug, use sample water in the jug (shaken to re-suspend particles **for at least 15 seconds**) before rinsing and or filling the unfiltered sample bottles.
3. Record data in the mobile app.
 - a. Scan the barcode label with the tablet (Figure 32).
 - Ensure barcode on tablet matches sample barcode, if not rescan barcode.
 - 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.
4. Immediately chill samples ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$). DO NOT FREEZE

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Figure 32. Barcode label scanning.

C.2 Collect Filtered Water Samples (FIL)

IN WADEABLE STREAMS SAMPLING, YOU CAN FILTER DIRECTLY FROM THE PUMP TUBING. FOR LAKES AND NON-WADEABLE STREAMS, YOU CAN FILTER DIRECTLY OUT OF THE 4 L JUG. YOU MAY ALSO WISH TO 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, AS DESCRIBED IN SECTION

B.5.4 Groundwater Field Filtering and Prioritization.

1. Set-up of Peristaltic Pump Apparatus (**Figure 33.** Pump and filter setup, including (a) a peristaltic sampling pump (modified from Woessner 2007), (b) a 4 L sample bottle, (c and d) tubing connectors to connect peristaltic and C-flex tubing, and (e) a capsule filter)
2.):
 - a. The peristaltic pump should be fitted with peristaltic tubing connected to $\frac{1}{4}$ in Inner Diameter (I.D.) C-Flex tubing on either end (**a**).
 - b. Place a **CLEAN** end of the tubing in 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 $\frac{3}{8} - \frac{1}{4}$ 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 $\frac{3}{8} - \frac{1}{4}$ in tubing connector.
 - e. Attach one end of $\frac{1}{4}$ 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 unused filter capsule fitted with a tubing connector (e).



NOTE: make sure to attach filter so that the direction of flow follows the flow arrow on the capsule filter.

- h. Filter approximately 100 mL of sample water to rinse the filter, and discard this rinse water.

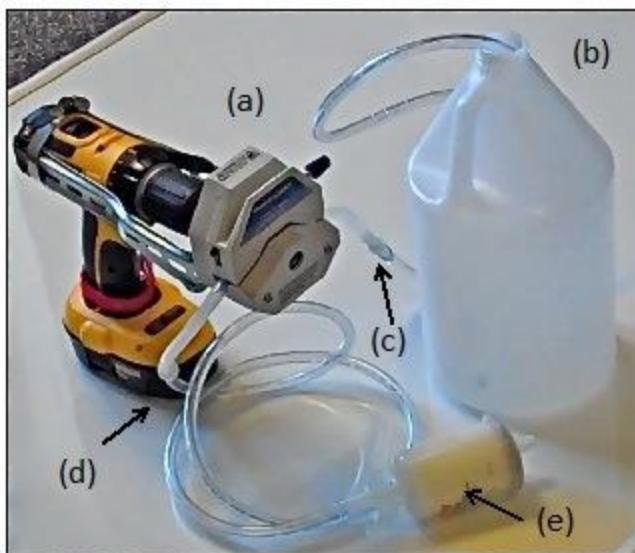


Figure 33. Pump and filter setup, including (a) a peristaltic sampling pump (modified from Woessner 2007), (b) a 4 L sample bottle, (c) and (d) tubing connectors to connect peristaltic and C-flex tubing, and (e) a capsule filter

3. Filter setup:
 - a. Use U-bolt to secure drill trigger at desired speed. Do not pump too fast, or you could blow out the filter.
 - b. When the tubing has been rinsed (Step 1), and is filled with water attach filter and begin pumping water through the filter. Making sure the tube is filled with water will reduce air being forced through the filter and the potential to blow a hole in the filter
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 250 mL HDPE bottle (ALK). Cap and shake to rinse.
 - b. Repeat rinsing 2 more times
5. **Fill filtered glass sample bottle (FIL) and ALK bottle completely (NO HEADSPACE).**



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- a. For low volume groundwater samples, use a 250 mL FIL bottle and the smallest ALK bottle possible in order to minimize chemical changes due to headspace.
- b. Because bubble-free sampling is time-intensive and the active layer often consists of low-volume water pockets, the FIL sample is further subdivided between .FIL and .DIC when using the Needle Method.
 - 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. **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 through two to three filters to improve clarity as much as possible.
 - ii. Murky water in groundwater wells with sufficiently thick water columns may indicate the need for well redevelopment.
7. Record data in the mobile app.
 - i. Scan the barcode label with the tablet (Figure 32. Barcode label scanning.). 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
8. Place samples in cooler with ice to keep cool ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$) until returned to lab. Group ALK and ANC samples together and ensure they will not be accidentally shipped to the water chemistry analytical laboratory.
9. Dispose of the capsule filter after all samples have been filtered per site per bout.
 - a. For lakes, these are one time-use filters, but can be used at multiple stations within a lake on the same day (Rinse ~100 mL of new station water through filter before sampling).
 - b. For groundwater, dispose after each well.

C.3 Total Particulate Carbon and Nitrogen (PCN) Sample Processing

1. Set up filter funnel, filter flask, and vacuum pump (Figure 34).
 - a. Either the hand vacuum pump with one filter flask and funnel attached or the filter manifold and electric pump with multiple filter funnels may be used.
 - b. Attach flexible tubing to from vacuum pump to hose connection on filter flask(s).
 - c. Make sure filter stem is inserted into the hole in the rubber stopper.



- d. Insert rubber stopper into the top of the filter flask. Push in tightly.
- e. Attach top of filter funnel to filter stem. This may be a magnetic connection or a screw-in connection.
2. Rinse filter unit, filter screen and filter funnel (Figure 34) with DI water, making sure no particulates remain on the filter screen or funnel. Note: Filter screen is easily lost. Be careful when rinsing.
3. Insert the stem of the filter unit into the hole in the middle of the rubber stopper and insert the stopper into the filter flask.
4. Remove the filter funnel from the base, leaving the filter unit and screen resting on the manifold stem.
5. Use filter forceps to remove a 25-mm pre-ashed GFF filter from the box and place the filter on the screen of the filter unit.
 - a. Place filter so that the smooth side is up/grid side is down.
6. Replace the filter funnel, rinsing with DI if necessary before replacing.
 - a. Make sure that the filter is in the center of the filter unit. Ensure there are no gaps between the side of the filter and the filter unit, and that there are no holes in the filter itself.
 - b. Take care note to over tighten the filter funnel on the filter as this will cut the filter around the edges.
7. Place the filter box back in the Ziploc bag to keep the filters from getting wet or blowing away.
8. Attach the vacuum pump tubing to the filter flask (Figure 34).
9. Rinse the filter with DI water. Use the vacuum pump to create suction in the flask and draw the DI water through the filter.
10. Shake the 4 L jug of water you collected at the lake/stream in order to resuspend and uniformly mix the particles (approximately 15 s).
11. RINSE the clean plastic 250 mL graduated cylinder with 25 mL of sample water. Turn cylinder on its side and rotate to rinse all sides of cylinder. Discard the rinse water.
12. Resuspend particulates (shake for 15 s) and immediately pour the water into the graduated cylinder, to be measured. You must resuspend particulates before every time you pour into your graduated cylinder.
 - a. Do NOT use the funnel as your measuring device, as it is not as accurate as the graduated cylinder.
13. Transfer appropriate amount of sample from the graduated cylinder to filter funnel. Be careful: the funnel only holds 200 mL of sample.
 - a. Only transfer what you can filter. You do not want to put too much volume in the funnel at once. If the filter clogs while there is still water in the funnel, and you cannot get the water through, you MUST restart with a new filter at STEP 1.
14. Use vacuum pump to pull water through the filter (do not exceed more than 15 in Hg).

IMPORTANT: BE CAUTIOUS OF THE VOLUME OF WATER IN THE FILTER FLASK SO YOU DO NOT SUCK WATER INTO THE VACUUM PUMP. DISCARD FILTERED WATER WHEN WATER IN FLASK REACHES THE FLASK NECK.

 - a. **NOTE:** Do not exceed 15 in. Hg vacuum on the pump gauge.





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15. Repeat previous 2 steps until water starts to move more slowly and particulates are visible on the filter. At that point, add water in smaller increments until the filter is nearly clogged and water no longer passes through. Do not collect so much material that you cannot fold it without sample squishing out (< 1 mm of particulates material thickness).
- In waters with low particulate (i.e., clearwater lakes), filter a minimum of 2 L of sample.
 - In high particulate systems, make sure there is not too much particulates on the filter that may squeeze out of the filter when folded
-  16. **IMPORTANT: Keep track of the amount of water you filter.** We will need the total volume filtered for the PARTICULATE calculation. See step 19 and 23.
17. Use a DI water squirt bottle to rinse down the particulates on the sides of the filter funnel.
18. Continue to pump until all the water is drawn through the filter.
19. Release the vacuum and **note** the TOTAL volume of sample water filtered. Be sure to include the appropriate units (mL). **NOTE: All the water in the tower should be filtered once poured because particles will start to settle. DO NOT add more water than you can filter.**
-  20. **Record total volume of sample water filtered** on datasheet (RD[05]) and the sample label (step 22). Do NOT include the DI rinse water in the TOTAL sample volume filtered.
21. Using clean filter forceps, remove filter funnel from the filter unit; **fold filter in half**. Folding filter helps reduce loss of particulate sample. DO NOT touch filter with your hands to reduce risk of sample contamination. Do not touch the sample (i.e., the colored part of filter) with forceps.
- To make the filter easier to remove, you may want to run the vacuum pump for a few minutes, turn the pump off, pull the stopper out and let the filter sit for a minute before trying to remove filter from unit. This ensures the filter is dry and helps remove suction.
22. **Be Careful.** If filter tears or rips, begin filtration over with a new filter and sample water.
- Note:** Some tearing of the filter edges may occur and this is OK, as long as you ONLY tear on the white section, not where the sample is located.
23. Place filter on 4 X 4 in piece of aluminum foil, fold foil around filter and add label and barcode. Circle lab code PCN and make sure volume filtered is filled out.
24. Record data in the mobile app.
- If available, scan the barcode label with the tablet (Figure 32). Ensure barcode on tablet matches sample barcode, if not rescan barcode.
 - Ensure that the human-readable sample ID matches the sample ID generated by the mobile app
25. Bag foiled filter in resealable plastic bag and place in cooler (Double bag if you are shipping in wet ice). If you have multiple filters, from different sites and or stations, it is OK to place them in the same bag.
26. Using 1 L DI water jug (or more, as necessary), rinse the filter set-up (filter unit, funnel and flask) and equipment (forceps, graduated cylinder).

a)



b)

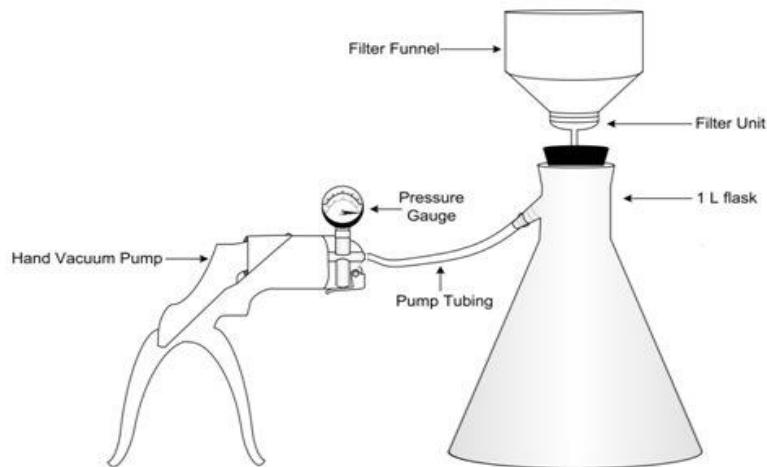


Figure 34. Filter apparatus set-up for particulates, using a) the vacuum pump and filter manifold, and b) the hand vacuum pump attached to the filter funnel



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C.4 End the Sampling Day

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, resealable plastic bags, foil, etc. Refer to section **Error! Reference source not found..**

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.

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 35**). 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.

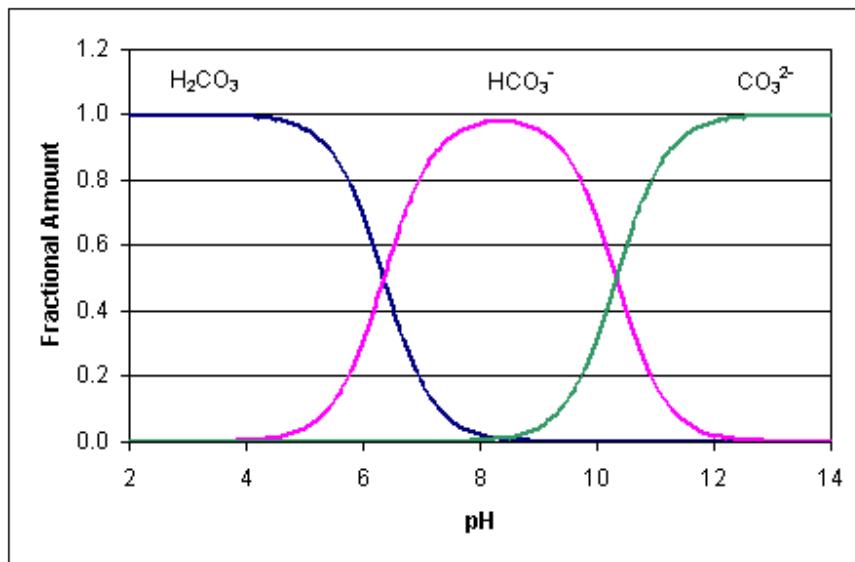


Figure 35. Fraction of carbonic acid(H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) as a function of pH (usu.edu).

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



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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 $\pm 5\%$. 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 $\pm 2^\circ\text{C}$, 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 period 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). Maintain pH meter appropriately. To avoid electrode solidification in the pH probe, the filling solution should be replaced with new and fresh KCl solution every 4-6 months.
 - 1) If present, open the vent at the top of pH probe to open while performing titrations. Ensure dial is closed when titrations are complete.
2. Ensure pH buffers and samples are at room temperature before calibrating and beginning titrations.
 - 1) Be sure to allow the sample bottle to sit on a lab bench until the temperature has equilibrated.
 - 2) 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 may also want to check, and recalibrate if necessary, the pH 10 buffer solution.
 - 3) Make sure buffer solution has not expired and is not reused.



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- 1) 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.
- 4) Ensure the bottle has been capped during storage to reduce contamination.
3. Check the pH meter calibration at pH 4 and 7. DO NOT use kimwipes on pH probe tip.
4. If the pH meter is off by ≥ 0.1 pH units, calibrate pH meter following pH meter manual.
5. 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.
6. 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.
7. 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. You can pour out the volume of sample you will use in the titration in a labeled glass beaker, covered with parafilm, to help sample come to room temperature more quickly.
 - a. **NOTE, GW ALK samples should remain in their bottle until they are measured to reduce exchange with oxygen.**
 - b. If you transfer surface water sample into beaker:
 - 1) Shake sample bottle for 15 s to homogenize before pouring.
 - 2) To ensure sample integrity and reduce chemical changes, do not allow the sample to warm in a covered beaker for more than 2 hours or the bottle for more than 3 hours before analyzing.



D.3 Titration Workflow

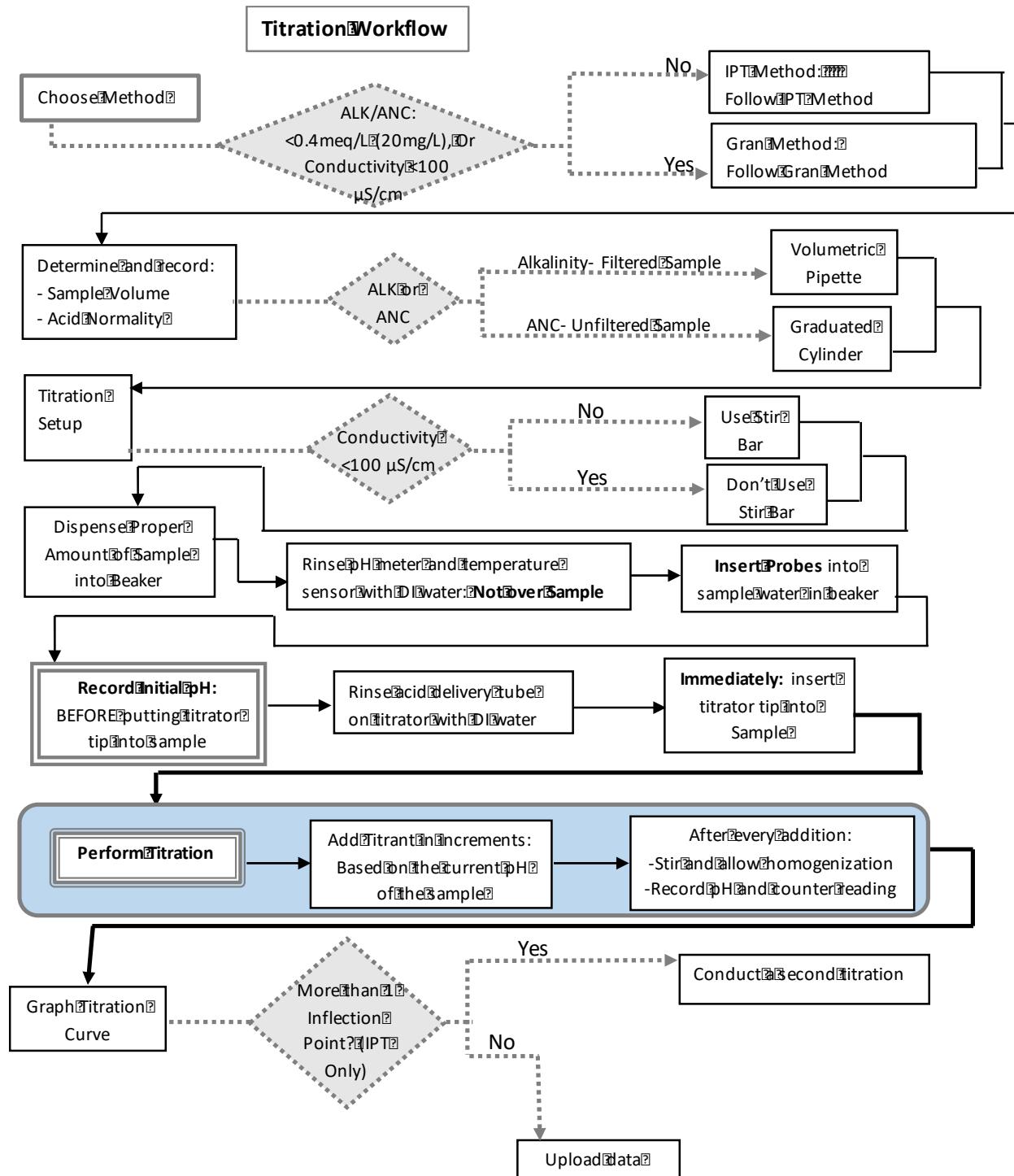


Figure 36. High Level titration workflow.



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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 (



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3. Table 8).

- The majority of 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 0.16N titrant, and adjust as necessary.
- 1.6N will only be used when alkalinity or ANC is greater than 4.0 meq/L, although it may not be necessary.
-



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- Table 8 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.
4. Record sample titration normality on the Datasheet (RD[05]).

Table 8. 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.

5. 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.

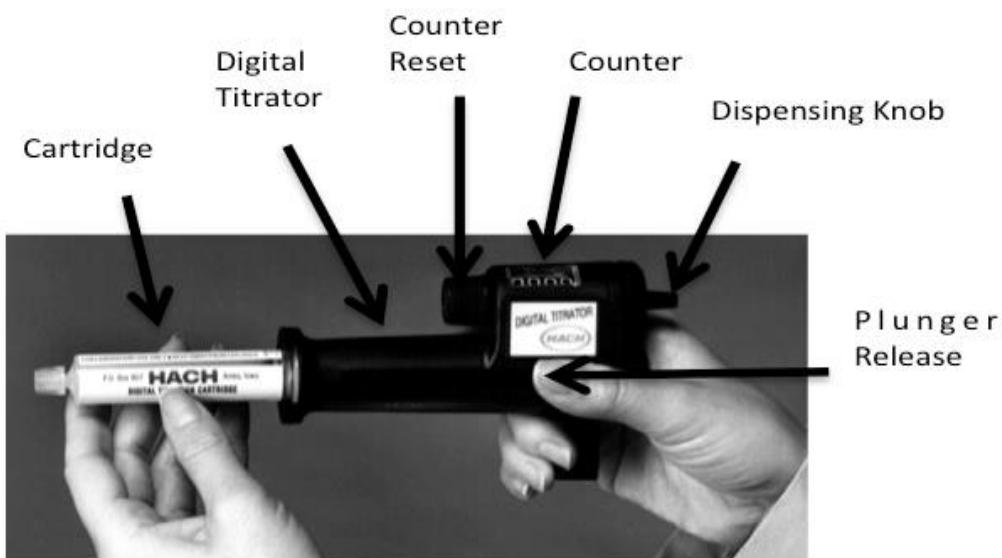


Figure 37. Inserting titrant cartridge into digital titrator. Photo from the Hach Digital titrator manual

- b. Insert cartridge into the end slot of the titrator (**Error! Reference source not found.**) 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.
6. 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.

7. Turn the dispensing knob to expel a few drops of titrant into a discard/acid waste container (**Figure 37**). This should remove air bubbles from the tube.

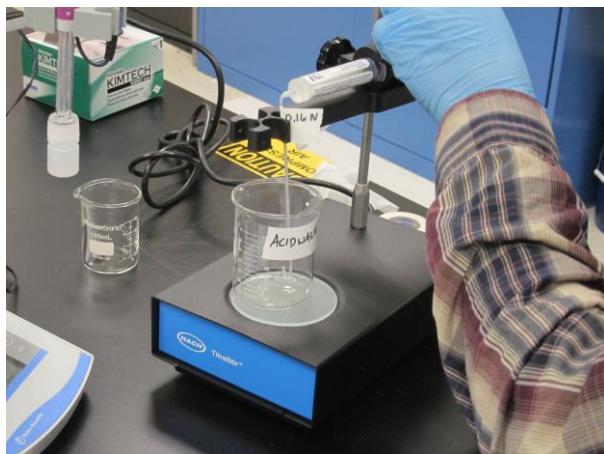


Figure 38. Diagram of procedure to expel acid from digital titrator set-up into a temporary acid waste container.

8. **Reset the counter to zero** and wipe the tip of the tube with a soft, lint-free tissue, such as a Kimwipe®.
 - a. Avoid dabbing at the delivery tube tip opening directly, because this can remove acid from inside the tube. Rinse tip of tube with DI, if necessary.
9. Once the counter has been set to zero, do not turn the delivery knob.
10. If conductivity is greater than **100 µs/cm**, place a clean, small, magnetic stirrer into the appropriate sized beaker (



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11. Table 8). **Do not use a stir bar if conductivity is less than 100 $\mu\text{s}/\text{cm}$. Using a stir bar in low conductivity water will increase the diffusion of gases into the sample and alter the pH.**
12. 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.
13. 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 (



14. Table 8).



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.

15. 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).
16. 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. Again, 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.
17. **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.
18. Rinse pH meter and temperature sensor with deionized water. Be cautious not to rinse probes over sample.
19. 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 39). 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. Stir sample briefly to ensure it is well-mixed.
20. **Record** on laptop using 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.

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21. 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 39).

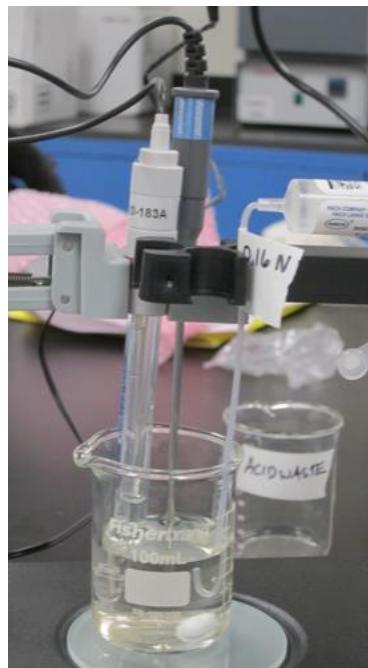


Figure 39. Image of titration set-up with digital titrator, stir bar, pH meter and temperature probe. Ensure nothing is touching the sides and bottom of the beaker or the stir bar

22. **Add Titrant** (Table 9). After each addition of titrant:

- Allow the stirrer to homogenize the sample for 15 s or gently, manually swirl the sample (~20 seconds followed by a 15 second rest) if you have a low conductivity sample.
- 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 40).

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.

- pH \geq 5.5 - 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. **After each addition of titrant, allow**



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the stirrer to homogenize the sample for 15 s. Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]).

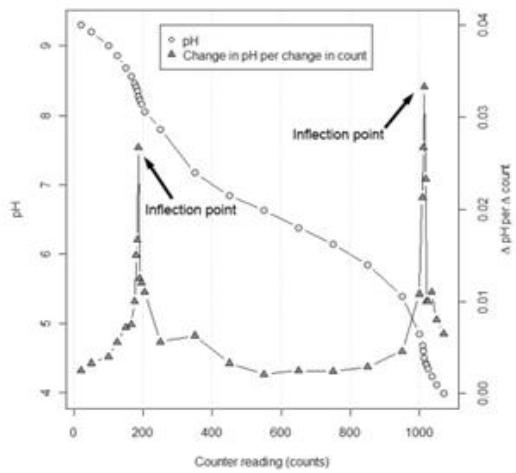
- d. pH <5.5 - Bicarbonate equivalence point. Cautiously and slowly add titrant in small (but do NOT add less than three counts on the digital titrator) increments from pH 5.0 to ≤4.0. If using the Gran method, add acid in small (**BUT NO LESS THAN 3 COUNTS**) increments (to change pH 0.2 - 0.3 pH units) to pH ≤3.5. Titrate to pH ≤3.0 for samples with high organic acids or if sample range is unknown. **After each addition of titrant, allow the stirrer to homogenize the sample for 15 s. Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]) or an electronic datasheet template.**

Table 9. 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

23. 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 40).
- 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.
 - 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.

a)



b)

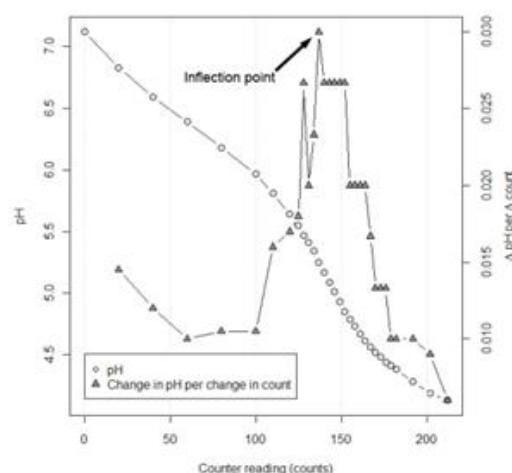


Figure 40. Example of inflection point titration using a digital titrator of a) a high alkalinity sample and b) a low alkalinity sample. Note difference in Y-axis scale. (Modified from USGS TWRI Book 9, Alkalinity, Version 3.0 7/2006).

24. 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.
25. Dispose of sample.
26. Repeat for all remaining samples at all stations.
27. Remove digital titrator from beaker. Depress plunger release and retract plunger to remove cartridge. Remove titrator tube. Cap cartridge tip.
28. Immediately double rinse titration tube and glassware with DI water and blot dry with lint-free soft paper tissue.
29. Place titration tubes in clean, sealable bag labeled with the titration normality (0.16 or 1.6 N).
30. 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.
31. Store all glassware, titrator, titrator tubes, and chemicals appropriately.
32. Triple-rinse and re-use 250 mL alkalinity and ANC sample bottles.



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D.5 Ending the Processing Day

Refreshing the laboratory supplies

1. Check expiration date of sulfuric acid titrant and pH buffer solutions. Order more if expiration has passed or will be passed within the next month.
2. Ensure you have enough equipment for the next sampling event.

Equipment maintenance, cleaning and storage

1. Check the expiration date of pH buffers and acid cartridges. Order more if necessary.
2. 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.
3. Titrators do not require calibration. Hach titrators have a lifetime warranty. Please contact the manufacturer for trouble shooting.



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SOP E 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. As a best practice, field data collected on paper datasheets should be digitally transcribed within 7 days of collection or the end of a sampling bout (where applicable). However, given logistical constraints, the maximum timeline for entering data is within 14 days of collection or the end of a sampling bout (where applicable). See RD[04] for complete instructions regarding manual data transcription.

E.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.



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SOP F Sample Shipment

Information included in this SOP conveys science-based packaging, shipping, and handling requirements, not lab-specific or logistical demands.

See the NEON Knowledge Base Article: Best Practices for Cold Chain Shipping.

F.1 Handling Hazardous Material

N/A

F.2 Supplies/Containers



NOTE: Shipping vessels and materials vary with the number of sites and site type.

1. Follow Best Practices for Cold Chain Shipping in Shipping Ecological Samples, Sensors and Equipment (RD[16]).

F.3 Timelines

1. Ship samples to the External Water Chemistry Laboratory immediately following processing, when possible. Ship water chemistry samples **overnight** to the external laboratory within 24 hours from sample collection in order to minimize chemical speciation and sample degradation. Ship only samples that will be analyzed by an outside laboratory. Make sure ALK and ANC samples remain at the Domain Support Facility.
2. Ship samples **“Priority Overnight.”**
 - a. **DO NOT** send them “FedEX First Overnight.”
 - b. **DO NOT ship samples on Friday.**

F.4 Conditions

Keep samples at 0.5°C – 6°C. DO NOT FREEZE. During summer months, it may be necessary to ship in larger cooler so you can get more ice in the cooler (site-specific). Place samples in the refrigerator until it is time to be shipped to help maintain temperature.

F.5 Grouping/Splitting Samples

N/A

F.6 Return of Materials or Containers

1. Include a return shipping label to your address with account information so the analyzing laboratory can return the cooler to you.



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2. Place return shipping label and the sample manifest in a resealable plastic bag and securely tape the bag to the inside cooler lid to help keep the forms dry.

F.7 **Shipping Inventory**

Whenever samples are shipped, they must be accompanied by a hard-copy Shipping Manifest enclosed within the shipping container. In addition, a corresponding electronic version of the Shipping Manifest (csv file), detailing the contents of the shipment, must be emailed to the taxonomic ID facility and NEON's CLA contact using the Stork Shipment Verification Tool as soon as possible after the samples have been shipped.

F.8 **Laboratory Contact Information and Shipping/Receipt Days**

See Inventory Fulcrum application.



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8**REFERENCES**

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APPENDIX A QUICK REFERENCES

The following datasheets are associated with this protocol:

Table 10. 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.



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APPENDIX B REMINDERS

Before heading into the field: Make sure you...

- Collect and prepare all equipment including labels and filters.
- 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).
- 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 RAW sample.
- DO NOT FREEZE samples.

Sample filtering: Be sure to...

- Keep track of the volume of sample water filtered for PCN.
- Once poured, filter all of the water in the tower because particles will start to settle.
- DO NOT add more sample into the filter tower than you can filter.

Sample titrations: Be sure to...

- Add titrant in smaller increments around equivalence points ($\text{pH} \sim 5$)
- After each addition of titrant, allow the stirrer to homogenize the sample for 15-30 s. In low conductivity samples, stir manually (~10 s).



APPENDIX C ESTIMATED DATES FOR ONSET AND CESSION OF SAMPLING

The seasonal timing of groundwater sample collection as shown in Table 11. Site-specific groundwater sampling windows and wells to samples. 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% ($\pm 5\%$) of cumulative annual discharge. The timing of groundwater chemistry sampling will be reassessed once a minimum of three years of water table data are available directly from the NEON wells to ensure that we are capturing seasonal variability in chemical and hydrologic conditions.

Table 11. 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



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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
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



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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 12**). 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 12. 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 13. Equipment list- Water chemistry sampling.

Item No.	Exact Brand? (Y/N)	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., suggested 4ft and 2ft in length	Pumping water into sample containers	2
GB0727000	Y	Pump Assembly <ul style="list-style-type: none">• 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 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



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	N	Squirt bottle (125mL)	Creating a flat surface for filtering water samples	1
	N	Non-porous flat surface	Creating a flat surface for filtering water samples	1
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: <ul style="list-style-type: none">• 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)	Collecting stream 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



Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	N	Adhesive barcode labels (Type 1)	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 14. Equipment list- Water chemistry bottles for dissolved and totals (see Figure 5).

Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
Durable items				
	N	250 mL HDPE ^a • 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				



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
HQ Field support orders form 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
HQ Field support orders form external lab.	Y	250mL 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
HQ Field support orders form external lab.	Y	60mL 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
	N	4 L jug	Collecting samples	1
GB08760000	N	Vacuum-pump filter manifold assembly, pre-made	Filtering samples	1
Part of GB08760000	N	Filter unit and 25mm, 200mL funnel (Part #: 0341440000)	Filtering samples- part of filter manifold assembly	1
Part of GB08760000	N	1L polypropylene vacuum flask (Part #: 0341520000)	Filtering samples- part of filter manifold assembly	
Part of GB08760000	N	2L polypropylene vacuum flask (Part #: 0342980000)	Filtering samples- part of filter manifold assembly	
Part of GB08760000	N	#8 rubber stopper for filter manifold (Part#: 0341450000)	Filtering samples- part of filter manifold assembly	
	N	Vacuum hand pump	Filtering samples- backup to filter manifold	1
	N	Graduated cylinder, plastic, 250mL	Measuring and adding the volume of sample into the filter funnel	1



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	N	Filter forceps- forceps with flat ends to not poke holes in filter	Handling filter	2
	N	Squirt bottle (125mL)	Rinsing the sides of the filter funnel and graduated cylinder	1
Consumable items				
	N	25mm pre-ashed GFF (0.7 µm) filters, filters are purchased as non-ashed but must be ashed before using	Filters for particulate sample (PCN)	20*
	N	Aluminum foil, pieces (~4x4")	Wrapping GF/F filters	20*
	N	DI water	Rinsing the sides of the filter funnel	As needed

*Take extras in field

Table 15. Additional equipment list – Sampling lakes and rivers for water chemistry.

Item No.	Exact Brand? (Y/N)	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



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	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 16. Equipment list – Sampling groundwater for water chemistry.

Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
Durable items				
	N	Clean 5 gallon bucket	Storing the groundwater well sensor and cable during sampling	1



Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
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 $\frac{1}{4}$ " x $\frac{1}{4}$ " 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 1 st 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 250mL 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 $\frac{1}{4}$ " tubing connector	[Minimum-purge Method Only] Pumping groundwater using the minimum purge method	1 dedicated tube per minimum



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	N	Stainless steel Quick Bullet weight for 1/4 th " OD tubing	[Minimum-purge Method Only] Optional weight used for minimum purge method to keep tubing in place	1 per minimum purge well
	N	3-way male slip stopcocks	[Needle Method Only] For bubble-free syringe sampling at D18/D19 sites	2 per well
	N	140mL Luer lock sterile syringe	[Needle Method Only] For bubble-free syringe sampling at D18/D19 sites	1 per well
	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	[Needle Method Only]	1 for D18, 1 for D19



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Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
			Filtering the pH and FIL subsamples in D18/19	
	N	pH calibration solution	Calibrating hand-held pH meter	1



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Table 17. Equipment list- Sample field storage and shipping. See RD[16] Shipping Ecological Samples, Sensors and Equipment.

Item No.	Exact Brand? (Y/N)	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
	N	shipping labels	Labeling shipment and cooler return	2

Table 18. Equipment list – Laboratory processing: Materials and supplies for the alkalinity and ANC laboratory measurement procedure

Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
Durable items				
	N	pH meter, with automatic temperature compensator <ul style="list-style-type: none"> • pH electrode, calibrated • Thermometer, calibrated 	Reading pH of the samples	1



Item No.	Exact Brand? (Y/N)	Description	Purpose	Quantity
	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 - 25mL - 50mL - 100mL	Measuring volume and transferring sample to glass beaker for ALK samples	1 1 1
	N	Graduated cylinders, class A "TD" ^b - 25mL - 50mL - 100mL	Measuring volume and transferring sample to glass beaker for ANC samples	1
	N	Pipette squeeze bulb	Used with volumetric pipet	1
	N	Glass beakers - 50mL - 100mL - 150mL (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
	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



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Item No.	Exact Brand? (Y/N)	Description		Purpose	Quantity
	N	Acid waste container			1
Consumable items					
	N	DI water (max conductivity of 1 $\mu\text{s}/\text{cm}$)		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) 0.16N - Sulfuric acid (H_2SO_4) 1.6N		Added to samples in order to measure AND and ALK	1
	N	Baking soda		Acid disposal	1