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

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See configuration management system for approval history.

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# Change Record

| REVISION | DATE | ECO # | DESCRIPTION OF CHANGE |
|---|---|---|---|
| A | 07/21/2015 | ECO-03068 | Initial release of merged protocols (Supersedes NEON.DOC.000694, NEON.DOC.001190 and NEON.DOC.001219 which are now OBSOLETE) |
| B | 02/16/2016 | ECO-03483 | Baseline review from FOPs, updated GW section. |
| C | 05/16/2016 | ECO-03871 | Minor update to GW section – setting the depth of pump in the well. |
| D | 02/07/2017 | ECO-04367 | 2016 updates following FOPS training and reviews; updated template; River stationID changed to ‘c0’, no longer ‘rs’; Updated shipping info and data entry; Updated field replicate strategy; Titration replicates on ALK only. Lake ALK/ANC only conducted at buoy station(s); GW ANC not collected; Updates to Gran titration instructions; Changes to under ice sampling |
| E | 01/10/2018 | ECO-05285 | Conductivity not needed on shipping manifest. Clarification that grid side of filter is down for 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. |

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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:

$$\mathbf{L = CQ}$$

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 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).

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.004104 | NEON Science Performance QA/QC Plan |
| AD[05] | NEON.DOC.050005 | Field Operations Job Instruction Training 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.002792 | AOS Protocol and Procedure: Secchi Disk and Depth Profile Sampling in Lakes and Non-wadeable Streams |
| RD[07] | NEON.DOC.001646 | General AQU Field Metadata Sheet |
| RD[08] | NEON.DOC.001152 | NEON Aquatic Sample Strategy Document |
| RD[09] | NEON.DOC.004257 | All Systems Standard Operating Procedure: Decontamination of Sensors, Field Equipment, and Field Vehicles |
| RD[10] | NEON.DOC.001197 | AOS Protocol and Procedure: Bathymetry and Morphology of Lakes and Non-Wadeable Streams |
| RD[11] | NEON.DOC.002494 | Datasheets for AOS Sample Shipping Inventory |
| RD[12] | NEON.DOC.004362 | NEON PREVENTIVE MAINTENANCE PROCEDURE: Groundwater Wells and associated instrumentation |

## 2.3 Acronyms

| Acronym | Definition |
|---|---|
| A/R | Acid-rinsed |
| ALK | alkalinity |
| ANC | Acid Neutralizing Capacity |
| ASR | Analytical Services Request |
| C/B | Cleaned and burned |
| $^{o}$C | Degrees Celsius |
| DI | Deionized |
| DO | Dissolved Oxygen |
| FIL | Filtered Chilled |
| GF/F | Grade F Glass Fiber Filter |
| GW | Groundwater |
| $H_2SO_4$ | Sulfuric acid |
| ha | Hectare |
| HDPE | High-density polyethylene |
| kg | Kilogram |
| L | Liter |
| lb/in | Pounds per inch |
| m | Meter |
| M | Molar |
| $m^3$ | Cubic meter |
| mg | Milligram |
| mg/L | Milligrams per liter |
| meq/L | Milliequivalents per liter |
| mL | Milliliter |
| µS/cm | Microsiemens per centimeter |
| mph | Miles per hour |
| MAD | Maximum Allowable Drawdown |
| N | Normal |
| OW | Observation Well |
| P&P | Procedure and Protocol |
| 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 |

## 2.4 Definitions

**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 ($m^3$) over a given time (s).

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

**Low Yield Well:** Groundwater wells with a recharge at a rate less than 100 mL/min

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

**Recharge Rate: T**he 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 $CO_2$.

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, station ID = 'ss') so that the sensor measurements can be validated with stream water chemistry samples (Figure 1). The sampling location should be typical of the entire reach. The sampling location should be located away from, or upstream of, any major local disturbances and other areas where NEON sampling activities commonly occur. In streams with a shallow water column, field personnel must be cautious not to disturb the benthic sediments when sampling. Disruption of the sediments by walking or by sampling too close to the stream bottom can contaminate samples. Thus, always sample upstream from wading activity and minimize suspension of sediments when sampling. If sediments are disrupted, wait until the area has cleared before sampling.

In **non-wadeable streams**, NEON will collect one sample in non-stratified rivers (station ID = 'c0') at 0.5 m depth just downstream of the sensor set (**Error! Reference source not found.**) in the area representing the steam thalweg (the deepest part of the stream, where access is possible). If the non-wadeable stream is stratified, an epilimnion sample at 0.5 m will be collected (stationID = 'c1') to align with dissolved gas sampling and a sample of the hypolimnion is taken if hypolimnion section depth (i.e. thickness) > 2m (station 'c2'), as in stratified lakes (Figure 8). 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.

In lakes, sample collection depends on lake depth and stratification, as detailed below (Figure 8). For all lakes, 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 with **very** shallow hypolimnions (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 with shallow hypolimnions (hypolimnion thickness 2-4 m), the sample is collected from the mid-point of the hypolimnion. In lakes with deep hypolimnions (hypolimnion thickness >4 m) an integrated sample is collected (Figure 8). Note that if 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 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 (**Error! Reference source not found.**). **Due to the limited number of samples available, a subset of 4 wells will be sampled twice per year at all sites.** Specific wells are selected for each site and the list of wells is available on the AOS-FOPS Sharepoint Page. For rivers and wadeable streams, the four sampling wells are selected to cover as much area as possible and ideally cover all of the following categories: upstream, downstream, right bank, left bank, near stream, far-from stream. 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.

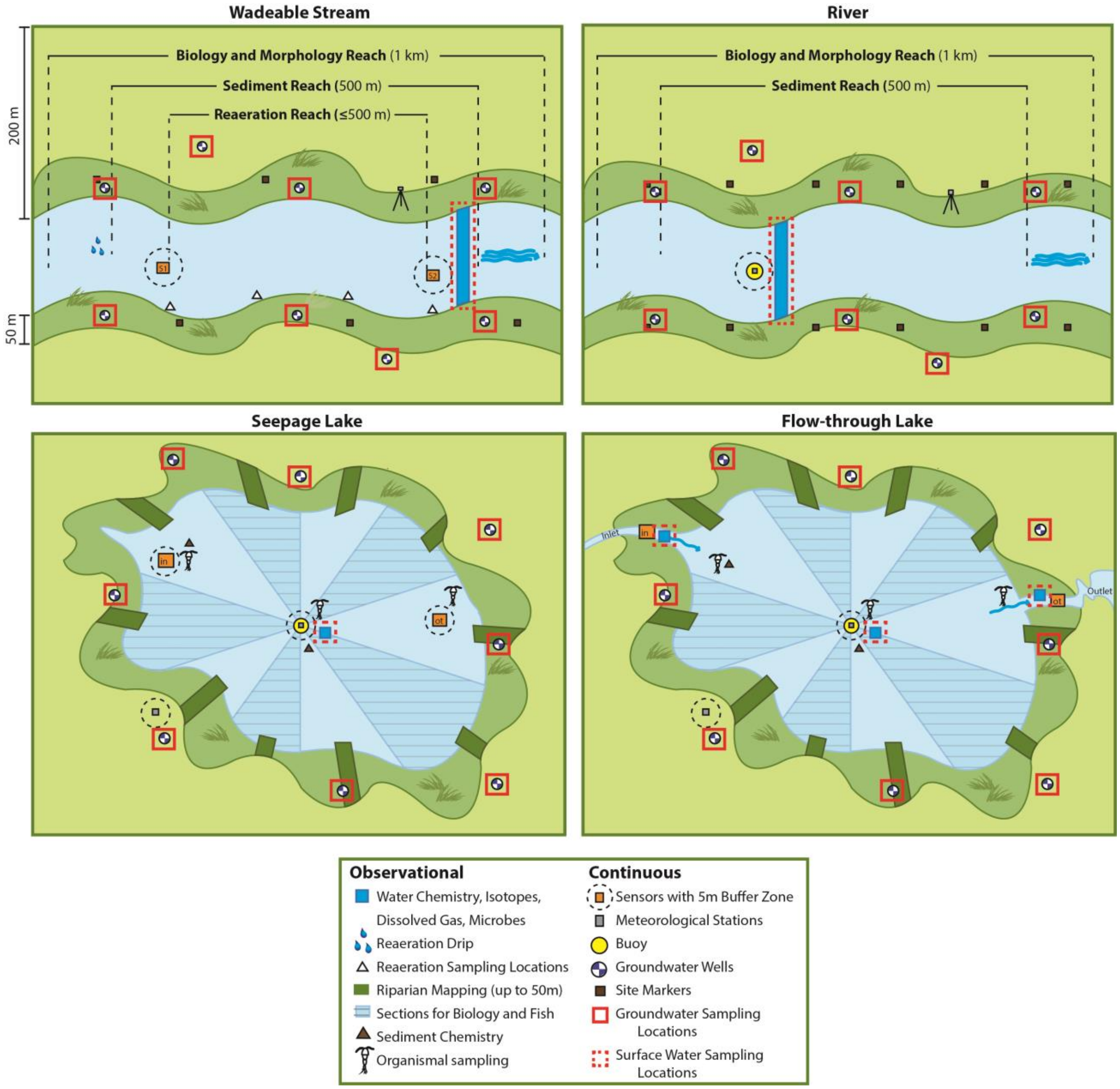


**Figure 1**. Generic site layouts for wadeable streams, rivers (AKA non-wadeable streams) and lakes surface water and groundwater sampling locations. Seepage lakes are lakes with no true inlet and outlet, while flow-through lakes have a true inlet and outlet.

Standard Operating Procedures (SOPs), in Section 7 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 field issues associated with implementing this protocol.

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

During Operations, NEON will quantify measurement uncertainty by collecting two additional replicate samples for external sample analysis on a minimum of 10% of surface water samples. This will result in a total of 3 samples for each sampleType (.FIL, .RAW, and .PCN) for that sampling event (1 set from the regular sample collection and 2 additional replicate sets).

For streams and rivers, collect replicates during 3 sampling events per year at all sites, resulting in an additional 6 samples per sample type per year.

For lakes, on 3 sampling events per year, collect replicate samples (3 total/2 additional samples per each sample type) at buoy stations only (c0 if non-stratified, c1 and c2 if stratified (in this case, 4 additional samples are collected per sampling event and 12 additional samples are collected per year).

No replicates will be collected on groundwater samples.

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

# 4 SAMPLING SCHEDULE

## 4.1 Sampling Frequency and Timing

**Wadeable and Non-wadeable stream** water chemistry sampling occurs up to 26 times per year (approximately every other week) at each NEON location. When applicable, chemistry samples should be collected on Tuesday to coincide with NEON atmospheric wet chemistry sampling, as well as the National chemistry sampling efforts. It is advised not to collect samples on Friday. A range of dates for each site will be determined *a priori*, based on historical stream discharge data. These criteria will be detailed in the NEON Aquatic Sample Strategy Document (RD[08]).

**Lake** water chemistry will be collected 12 times per year (approximately monthly and during shoulder seasons to capture ice-on and ice-off events). Other than event based sampling, chemistry samples are preferably collected on Tuesday to coincide with other National chemistry sampling efforts. Sampling timing is provided annually by Science Operations and shall be outlined in the NEON Aquatic Sampling Strategy Document (RD[08]).

**Groundwater** chemistry samples are collected up to twice per year from a subset of wells, selected on a site-by-site basis, during each sampling event. 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). Groundwater chemistry samples shall be collected within +/- 1 day of the surface water chemistry sampling event, when possible.

## 4.2 Criteria for Determining Onset and Cessation of Sampling

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

For example, **wadeable streams** with little or no flow during the summer dry-season or completely frozen streams during the winter are sampled more intensively during wet periods. Systems that have a 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.

**Non-wadeable streams** 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 fall of 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 sample occurring when the stream is between 20-30% and the second sample 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 stream sampling event. 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, samples should be processed (i.e. filtered) as soon as possible, preferably within 3 hours, and shipped to the water chemistry lab within 24 hours, when possible, to ensure sample integrity. Samples must be kept cold (~4 ± 2°C) to reduce nutrient transformation. Water jugs must be shaken before filtration to re-suspend particulates and homogenize water. For further storage and shipping information see SOP 7: Standard Operating Procedures.

For internal laboratory analysis, samples for alkalinity and ANC should be kept on ice or refrigerated at 4°C ± 2°C. 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. For **groundwater**, only alkalinity samples are collected (no GW ANC samples collected), and ALK samples should be processed within 24 hours, when possible. However, given that groundwater chemistry sampling logistics may make titrations within 24 hours impossible, the maximum allowable time period between sample collection and analysis is 72 hours.

It is advised to not collect field samples on Friday given shipping and domain laboratory processing requirements.

### 4.4 Sampling Timing Contingencies

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

**Table 1.** Contingent decisions

| Delay/ Situation | Action | Outcome for Data Products |
|---|---|---|
| Hours | If weather conditions deteriorate and conditions become unsafe (e.g. approaching thunderstorm, rapid increase of water level in the **wadeable stream**), or the **lake/non-wadeable stream** becomes too windy (>20 mph) and has unsafe wave heights (>1 m) to hold the boat stationary over a sampling point) return to shore and wait in a safe location for 30 minutes. If conditions improve, resume sampling, if not, return to the Domain Support Facility and sample at another time. | No adverse outcome. |
| | If wadeable stream is ice-covered but still flowing, the ice should be broken in order to sample the stream, as long as it is safe to do so. Be sure to bring a shovel or other long-handled tool if the surface ice is expected to be hard to break. If necessary, move to a nearby sampling location that is safe to sample and ice can be broken. Make note of the new location on the datasheet. | No adverse outcome. |
| | If lake sureface has a think 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. |
| | If the lake surface is frozen and safe to walk on (minimum of 15 cm thickness for walking and 20 cm thickness for use of UTV/snowmobiles, etc.) make a hole in the ice and proceed with sampling. The thickness of the ice shall be tested on the near shore environment prior to walking on the lake, by drilling a hole in the ice and measuring the ice thickness and consistency (RD[08]). | No adverse outcome. |
| | If lake surface is frozen, and the lake has in-lake inlet and outlet sampling locations, only sample at buoy location. Lakes with inlet and outlet streams should follow stream ice recommendations for inlet and outlet locations. | No adverse outcome. |
| | If sampling stirred up sediments or added chemical constituents to the water within the past hour, allow the water to clear and disturbance to pass or sample in a different location upstream/upwind of the disturbance. | No adverse outcome. |
| | If water samples cannot be processed in situ (due to field conditions, time limits, etc.), collect water samples in two 4 L jugs and return the samples on ice to the designated sample processing location to filter. The filtration should be completed in 3 hours and must be completed within 6 hours of sample collection. Samples must be kept cold (~4°C) to reduce nutrient transformation. Water jugs must be shaken before filtration to re-suspend particulates and homogenize water. | No adverse outcome. |
| | If the water chemistry sampling location is too shallow to obtain a sample, sample in a nearby location where water is deep enough to obtain a clean, sediment free, sample, and note this change during data collection by noting the new GPS position on the field sheet. | No adverse outcome. |

| | | |
|---|---|---|
| | If low discharge or lake levels render some habitat dry or the flow is so low that the stream appears to be a series of pools not connected by surface water, continue sampling in the water chemistry sampling locations provided the sample bottle could be filled without disturbing sediments. Be sure to note this in the comments section of the field sheet during data collection. | No adverse outcome. |
| | When sampling a groundwater well following the low flow method, if the well goes dry at the lowest flow rates, contact Science about the possibility of implementing the low yield method. | No adverse outcome. |
| | If temperatures are below freezing and filtration equipment is not functional in situ, collect sample and filter in a sheltered area, such as the field vehicle or return to the Domain Support Facility for filtration. | No adverse outcome. |
| Days – Months | If the water body is entirely dry or frozen to the ground, note during data collection. Postpone sampling until water is available for sampling. | No adverse outcome. |
| | If site conditions dictate that **stream** sampling is not possible due to the stream being dry, then postpone the **groundwater-sampling** event until flow returns in the stream. | No adverse outcome |
| | If temperatures are below freezing and water in the **groundwater** pump discharge line is freezing, stop sampling and reinitialize the sampling effort when ambient temperatures are above freezing. Since GW sampling occurs at most twice a year, the events should be timed with above freezing weather conditions. | No adverse outcome. |
| | In some locations the **groundwater** level will drop below the bottom of the well either seasonally (e.g. Taiga and Tundra sites) or in periods of drought, which are likely to occur at some point during the life of the Observatory. Under these conditions sampling of groundwater is not possible and timing of the sampling bout should be reevaluated. | No adverse outcome |
| | Though **groundwater** wells are generally sited for slightly elevated locations, times will occur when standing water surrounds the base of the well. In this condition postpone sampling until the ground near the base of the well is free of standing water. | No adverse outcome. |
| | For sites that have the "generation" **of groundwater** resulting from seasonal thawing of permafrost, sampling is targeted for times when the permafrost is sufficiently thawed to allow for collection of groundwater samples. | No adverse outcome |

### 4.5 Criteria for Permanent Reallocation of Sampling Within a Site

Water chemistry sampling will occur on the schedule described above at 1 (streams/rivers) and1-4 (lakes) sampling stations per site. 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, circumstances may arise requiring that sampling within a site be shifted from one particular location to another. In general, sampling is considered to be compromised when sampling at a location becomes so limited that data quality is significantly reduced. If sampling at a given station becomes compromised, a problem ticket should be submitted by Field Operations to Science.

There are two main pathways by which sampling can be compromised. Sampling stations can become inappropriately suited to answer meaningful biological questions (e.g., a terrestrial sampling plot becomes permanently flooded or a stream moves after a flood and the location is no longer within the stream channel). Alternatively, sampling locations may be located in areas that are logistically impossible to sample on a schedule that that is biologically meaningful.

## 4.6 Sampling Specific Concerns

Samples should be processed (filtered and chilled at 4 ± 2°C) as soon as possible to reduce nutrient transformation. If necessary, sample water may be collected in a large container (may require up to three 4 L jugs in clear systems), kept on ice or ice packs, and filtered within 3 hours (maximum of 6 hours) at a base camp or Domain Lab (i.e., if weather dictates the need to get out of the field immediately and stream discharge is increasing). Water jugs must be gently shaken before filtration to re-suspend particulates and homogenize water.

Always make note of any weather or stream conditions that could influence chemistry, including but not limited to wind, activities in the surrounding watershed, prior flood or rain events, ice, and changes in sampling locations (RD[05]). Sample collection time, processing station and processing time must be recorded on the Water Chemistry Data Sheet (RD[05]).

No other protocols should be done upstream or upwind during surface **water** chemistry sampling.

**Groundwater** sampling should be timed to occur on the same day (preferred) or within 1-2 days (preferably 1 day) of the surface water collection. GW sampling can be time consuming, as such, conducting the groundwater chemistry sampling event over two days is also acceptable. The order in which the wells are sampled does not matter, though specific wells are designated for each site.

**Table 2.** Groundwater sampling specific contingent decisions

| Delay/ Situation | Action | Outcome for Data Products |
|---|---|---|
| If a groundwater well is damaged (i.e. casing is broken internally) or bent | Do not try to sample this well. It is likely that the pump may get stuck inside the well due to the limited tolerance between the pump and well casing. If this condition is observed submit a trouble ticket for a new well to be selected for sampling. | No adverse outcome. |

## 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 fieldwork 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 ≥ 10 $ft^2/s$ (0.93 $m^2/s$). When working around ice, refer to (AD[02], Section 10.3 Winter Water Safety. Do not attempt to walk on frozen lake is depth of ice is less than 6" (+15cm) or operate UTV or snowmobile on frozen lake if depth of ice is less than 8" (20cm). Use caution and good judgment to carefully evaluate site conditions including ice strength. Local guidelines from natural resource officials, property owners or hosts, and domain managers should be consulted regarding work on ice, prior to deploying employees and equipment. Do not continue if the risk is too great.

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

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

1. Due to site-specific hazards that may be encountered, technicians may perform GPS positioning around the lake, and measurements for inflow and outflow, without dismounting from the vessel. In addition, technicians are required not to put hands and feet in waters where alligators are present and to make sure a safe distance from hazards is maintained.
2. All personnel must be wearing a personal flotation device prior to entering the boat.
3. All employees shall have access to a form of communication with other team members such as a two-way radio.
4. Technicians should be aware of any site-specific hazards and 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.
7. Access to Safety Data Sheet shall be available for work with chemicals associated with this protocol.

# 6 PERSONNEL AND EQUIPMENT

## 6.1 Equipment

The following equipment is needed to implement the procedures in this document. The first two lists are specific to sampling of lakes/non-wadeable streams and groundwater (no additional, specific equipment is needed to sample wadeable streams). All remaining lists are organized by task and apply to all waterbodies and groundwater. They do not include standard field and laboratory supplies such as charging stations, first aid kits, drying ovens, ultra-low refrigerators, etc.

This protocol suggests the use of a GPS unit with WAAS, specifically a Hummingbird 1198c, used for navigating to lake sampling locations. Any GPS unit can be used as long as the navigation accuracy is <4 m for lake navigation.

**Table 3.** Equipment specific to sampling lakes

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| | | | R | Boat | | 1 | Y |
| MX107097 | Amazon Capital Services Inc. | B003ZZG5EM | R | Anchor with rope | | 2 | N |
| MX100457 | | | R | Oars | | 2 | N |
| MX100458 | West Marine Products, Inc. | 13487178 | R | Trolling Electric Motor | | 1 | Y |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| | | | R | Marine deep cycle battery | Powering trolling boat motor | 1 | Y |
| MX100435 | Amazon Capital Services Inc. | B003QKQ4V0 | R | Safety kit for boat (e.g., flares, bailer, float with rope) | | 1 | Y |
| MX102603 | Grainger, W.W. | 11C657 | R | First Aid Kit | | 1 | N |
| | | | R | Personal Flotation Devices (PFDs) | | 1 per person | N |
| MX100393 | Fisher Scientific Company, LLC | EW0548610 | R | Kemmerer sampler with rope and messenger | Collecting samples | 1 | |
| MX110075<br>MX102739 | Forestry Suppliers, Inc.<br>Cabela's Inc.<br>Recreational Equipment Inc. | 39481<br>IK-270217<br>895022 | R | GPS (Accuracy <4 m) | Navigating to sampling locations | 1 | |
| MX100447 | Grainger, W.W. | 9CJR8 | R | Secchi Disk | Determining the depth of the euphotic zone | 1 | |
| **Consumable items** | | | | | | | |
| | | | | (none) | | | |

R/S=Required/Suggested

**Table 4**. Equipment specific to sampling groundwater

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| MX101740 | Uline | S-7914 | R | Clean 5 Gallon Bucket | Storing the groundwater well sensor and cable during sampling | 1 | N |
| 318830003 | QED Environmental Systems | MPSP4P | R | QED Sample Pro Pump | Pumping groundwater from the well | 1 | N |
| 318830001 | QED Environmental Systems | MP50 | R | QED MP-50 Compressor / Controller | Pumping groundwater from the well | 1 | N |
| MX100899 | Grainger, W.W. | 2UKJ5 | R | Battery (12V, minimum of 3.6 Ah) | Pumping groundwater from the well | 8 | N |
| 318830002 | QED Environmental Systems | DTTP4B | R | Bucket of ¼" x ¼" dual bonded tubing (250 ft of tubing in each bucket). Tubing is dedicated per each well for the duration of the sampling events. | Pumping groundwater from the well | 1 per site, required for 1st sampling event. | Y, Must Remain Clean |
| Cut tubing from 0318830002 | QED Environmental Systems | DTTP4B | R | Dedicated tubing for wells (in large plastic bags). Make sure to get the | Pumping groundwater from the well. One piece | 1 dedicated piece of | Must Remain Clean |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| | | | | tubing identified for the well that is sampled. The sealable bags shall be labeled with the Well ID. | of tubing dedicated to each well. | tubing per well sampled (after 1st sampling event) | |
| MX110049 | In-Situ, Inc. | 73310 | R | Water level tape (metric) | Measuring water height | 1 | N |
| MX100391 | Fisher Scientific Company, LLC | 300742 | R | Collection cell, such as a 250 mL graduated cylinder | Monitoring groundwater well chemistry | 1 | N |
| MX100364<br>MX109123 | Thomas Scientific, Inc.<br>Cole-Parmer<br>Fisher Scientific Company, LLC<br>Fisher Scientific Company, LLC | 1207W05<br>EW0640776<br>14171212<br>4151836 | S | For minimum purge wells only: 1/8” ID tubing and 1/8” to 1/4” tubing connector | Pumping groundwater using the minimum purge method | 1 dedicated tube per minimum purge well | Must Remain Clean |
| | | | S | Stainless steel Quick Bullet weight for ¼” OD tubing | Optional weight used for minimum purge method to keep tubing in place | 1 per minimum purge well | N |
| **Consumable items** | | | | | | | |
| | | | | (none) | | | |

**Table 5.** Equipment list – Sampling equipment

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| MX111388 | CDW-G | 4452963 | R | Mobile data entry tablet, fully charged and synced before field work | Field data entry | 1 | N |
| MX105571 | Cole-Parmer<br>Fisher Scientific Company, LLC<br>Thomas Scientific, Inc. | EW0608953<br>0343814B<br>1212W94 | R | 4 L jug | Collecting water | As needed, suggest 4 (GW and Lakes) and 2 (streams) | N |
| MX100374 | Fisher Scientific Company, LLC | 14171104 | R | Pieces of C-Flex® tubing, 1/4 in I.D. and 3/8 in outer O.D., suggested 4 ft and 2 ft in length | Pumping water into sample containers | 2 | N |
| GB07270000 | | | R | Pump Assembly<br>• Easy-Load Peristaltic pump head (e.g., Masterflex® L/S® | Pumping stream water into sample containers | 1<br>1 | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| | | | | Easy-Load® pump head) with Peristaltic pump tubing (e.g., L/S® 15 or L/S® 24)<br>• 18-V Drill Pump (Power source for pump head)<br>• Tubing connectors | | 1<br>2 | |
| | | | R | 18-V Drill battery charger | Pumping water into sample containers | 1 | N |
| | | | S | U-bolt | Keeping the drill in the “on” position to pump stream water continuously. | 1 | N |
| MX100346 | Fisher Scientific Company, LLC<br>Thomas Scientific, Inc. | 0340910C<br>1207M51 | R | Squirt bottle (125 mL) | Rinsing tubing before placing in 4 L jug | 1 | N |
| | | | S | Non-porous flat surface | Filtering and processing water samples | 1 | N |
| MX100514 | Thomas Scientific, Inc.<br>Fisher Scientific Company, LLC | 1185K52<br>15177622 | R | Meter, Dissolved Oxygen and Conductivity, | Temperature and Conductivity Meter – must order Probes and cable | 1 | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| | | | | Handheld, Backlit LCD Display; YSI Pro 2030 or Equivalent – Cable and probes sold separately | separately (MX110375 and MX107555) | | |
| MX107555 | Fisher Scientific Company, LLC | 15177490 | | Cable, 4m Length, for YSI Pro 2030 or Equivalent, including conductivity and temperature sensors<br>• Adjust cable length as needed for lake and river sites | 4 m cable for handheld with Conductivity and Temperature sensors | 1 | N |
| MX110375 | Fondriest Environmental, Inc.<br>Fisher Scientific Company, LLC | 605202<br>15177458 | R | DO probe, galvanic, Item includes DO Probe and 1 set of 6 replacement tips for conductivity/temperature handheld meter (MX100514/MX10755) | DO Galvanic Probe and replacement tips –must order separately. | 1 | N |
| MX107554 | Fondriest Environmental, Inc.<br>Fisher Scientific Company, LLC | 605913<br>15176211 | | Replacement DO sensor tips for MX110375 | Replacement part for DO sensor tips – order when appropriate | As needed | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Consumable items** | | | | | | | |
| MX109336 | Fisher Scientific Company, LLC | GWSC04510 | R | Pall Supor capsule filter (0.45 µm) | Collecting stream water for filtered samples | 1 | N |
| MX100904 | Amazon Capital Services Inc. | B00006IBUW | R | Sample labels (2”*4” in waterproof) | Labeling samples, human readable | 10 | N |
| | | | S | Adhesive barcode labels | Labeling sample bottles with barcode-readable | 1 sheet | N |
| MX102002 | | | R | Permanent marker | Labeling samples | 2 | N |
| | | | R | 1 L jug of DI | Rinsing tubing before placing in 4 L jug | 1 | N |
| MX108570 | Thomas Scientific, Inc. | 3241M10 | R | Conductivity calibration solutions | Calibrating hand-held conductivity meter | 1 | N |

R/S=Required/Suggested

**Table 6.** Equipment list – Water chemistry bottles for dissolved and totals (see also Figure 2)

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| MX100574 | Fisher Scientific Company, LLC<br>Thomas Scientific, Inc. | 2912034<br>1709C02 | R | 250 mL HDPE [a]<br>• Alkalinity<br>• Acid Neutralizing Capacity (ANC) | ALK and ANC sample containers, per site | 2 per station | N |
| **Consumable items** | | | | | | | |
| Order form HQ MX108305 | Colorado State University | | R | 1 L amber bottle – A/R and C/B – Order from HQ Warehouse (MX108305) | Prepared bottle for filtered water sample (FIL) | 1 per station | N |
| Order from HQ MX108304 | Colorado State University | | R | 250 mL amber bottle – A/R and C/B – Order from HQ warehouse (MX108304) | Prepared bottle for unfiltered water sample (RAW) | 1 per station | N |

R/S=Required/Suggested

[a] indicates sample bottles that will remain at NEON Domain Support Facilities to be analyzed. These bottles are labeled with different labels (Figure 4) and bottles can be re-used.

**Table 7.** Equipment list – Total Particulate Carbon and Nitrogen (PCN)

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| MX105571 | Cole-Parmer<br>Fisher Scientific Company, LLC<br>Thomas Scientific, Inc. | EW0608953<br>0343814B<br>1212W94 | R | 4 L jug | Collecting samples | 1 | N |
| GB08760000 | | | R | Vacuum-pump filter manifold assembly, pre-made | Filtering samples | 1 | N |
| Part of GB08760000 | | | R | Filter Unit and 25 mm, 200 mL funnel (Part #: 0341440000) | Filtering samples – part of filter manifold assembly | 1 | N |
| Part of GB08760000 | | | R | 1 L Polypropylene vacuum flask (Part #: 0341520000) | Filtering samples – part of filter manifold assembly | | N |
| Part of GB08760000 | | | R | 2 L Polypropylene vacuum flask (Part #: 0342980000) | Filtering samples – part of filter manifold assembly | | N |
| Part of GB08760000 | | | R | #8 rubber stopper for filter manifold (Part #: 0341450000) | Filtering samples – part of filter manifold assembly | | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| MX111134 | Amazon Capital Services Inc. | MV8510 | S | Vacuum hand pump | Filtering samples – backup to filter manifold | | |
| MX100391 | Fisher Scientific Company, LLC | 300742 | R | Graduated Cylinder, plastic, 250 mL | Measuring and adding the volume of sample into the filter funnel | 1 | N |
| MX100387 | Fisher Scientific Company, LLC | 975350 | R | Filter Forceps – forceps with flat ends to not poke holes in filter | Handling filter | 2 | N |
| MX100346 | Thomas Scientific, Inc.<br>Fisher Scientific Company, LLC | 1207M51<br>0340910C | R | Squirt bottle (125 mL) | Rinsing the sides of the filter funnel | 1 | N |
| **Consumable items** | | | | | | | |
| MX106350 | Fisher Scientific Company, LLC | 987464 | R | 25 mm 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 |
| MX100589 | Grainger, W.W. | 6CHG5 | R | Aluminum foil, pieces (~4X4 in) | Wrapping GF/F filters | 20* | N |

| **Item No.** | **Supplier** | **Supplier ID** | **R/S** | **Description** | **Purpose** | **Quantity** | **Special Handling** |
|---|---|---|---|---|---|---|---|
| | | | R | DI water | Rinsing the sides of the filter funnel | As needed | N |

R/S=Required/Suggested

*Take extras in field

**Table 8.** Equipment list – Sample field storage and shipping

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| | | | R | Shipping cooler | Shipping samples | 1 | N |
| **Consumable items** | | | | | | | |
| | | | R | Packing material | Filling up extra space and adding absorbent material | As needed | N |
| MX104844 | Grainger, W.W. | 5LH30 | R | Resealable plastic bags (gallon and quart size) | Separately enclosing the shipping labels, ice packs and samples | As needed | N |
| MX105088 | Fisher Scientific Company, LLC | 3532100 | R | Ice or ice packs (< or = 0 degree C packs) | Keeping the samples cool (water ice is preferable if logistically feasible). | As needed | N |
| MX105587 | Grainger, W.W. | 15F814<br>31HJ31 | R | Clear packing tape, roll | Labeling shipment | 1 | N |
| | | | R | FedEx shipping labels | Labeling shipment and cooler return | 2 | N |

**Table 9.** Equipment list – Laboratory processing: Materials and supplies for the alkalinity and ANC laboratory measurement procedure

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| **Durable items** | | | | | | | |
| MX100556 | Fisher Scientific Company, LLC | 13636AB15PB | R | pH meter, with automatic temperature compensator<br>• pH electrode, calibrated<br>• Thermometer, calibrated | Reading pH of the samples | 1 | N |
| MX110707 | Fisher Scientific Company, LLC | S88857200 | R | Magnetic stirrer | Mixing the sample with the titrant solution | 1 | N |
| MX100563 | Amazon Capital Services Inc. | 41121802 | R | Stir bars, Teflon® coated, smallest size | Mixing the sample with the titrant solution | 2 | N |
| MX100572<br>MX100888<br>MX105514 | Fisher Scientific Company, LLC<br>Fisher Scientific Company, LLC<br>Grainger, W.W. | 136502P<br>136502S<br>5PTF0 | R | Volumetric pipets, Class A "TD" [a]<br>– 25 mL<br>– 50 mL<br>– 100 mL | Measuring volume and transferring sample to glass beaker | 1<br>1<br>1 | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| MX100379<br>MX100380<br>MX100381 | Fisher Scientific Company, LLC<br>Thomas Scientific, Inc.<br>Fisher Scientific Company, LLC | 0300739<br>3571A20<br>085726D | R | Graduated cylinders [b]<br>– 25 mL<br>– 50 mL<br>– 100 mL | Measuring volume and transferring sample to glass beaker | 1<br>1<br>1 | N |
| MX100571 | Thomas Scientific, Inc.<br>Fisher Scientific Company, LLC | 7775B10<br>1368151 | R | Pipette squeeze bulb | Used with volumetric pipet | 1 | N |
| MX100650<br>MX100559<br>MX100558 | Thomas Scientific, Inc. | 1531H66<br>1530L76<br>1531H86 | R | Glass beakers<br>– 50 mL<br>– 100 mL<br>– 150 mL<br>(or larger as needed) | Sample container for pH readings | 1 | N |
| MX100346 | Thomas Scientific, Inc.<br>Fisher Scientific Company, LLC | 1207M51<br>0340910C | R | Squeeze bottle with DI water | Rinsing pH probe | 1 | N |
| MX100384 | Hach Company | 2063700 | R | Digital titrator and mounting assembly | Adding titrant solution to sample | 1 | N |
| MX100565 | Hach Company | 4157800 | R | Delivery tubes, 90° angle, transparent | Adding titrant solution to sample, 1 per titrant solution | 2 | N |

| Item No. | Supplier | Supplier ID | R/S | Description | Purpose | Quantity | Special Handling |
|---|---|---|---|---|---|---|---|
| MX103145 | Amazon Capital Services Inc. | B005IQTSE0 | S | Plastic squeeze bulb pipette (3 mL) | Rinsing acid deliver tube after use | 1 | N |
| | | | R | Safety – gloves, glasses, acid spill kit, lab coat | Safety | 1 | N |
| MX100523 | Fisher Scientific Company, LLC | 146483 | S | Stopwatch | Titraiton stir timing. | 1 | N |
| | | | S | Acid waste container | | 1 | N |
| **Consumable items** | | | | | | | |
| | | | R | DI water (max conductivity of 1 µs/cm) | Rinsing pH probe | 1 | N |
| MX100566<br>MX105772 | Hach Company<br>Thomas Scientific, Inc. | 1438801<br>9866L41 | R | Titrant solution<br>- Sulfuric acid ($H_2SO_4$) 0.16*N*<br>- Sulfuric acid ($H_2SO_4$) 1.6*N* | Added to samples in order to measure ANC and ALK | 1 | Y |
| MX106431 | Grainger, W.W. | 33X679 | R | Baking Soda | Acid disposal | 1 | N |

R/S=Required/Suggested

[a] indicates equipment specific to alkalinity measurements.

[b] indicates equipment specific to ANC measurements.

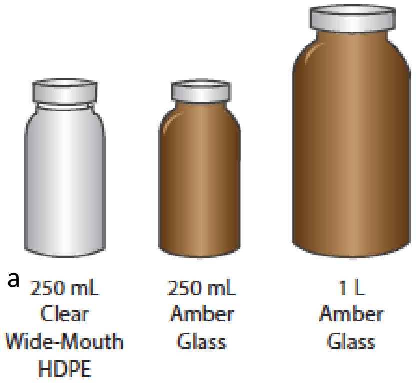


**Figure 2.** Water chemistry bottle types. [a] indicates sample bottles that will remain at NEON Domain Support Facilities to be analyzed. These bottles are labeled with different labels (Figure 4) and bottles can be re-used. 125 mL bottles may be used if less volume is needed – site specific.

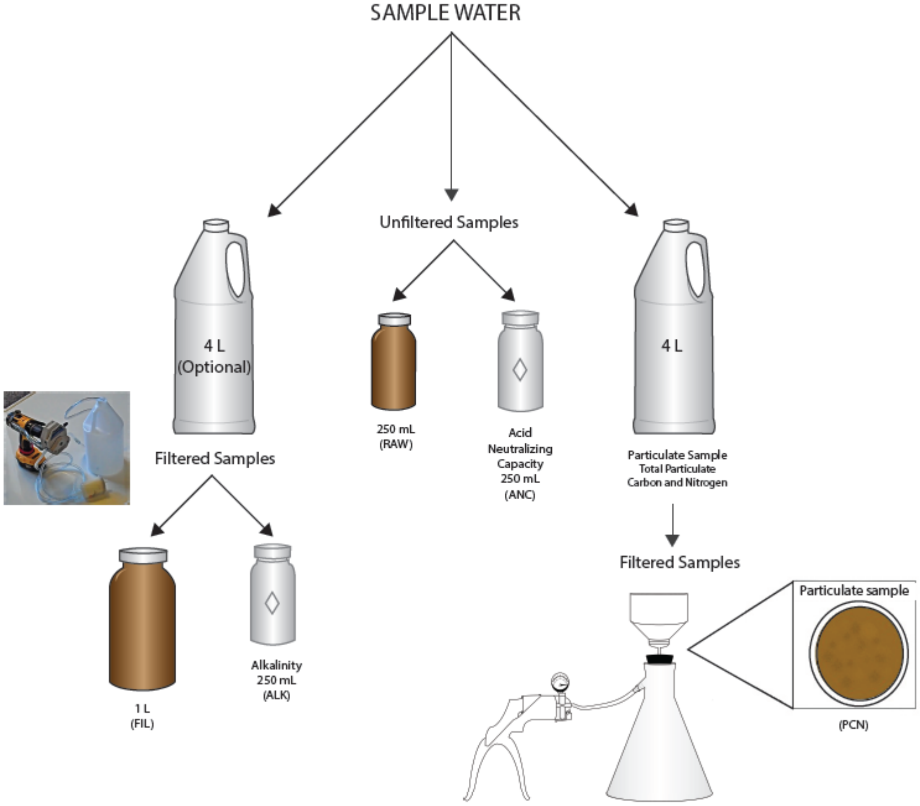


**Figure 3**. Flowchart of Water Chemistry Sample Collection and Filtration. ◊ Indicates 250 mL, wide-mouth sample bottles that remain at the Domain Support Facility for analysis. Letters in parenthesis indicate the codes that correspond to the chemistry labels (see Figure 4).

## 6.2 Training Requirements

Technicians must complete protocol-specific training for safety and implementation of this protocol. 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.

## 6.3 Specialized Skills

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

## 6.4 Estimated Time

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

We estimate that surface water sampling requires 2 technicians for 1-2 hours in **wadeable and non-wadeable streams** or 1-2 hours per station in **lakes** (~ 3-5 hours per lake) each sampling day plus travel to and from the site. An additional 1-2 hours per station (l**ake buoy, wadeable streams, and non-wadeable streams**) of laboratory work at the Domain Support Facility is expected. NOTE: Lake ALK and ANC are only completed at buoy station(s), unless lakes have a defined stream inlet and outlet.

**Groundwater** sampling is estimated to require 1 technician up to 1-2 hours for each well that is sampled plus travel to and from the site. Sampling 4 observation wells should be able to be completed in 6-8 hours as an average. Shallow wells will require significantly less time than deeper wells to sample. For the low-yield protocol, an additional hour should be set aside in the week prior to sampling to place the dedicated tubing in the low yield well(s). An additional 1-2 hours (per well) for laboratory work at the Domain Support Facility is expected. Note: for GW domain lab activities: Only GW ALK is collected.

# 7 STANDARD OPERATING PROCEDURES

## SOP A Preparing for Sampling

### A.1 Preparing for Data Capture

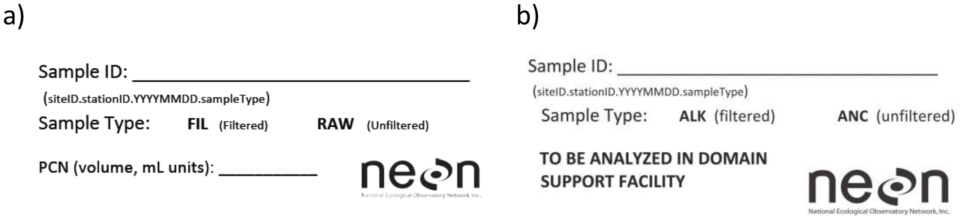
Mobile applications are the preferred mechanism for data entry. Mobile devices should be fully charged at the beginning of each field day, whenever possible. For detailed instructions on protocol specific data entry into mobile devices, see the NEON Internal Sampling Support Library (SSL).

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.

### A.2 Preparing for Sampling

1. Check the water chemistry field sampling kit to make sure all supplies are packed and ensure batteries for the peristaltic pump are charged.
2. Check the hand-held conductivity calibration and recalibrate if necessary. We suggest conductivity sensor should be calibrated monthly. See Conductivity 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 3). *Note: prepare 2 sets of bottles; the second set will be used as a backup.
4. **Groundwater sampling only:** Pack tubing individually into large sealable bags labeled for the corresponding well. 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.3).
5. 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.
    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.
    a. After furnace has cooled, remove from the furnace and stack filters using filter forceps, and place in original box. CAUTION: Ashed filters may be hot. Use designated safety equipment at all times.
    b. Label box with permanent marker to read "ASHED, Your Name, Date".
    c. Place box in in sealed zip-top bag.
    d. Ashed filter may be stored indefinitely, as long as they remain in the box and stay dry.

6. Attach pre-printed labels (Figure 4 a and b) to bottles (**Figure 2**).
7. Use a permanent marker to fill out bottle labels (Figure 4) 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 4a) or will be analyzed at the Domain (Figure 4b). **Labels are waterproof but should be filled out before getting wet to ensure ink is dry. SampleID** should be **siteID.stationID.date.sampleType.**
    a. **StationID** is the 2-digit station code where sample was taken (i.e. **stationID** for stream samples ='*ss*', river samples = '*c0*' (or '*c1*' and '*c2*' if river is stratified, with '*c1*' being the top-most layer)), in Lakes '*in*', '*ot*', '*c0*', if center is stratified: '*c1*', '*c2*', '*c3*', with '*c1*' being the top-most layer. Note, chose c1 for sampleID if lake is stratified, even if c2 hypolimnion depth is too shallow to sample. This allows users to quickly identify a stratification was present. '*w1*'-'*w8*' for groundwater wells).
        a) Use **stationID** of '*re*' if the sample cannot be collected at the defined spot (e.g., that location is dry). This indicates you collected the sample somewhere else in your reach. If using 're' you **must** use that as the stationID for your field, domain, and external samples. Ex) KING.re.20160205
    b. **SampleType** for external lab is 'FIL', 'RAW', or 'PCN', with 'FIL' indicating a filtered sample, 'RAW' indicating an unfiltered sample, 'PCN' indicating the particulate carbon and nitrogen filter sample. Domain Lab **sampleType** is ALK (filtered sample) and ANC (unfiltered sample). Circle the correct bottle type code (Figure 3 and Figure 4) for each bottle.
    c. On the occasions when additional replicates are collected (3 times per year), replicate sampleID convention should be site.station.YYYYMMDD.sampleType.2 and site.station.YYYYMMDD.sampleType.3. There is no need to place a '.1' after the first replicate, we will treat that as our normal sampleID.
8. Organize bottles as appropriate for your study sites.


a)

Sample ID: ______________________________
(siteID.stationID.YYYYMMDD.sampleType)
Sample Type: **FIL** (Filtered) **RAW** (Unfiltered)
PCN (volume, mL units): __________

b)

Sample ID: ______________________________
(siteID.stationID.YYYYMMDD.sampleType)
Sample Type: **ALK** (filtered) **ANC** (unfiltered)
**TO BE ANALYZED IN DOMAIN SUPPORT FACILITY**

**Figure 4.** Blank NEON Chemistry Labels for a) the External Analytical Laboratory and b) Internal NEON Domain Support Facility Measurements.

9. When the system is available, adhesive barcode labels will be added to the sample containers and scanned by the mobile app (**Figure 5**). Add adhesive labels to sample bottles prior to going in the field and getting the bottle wet. **Figure 5**). Add adhesive labels to sample bottles prior to going in the field and getting the bottle wet.
    a. Keep a human-readable label on each bottle with a minimum of the sample ID printed to assist with organization and shipping.

**Figure 5.** Example of adhesive barcode labels.

## SOP B Field Sampling

**For all water chemistry samples:**

In the field, fill out the General AQU Field Metadata Sheet (RD[07]) before collecting samples. You only need to fill out one AQU Field Metadata Sheet 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]).
    a. Measure and record water temperature, temperature-corrected conductivity, DO, and DO percent saturation on the mobile application or datasheets for Water Chemistry Sampling in Surface Waters and Groundwater (RD[05]).
        a) 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).
        b) Conductivity sensor is located at the top of the probe tip, so ensure probe is completely submersed in the water or readings will be inaccurate (Figure 6).

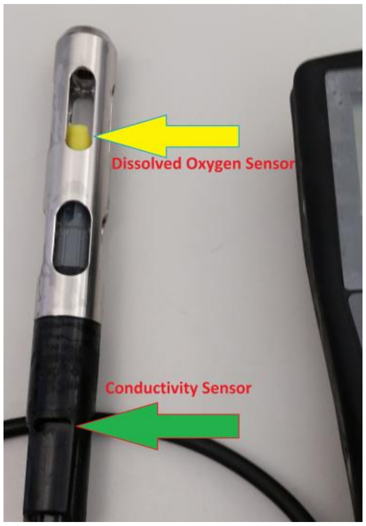


**Figure 6.** Picture of handheld meter showing location of sensors on probe.

## B.1 Wadeable Stream Collection

### FIELD SAMPLING –WADEABLE STREAMS

1. ALWAYS sample in the THALWEG (the deepest location in the stream cross-section) with the bottle opening pointed upstream and into the main flow of water (Figure 7) and several centimeters below the surface (to avoid sampling floating material or surface film). You may step into the stream, but disturb the stream bottom as little as possible as you walk. Take samples UPSTREAM from where you are standing. **Be cautious when sampling. Items can easily fall into stream while bending to sample.**

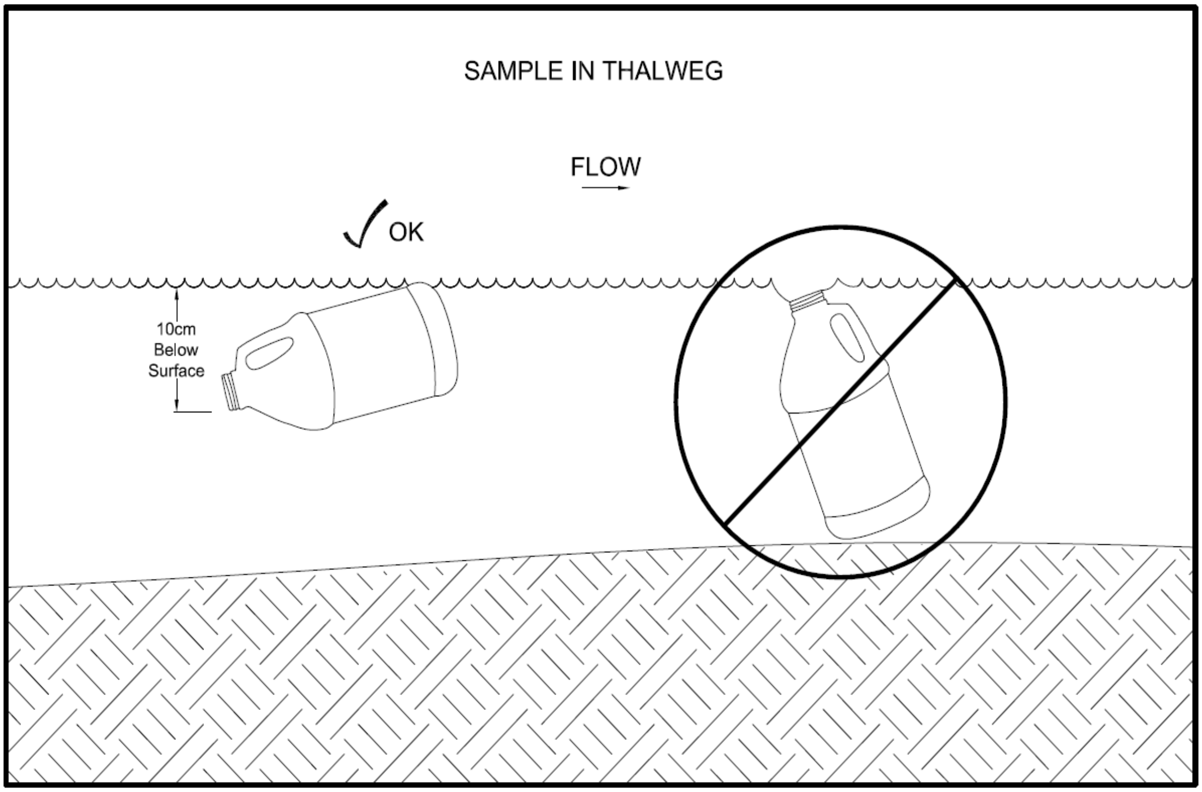


**Figure 7**. Diagram of proper and poor placement of a water sampling bottle

2. Rinse the collection 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:
        a) 4 L jug (can be used for filtered samples and/or PCN, see below)
        b) 250 mL burned amber glass bottle for external lab
        c) 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).

a) 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 $^1/_5$ of the collection bottle. Remove bottle from stream, cap and shake. Discard water downstream. Repeat 2 more times.

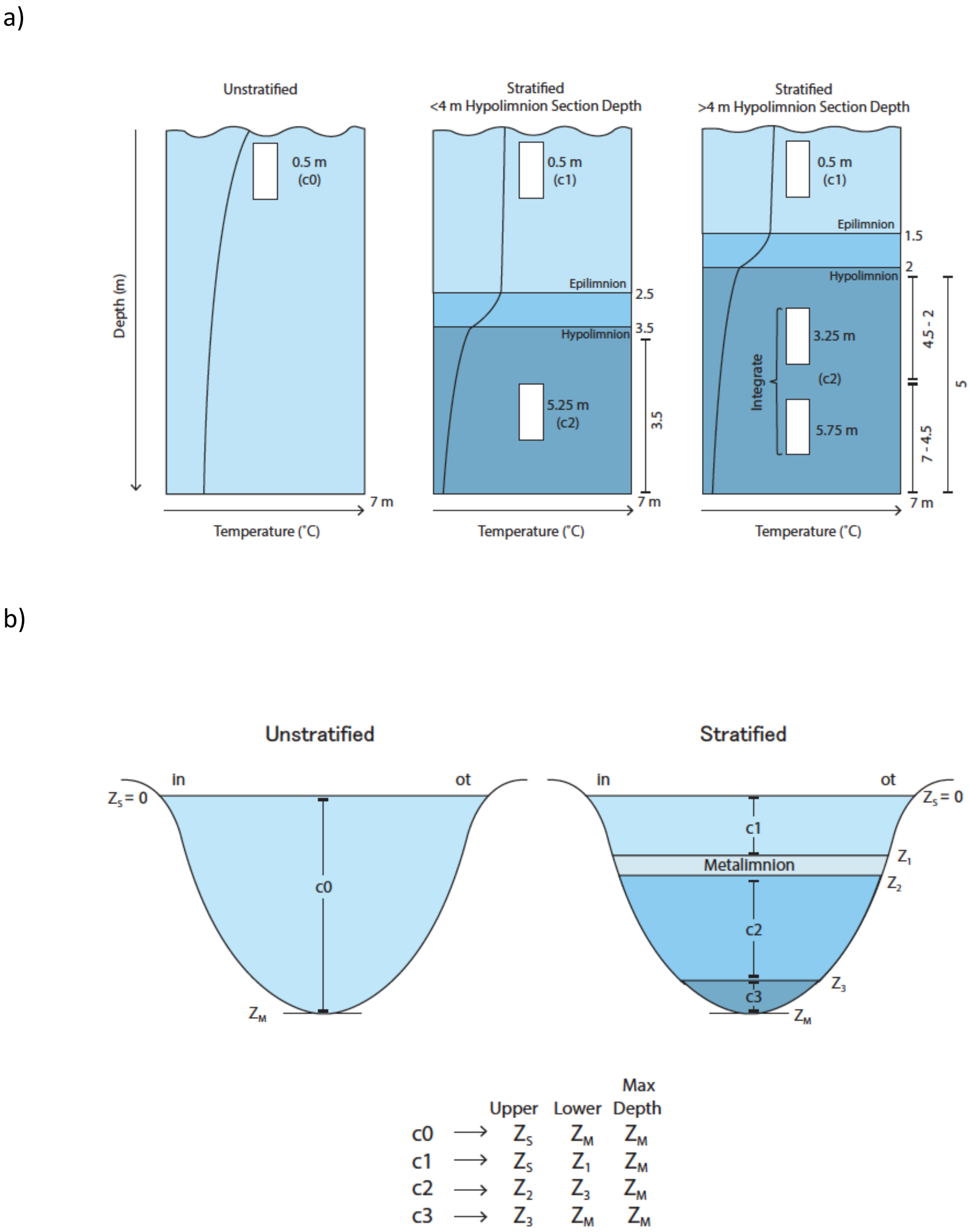
b) NOTE: You may also use the field pump to pump water out of the stream (from just below the surface) and into your bottles for rinsing.

3. Proceed to SOP C.

## B.2 Lake and Non-Wadeable Stream Collection

### DETERMINE SAMPLING DEPTH BASED ON STRATIFIED OR NON-STRATIFIED WATERBODY

1. Determine the stratification conditions from the Secchi Disk and Depth Profile Sampling in Lakes and Non-Wadeable Streams (RD[06]), Section 7, SOP C
2. Take one sample at a 0.5 m depth at the buoy (the bottom of the Kemmerer should be located at 0.65 m). Be sure to pre-mark depth marks on your Kemmerer rope.
3. Is the lake thermally stratified?
   a. If NO, do not take any more samples.
   b. If YES, calculate the depth of the **hypolimnion** section (i.e. hypolimnion thickness) at the buoy. Ensure you are calculating the hypolimnion section depth, NOT the maximum lake depth (Figure 8a).
      i) If hypolimnion section depth (i.e. hypolimnion thickness) is <2 m, do not take any more samples.
      ii) If hypolimnion depth/thickness > or = 2 m but < or = 4 m, then collect a sample from the midsection of the hypolimnion depth.
      iii) 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.
4. If there is a true (i.e. continuous flow-through) inlet and outlet (**Figure 8**), collect inlet and outlet samples just downstream of the inlet and outlet infrastructure, following the wadeable stream protocol. Note, if your inlet and outlet infrastructure is located within the lake, you do not have a flow-through system and will not sample inlet and outlet.
5. 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 8). 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 8).
6. During winter sampling:
   a) Core through the ice. Ensure safe conditions (See Section 5 Safety).
   b) Determine the total depth of water below the ice.
   c) Take samples from below the ice as per an unstratified lake or non-wadeable stream.
      i. A minimum of 0.5 m of water below the ice is required to sample.
      ii. If < 0.5 m of water depth is available in the central (buoy) location, then move to a location that is within 10 m of the original location and note the new GPS location.



| | | Upper | Lower | Max Depth |
|---|---|---|---|---|
| c0 | ⟶ | $Z_S$ | $Z_M$ | $Z_M$ |
| c1 | ⟶ | $Z_S$ | $Z_1$ | $Z_M$ |
| c2 | ⟶ | $Z_2$ | $Z_3$ | $Z_M$ |
| c3 | ⟶ | $Z_3$ | $Z_M$ | $Z_M$ |

**Figure 8.** 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.

## FIELD SAMPLING –LAKES AND NON-WADEABLE STREAMS: USING A KEMMERER SAMPLER

1. Take your water sample from the windward (the upwind) side of the boat to lessen any contamination from the boat.
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 jig 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 9b). 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 9a).
11. Repeat steps 1 through 10 for each sample.

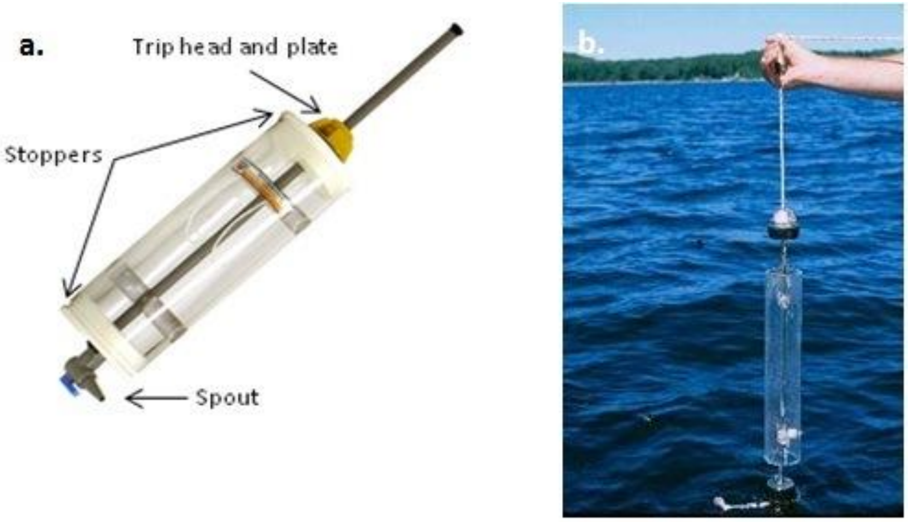


**Figure 9**. Illustration of Kemmerer sampler for water sampling (a). Illustration of how the Kemmerer is lowered into the water by holding the rope and messenger (b)

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:
        a) 4 L jug(s) (can be used for filtered samples and/or PCN, see below)
        b) 250 mL burned amber glass bottle for external lab (code RAW)
        c) ANC - 250 mL wide-mouth, HDPE – ***to be analyzed at the Domain Support Facility**.

        <u>To rinse:</u> 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 $^{1}/_{5}$ 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. Proceed to SOP C.

## B.3 Groundwater Collection

Several groundwater extraction methods are used by NEON for obtaining groundwater samples from the wells. The method will vary with site conditions and should be selected based on the decision tree below (Figure 10) 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 low-yield sampling, the bailer method, and purging to dryness methods.

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

### B.3.1 DETERMINE BEST SAMPLING METHOD

Which sampling method to use is determined by evaluating the recharge rate and water column height of a given well (Figure 10).

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). Recharge rate is determined as shown in section B.3.2.A.7. 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 **purging the well dry** and sampling once replenished (Figure 10).

1. Attempt low-flow sampling (B.3.3.A) for water column heights > 0.5 m or the bailer method (B.3.3.B.) for water column heights < 0.5 m.
2. Calculate recharge rate (B.3.3.A.7).
3. If recharge rate <100 mL/min, select “sampling impractical, low yield well”
4. Write a trouble ticket to Science detailing the issue and include depth to water table for the well. There are 2 possible remediation’s:
    a. Change in sampled wells. Science may reconsider the wells chosen for sampling in the site sampling strategy if other non-sampled site wells show higher yield.
    b. Change in sampling method. Science will help determine if the low yield method (B.3.3.B.) or purging to dryness (B.3.3.D.) 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.

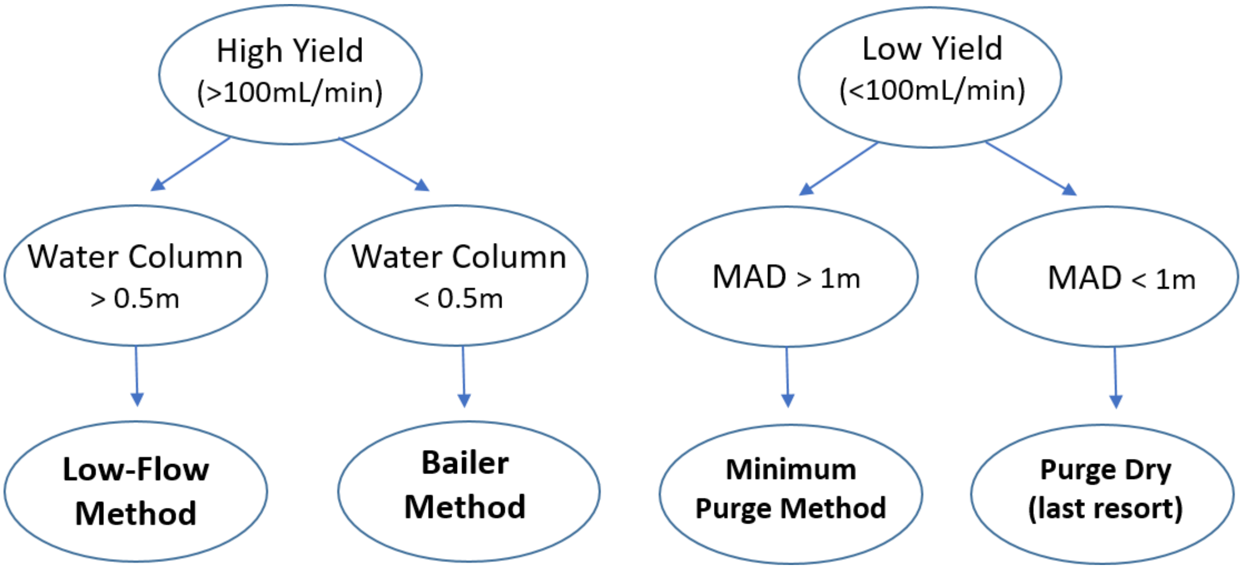


Figure 10. Decision tree for determining appropriate groundwater sampling method. MAD is the maximum allowable drawdown as described in section B.3.3.B.3.

### B.3.2. LOCATE WELL AND MEASURE DEPTH TO WATER

1. Locate Well. The NEON groundwater observation wells (OW) will look different depending on site host requirements and may be camouflaged at National Parks sites. Wells can be difficult to locate the first time, therefore a well map with GPS coordinates should be taken to the field the first time.

2. Unlock the Well. Open the lock and flip open the protective well lid, then remove the white PVC cap from the well.

3. 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. Disconnect the sensor from the cable to stop the data stream. Directions for removing and reconnecting the sensor from the cable can be found in the groundwater PM [RD12].
    c. 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.

2. Take key groundwater measurements prior to starting the groundwater extraction process (Figure 11).

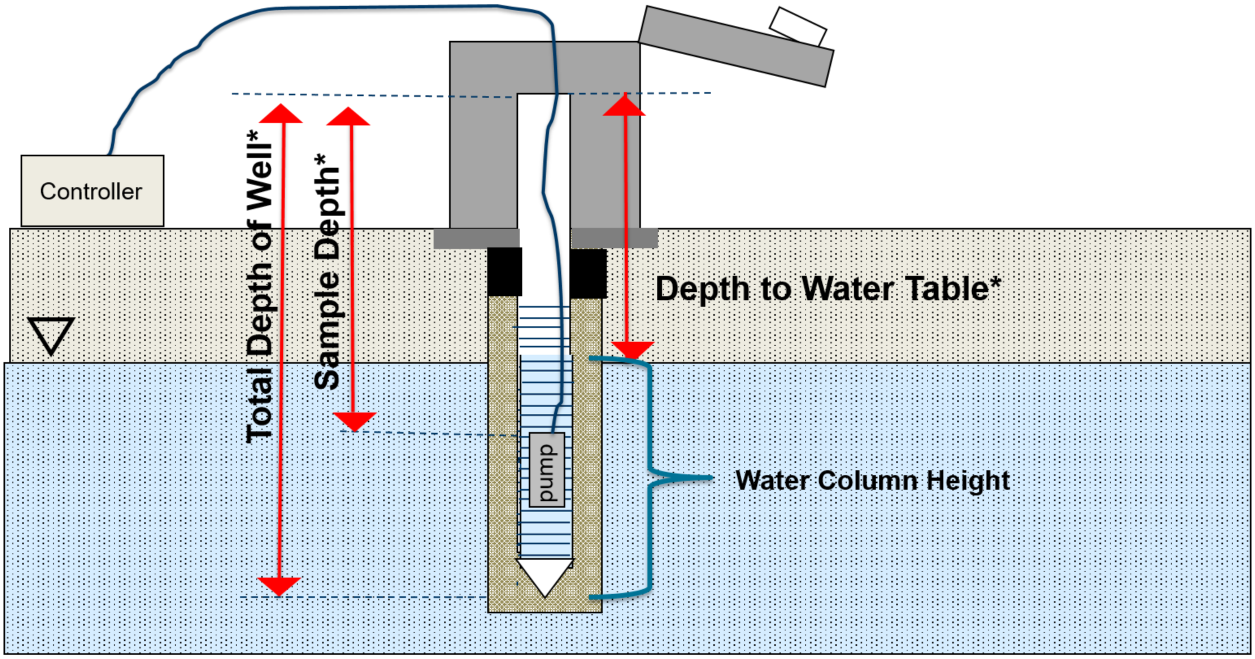
   a. Measure the **depth to water table** by measuring the depth from the top of the PVC well casing down to the water surface using the water level tape.

      (1) Attach the water level tape to the outer steel casing of the well (**Figure 12**b). 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.

      (2) Note the depth to water and time on the datasheet (RD[05]). 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 12**Figure 11c.

   b. Calculate **water column height.** 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 on the data sheet. (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 11. Key groundwater measurements

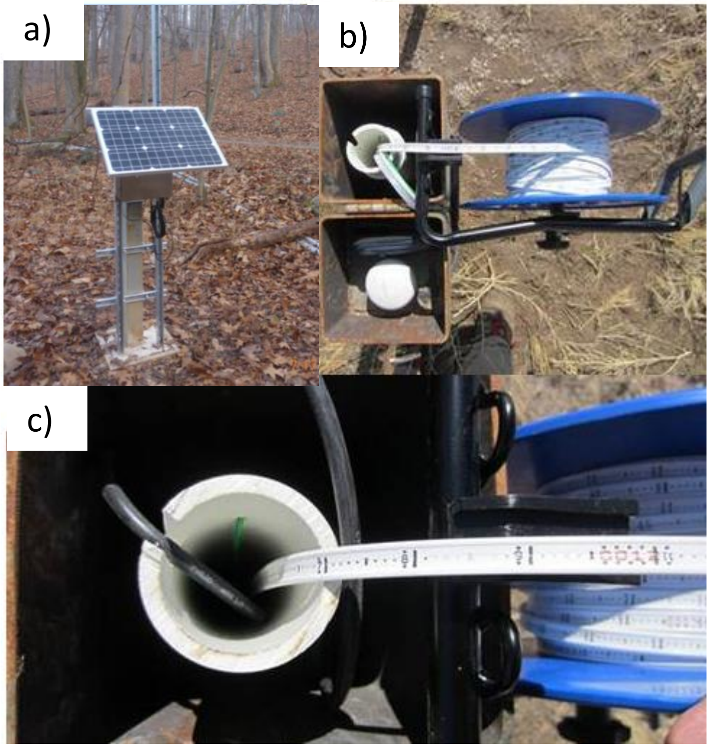


**Figure 12** (a) Standard groundwater well at a NEON site (b) Water-level tape attached to outer well casing. (c) Reading the depth to water from the water-level tape. The tapes are marked in "meters" with each foot increment marked in red. Readings are taken at the top of the inner PVC casing.

## B.3.3. EXTRACT GROUNDWATER FROM WELL

### A. 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 11) as shown in section B.3.2.2.c.
2. Calculate the depth to set the sampling pump as follows:

| Water Column Height (m) | Sample Depth (Top of Pump) |
|---|---|
| ≥ 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 m
Sample Depth: (5.55 m + 1 m) = 6.55 m

Example 2:
Total Depth of Well = 7.25 m
Depth to Water Table = 5.85 m
Water Column Height = (7.25 – 5.85) = 1.4 m
Sample Depth: (7.25 m –0.5 m) = 6.75 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. you may have your first groundwater chemistry sampling bout during a season high water time, and need to make sure there is sufficient tubing available if the water table is lower for your next event) 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 “gab 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" 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 14 (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.)

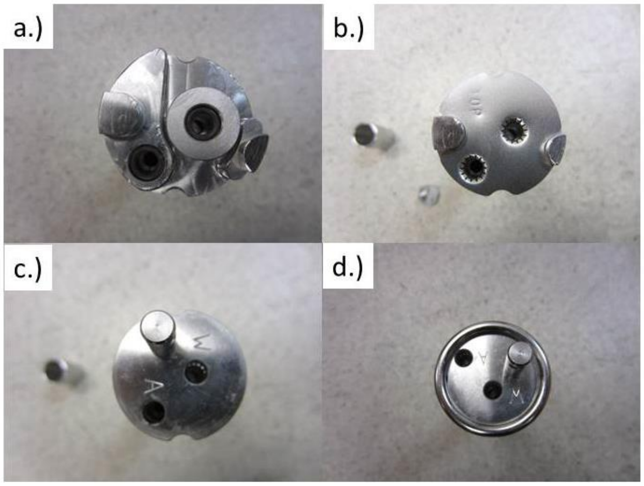


**Figure 13**. Assembly of the fitting plate at the top of the pump for holding the air and water lines. (a) Bare top of pump. (b) Fitting/grab plate added ("TOP" must face upwards). (c) Top plate added. (d) Collar added to lock parts (a-c) together.

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. Periodically this bladder will need to be replaced as it may develop holes from use or become heavily contaminated with sediment. 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 14** shows the components of the pump including the bladder.

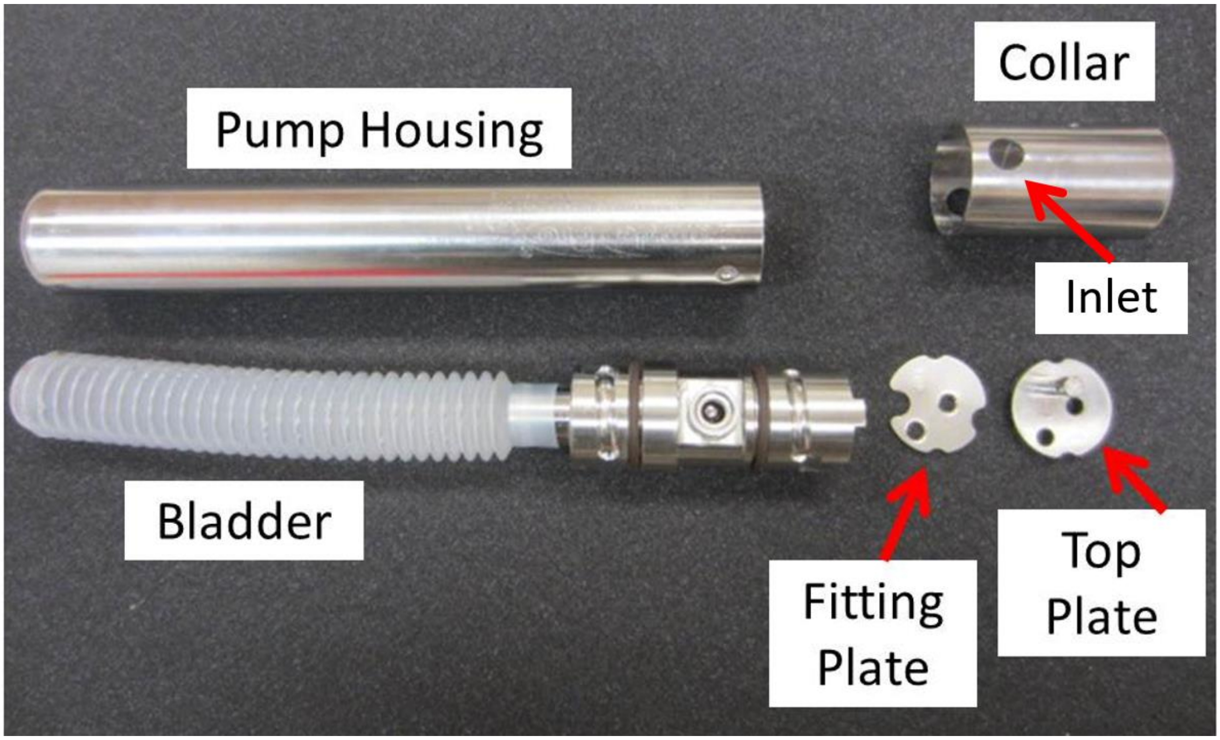


**Figure 14.** Components of the sampling pump

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 15**. (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 16**. Note: once attached, the post and cable can remain attached to the top plate/collar of the pump for future collections.

**Figure 15.** Attaching grey air-line and white water-lines to pump
(top-right photo shows lines pushed through top plate and “teeth” of grab plate)

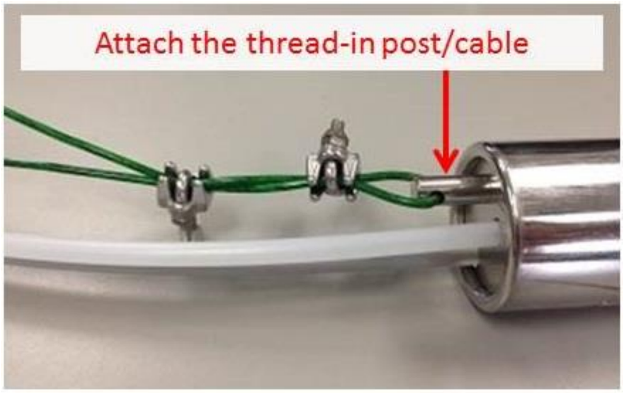


**Figure 16.** Attach post and cable to the pump via the top plate

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 17), 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 18).

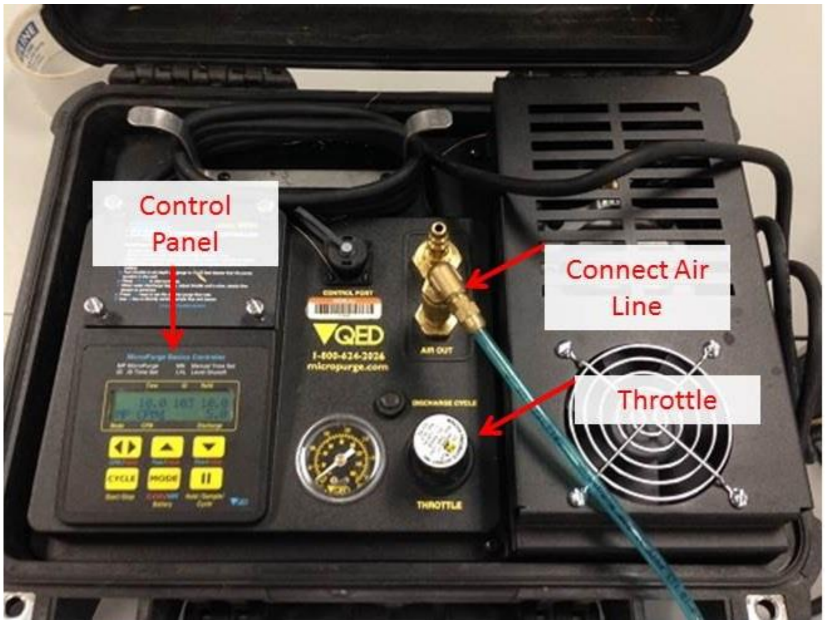


**Figure 17**. Attach blue air-line to controller

**Figure 18**. Attach grey air-line to blue air-line

b. Place the water discharge line into your collection cell (a 500 - 1000 mL plastic graduated cylinder works well). Place the hand-held water quality probe (YSI PRO2030) into the collection cell.

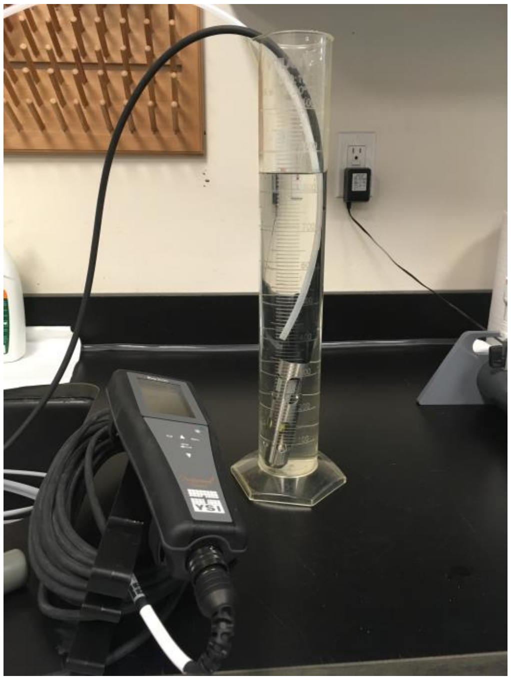


**Figure 19**. Groundwater Chemistry Collection cell using a 1000 mL graduated cylinder.

c. Operation of the Controller:

a) 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.

b) 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.

c) 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 on the data sheet.

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 20). 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 sec or 1 min intervals periodically throughout 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.

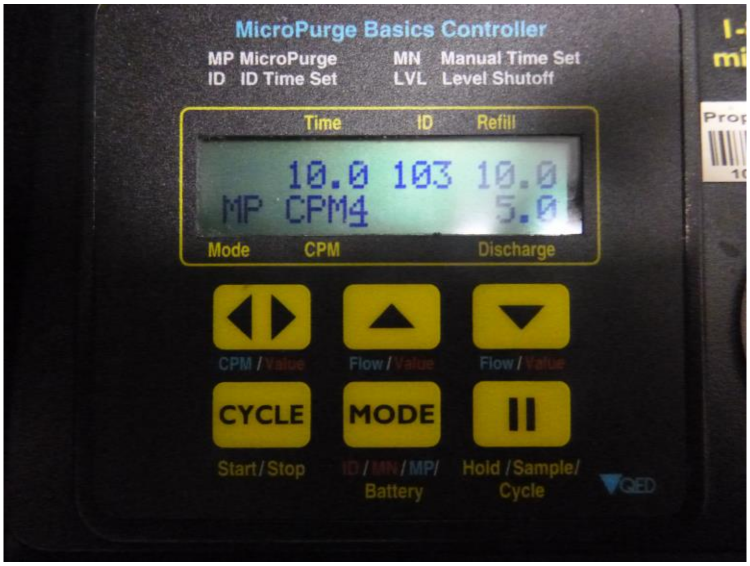


**Figure 20**. Groundwater pump control panel screen. Note the Refill and Discharge times on the right.

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.

10. Monitor water quality: While the pump is discharging water from the well, monitor the water quality parameters Dissolved Oxygen Saturation (%), Specific Conductance (uS/cm), and Water Temperature (°C) to provide a metric to determine when the water is ready to be collected for sampling.
    a. Specific conductance should be measured as temperature-corrected conductivity at 25°C, whenever possible. Ensure conductivity measurements are on the appropriate temperature-corrected and unit setting (i.e., setting SPC, uS/cm).
    b. 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.
    c. Once 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. 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.

11. Collect samples: The following sections detail the actual water samples to be collected and the procedure to do so. One 4 L jug of water will need to be collected from each well and should be collected all at one time.
    a. **Record** water quality parameters (SPC, DO, and Temp) at the time of sampling using the hand-held meter on the field datasheet (RD[05]).
    b. **Record** the sampling method and collect the sample.
    c. If you cannot get enough water for all GWW chemistry analysis, please prioritize in the following order and complete a trouble ticket:
        (1) $H_2O$ isotope
        (2) FIL*
        (3) RAW
        (4) ALK
        (5) PCN filter

    *If there is less than 1 L available, fill one 250 mL bottle rather than sending a partially full 1 L bottle.

## B. MINIMUM PURGE SAMPLING 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.

### Requirements for Feasibility

#### i. 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, FIL, RAW, ALK, PCN filter. However, it is necessary to discontinue the sampling once maximum allowable drawdown is reached (SOP B.3.b.ii.). If maximum allowable drawdown is less than 1 m do not use this method.

#### ii. 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.

### Methodology

1) 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 21). Tubing with 1/8"ID will fit in the same slot as the cable.
    - **a.** 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.
    - **b.** Care should be taken to cause minimal disturbance to the water column.

Figure 21. Pump tubing secured in place with zip tie.

2) 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 14). This is the specific point on the pump to set to the specified depth. When placing the pump, measure from this point.**
3) 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. 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.

    a. If water table is above the screened interval of the well:
        MAD = depth to pump placement – depth to top of screen - 0.5m

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

    b. If water table is within the screened interval of the well:
        MAD = depth to pump placement – depth to water table - 0.5m

    Example 2:

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

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

4) Prior to sampling, remove a set volume based on tube length (Table 10). Measure and record water temperature, temperature-corrected conductivity, and DO percent saturation for the discharged water. Divide the volume removed into thirds and use it to rinse the 4L jug 3 times.
5) 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 in the following order and submit a trouble ticket: H2O isotope, FIL*, RAW, ALK, PCN filter.
*If there is less than 1 L available, fill one 250 mL bottle rather than sending a partially full 1 L bottle.

Table 10. 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 |

6) 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.
7) 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.
    a. Weight the end of the peristaltic pump tubing with stainless steel nuts as shown in figure 22. 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.
    b. 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.
    c. Proceed to sample using method 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 in to the field.

Figure 22. Nuts added to peristaltic pump tubing for weight.

## C. BAILER TUBE METHOD

Domains with shallow groundwater, such as in the Tundra and Taiga domains where there is a limited liquid on top of the permafrost layer, will require the bailer tube method. This method is applied for shallow wells that are high yield, but have less than 0.5 m of water. 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 23**). Note: you may also use the peristaltic pump instead of the bailer tube to remove the three well volumes, as indicated below.

**Figure 23**. Image of bailer tube

1. Lower the tube into the well on the end of a rope below the static water level filing-up the bailer tube with water.

2. 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 <u>**three**</u> "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:

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

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, $\pi\ r^2 = 8.03\ cm^2$). **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 (0.66m)x(0.8L/m of water) = 0.53L of water. The three well volumes are equivalent to 1.59L of water.

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.

3. **Record** water quality parameters (SPC, DO, and Temp) 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 on the field datasheet (RD[05]).

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

### D. 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 bailer or peristaltic pump at a high rate to drain the well. 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.
2) Return within 24 to 48 hours to directly sample the volume that has return to the well.
    a. Remove 100mL from well. Record pre-sampling information on this volume and use it to rinse the 4L jug.
    b. Sample well. When obtaining the full sample volume is not possible, prioritize in the following order: H2O isotope, FIL, RAW, ALK, PCN filter.

### B.3.3 FIELD SAMPLING – GROUNDWATER (ALL METHOD EXTRACTION TYPES)

After recording water quality parameters, sampling method, and approximate volume of water discharged:

1. Rinse a 4 L 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 the minimum purge method and purge dry method, a modified rinse may be used as described above.
2. Collect an unfiltered water sample: Fill the 4 L jug (or more if necessary).

Collect water in a 4 L jug to be divided and filtered into appropriate containers (Figure 3). Cap the jug, set aside for SOP C. Set the jug in a cooler with ice.

## SOP C Sample Processing

In **wadeable streams**, fill the collection bottle by placing the bottle 10 cm below the water surface with the opening pointed upstream (Figure 7) or pump water directly out of the stream from 10 cm below the water surface. If you are not filtering directly out of the stream, collect water in a 4 L jug to be filtered into appropriate containers (**Figure 3**). In **lakes and non-wadeable streams**, use the Kemmerer to collect unfiltered water in one - two 4 L jugs from the desired depth. Cap the jug, set aside for Section C.2 (Collect Filtered Water). For **groundwater** sampling, collect water from the white/clear tubing coming out of the well while the pump is running (after values have stabilized, as described above).

### C.1 Collect Unfiltered Water (RAW)

1. After triple rinsing, collect unfiltered water samples using the appropriate sampling method, described above. Be sure to loosely cap bottle while lowering the bottle 10 cm below surface so as not to collect surface film. Remove cap and allow container to fill, keeping the container horizontal to the stream. Recap bottle under stream.
2. If you collected the sample in a 4 L jug, use sample water in the jug (shaken to re-suspend particles) to rinse (3 times) the sample bottles for the 2 samples that do not require filtering (**Figure 3**):
   a. 250 mL burned amber glass bottle for external lab (Code RAW) – with headspace, filled to just below the neck to reduce potential for breakage if bottle freezes during shipment.
   b. Acid Neutralizing Capacity: 250 mL wide mouth HDPE – **FILLED/NO HEADSPACE** (Code ANC) ***to be analyzed at the Domain Support Facility.**
      a) Fill the ALK collection bottle **COMPLETELY** to the rim and close cap tightly to minimize headspace.
3. Record data in the mobile app.
   a) If available, scan the barcode label with the tablet (Figure 24).Figure 22).
   b) Ensure that the human-readable sample ID matches the sample ID generated by the mobile app.

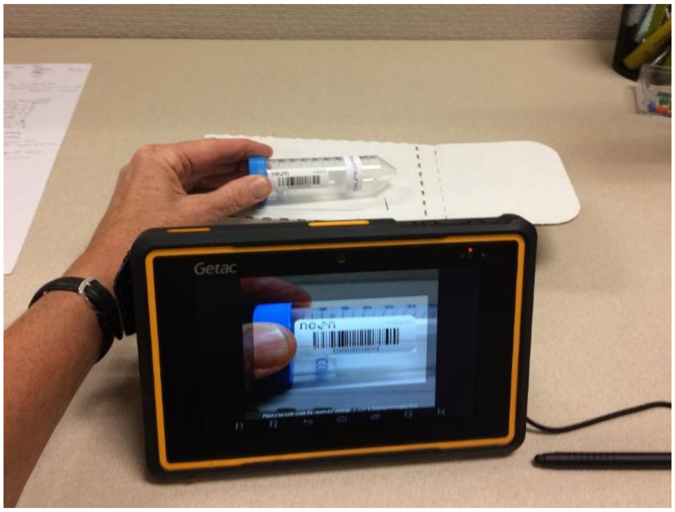


**Figure 24**. Barcode label scanning.

4. Collect an additional 4 L jug to be filtered for Total Particulate Carbon and Nitrogen (code PCN) analysis (NOTE: the **filter** is your sample and will be analyzed for PCN; SOP C.5). You may need less than 4 L. This is site specific.
5. IMMEDIATELY chill samples (4°C ± 2 °C). DO NOT FREEZE.

## C.2 Collect Filtered Water Samples (FIL)

In **wadeable streams** and **groundwater** 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.

1. Set-up of Peristaltic Pump Apparatus (**Figure** 25):
   a. The peristaltic pump should be fitted with peristaltic tubing connected to ¼ in Inner Diameter (I.D.) C-Flex tubing on either end (**a**).
   b. Place a **CLEAN** end of the tubing in the 4 L collection jug (**b**). Rinse tubing with DI water before placing in jug if necessary.
   c. Attach the other end of the tubing to a $^3/_8$ – ¼ in tubing connector, which is then attached to the peristaltic tubing and pump (**c**).
   d. The other end of the pump should connect to a $^3/_8$ – ¼ in tubing connector.
   e. Attach one end of ¼ in C-flex tubing (2 ft long) to the tubing adaptor (**d**).
   f. Using the drill peristaltic pump, rinse tubing with approximately 100 mL of sample water. The direction of the drill pump can be changed, if necessary.
   g. When tubing has been rinsed and is mostly filled with water (i.e., no large air pockets), attach the end of the outflow tubing to an unused filter capsule fitted with a tubing connector (**e**).

   a) **NOTE:** make sure to attach filter so that the direction of flow follows the flow arrow on the capsule filter.
   b) Filter approximately 100 mL of sample water to rinse the filter, and discard this rinse water

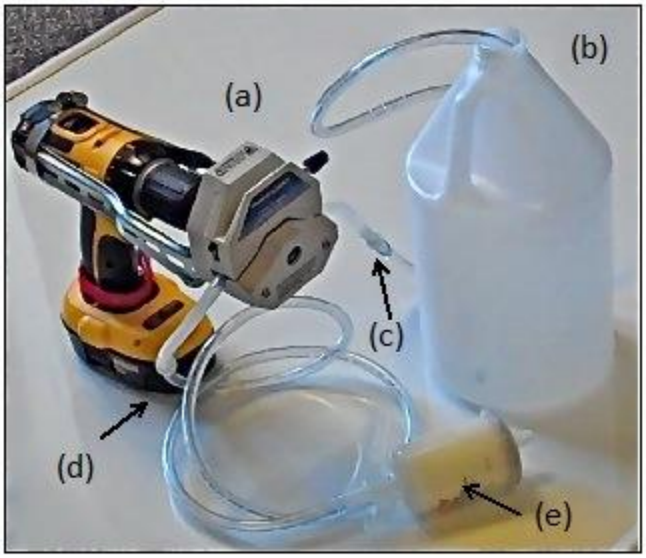


**Figure 25.** Pump and filter setup, including (a) a peristaltic sampling pump (modified from Woessner 2007), (b) a 4 L sample bottle, (c and d) tubing connectors to connect peristaltic and C-flex tubing, and (e) a capsule filter

2. 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
3. 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
4. Ensure the tubing stays completely submerged in the water at all times.
5. **Fill filtered glass sample bottle (FIL, Figure 3) and ALK bottle completely (NO HEADSPACE).**
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.
7. Record data in the mobile app.
   a) If available, scan the barcode label with the tablet (Figure 24).Figure 22).

   b) 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°C ±2°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. 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).

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

Use the water collected in a 4 L jug as described in step 5 of SOP C.1. Filter with vacuum pump and filter funnel to obtain a particulate sample on filter (Figure 26).

1. Rinse filter unit, filter screen and filter funnel (Figure 26) with DI water, making sure no particulates remain on the filter screen or funnel. Note: Filter screen is easily lost. Be careful when rinsing.
2. 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.
3. Remove the filter funnel from the base, leaving the filter unit and screen resting on the manifold stem.
4. 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 grid side is down.
5. Replace the filter funnel, rinsing with DI if necessary before replacing. 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.
6. Place the filter box back in the Ziploc bag to keep the filters from getting wet or blowing away.
7. Attach the vacuum pump tubing to the filter flask (Figure 26).
8. Rinse the filter with DI water. Use the vacuum pump to create suction in the flask and draw the DI water through the filter.
9. 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).
10. 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.
11. Resuspend particulates (shake for 15 s) and immediately pour the water into the graduated cylinder, to be measured. You must resuspended 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.

12. 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.
13. 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.
14. 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).
    a. In waters with low particulate (i.e., clearwater lakes), filter a minimum of 2 L of sample.
    b. In high particulate systems, make sure there is not too much particulates on the filter that may squeeze out of the filter when folded
15. **IMPORTANT: Keep track of the amount of water you filter**. We will need the total volume filtered for the PARTICULATE calculation. See step 18 and 22.
16. Use a DI water squirt bottle to rinse down the particulates on the sides of the filter funnel.
17. Continue to pump until all the water is drawn through the filter.
18. 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.**
19. **Record total volume of sample water filtered** on datasheet (RD[05]), sample label (step 22) and the shipping inventory (RD[11]). Do NOT include the DI rinse water in the TOTAL sample volume filtered.
20. 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 on the filter with forceps.
    a. 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.
21. **Be Careful.** If filter tears or rips, begin filtration over with a new filter and sample water.
    a. **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.
22. Place filter on 4 X 4 in piece of aluminum foil, fold foil around filter and add label. Circle lab code PCN and make sure volume filtered is filled out.
23. Record data in the mobile app.
    a) If available, scan the barcode label with the tablet (Figure 24).Figure 22).

   b) Ensure that the human-readable sample ID matches the sample ID generated by the mobile app

24. Double bag foiled filter in resealable plastic bag and place in cooler. If you have multiple filters, from different sites and or stations, it is OK to place them in the same bag.
25. 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)

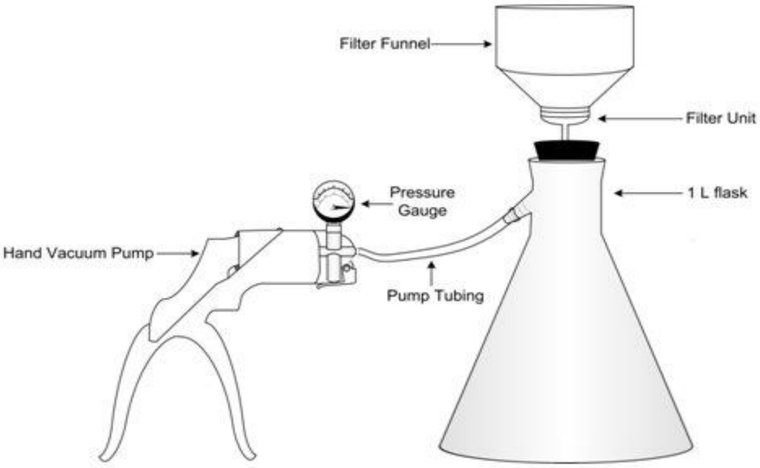


**Figure 26.** Filter apparatus set-up for particulates, using a) the vacuum pump and filter manifold, and b) the hand vacuum pump attached to the filter flask and filter funnel.

## C.4 Ending 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 6.1.

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.

## SOP D Laboratory Sampling and Analysis

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. 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.

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

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

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

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

## D.1 Sample Processing Timing

Following sample collection, alkalinity and ANC samples should be kept on ice or refrigerated at 4°C ±2°C, unless they are processed immediately. Laboratory analysis should be completed as soon as possible after returning from the field. Alkalinity and ANC samples should be processed within 24 hours. Samples analyzed after the 24 hours window will be flagged. The maximum allowable time period between sample collection and analysis is 72 hours. It is advised to not collect field samples on Friday, unless alkalinity and ANC can be measured in the Domain Support Facility on Friday afternoon.

## 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.
    a. If present, turn dial at top of pH meter to open while performing titrations. Ensure dial is closed when titrations are complete.
2. Allow pH buffers 4 and 7 to come to room temperature before calibration by allowing the sample bottle to sit on a lab bench until the temperature has equilibrated. 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.
    a. Make sure buffer solution has not expired and is not reused.
        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.
    b. 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 plastic, to help sample come to room temperature more quickly. 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 Sample Processing in the Lab

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

    Note for Gran Method Users: This protocol details the IPT Method, although the information in the steps is still useful to the Gran Method users. See USGS Gran method (Rounds 2012) for detailed instructions on using the Gran Method to calculate alkalinity. Contributing carbonate species will not be determined). In short, titrate **to change pH 0.2 – 0.3 pH units (**DO NOT GO TOO FAST). Titrate to pH of 3.5. Do NOT use a stir bar if conductivity is < 100 µS/cm, but swirl solution gently (20 seconds, do not create a vortex) between additions. Wait 15 seconds before recording data and adding more acid. NOTE: You do not need to wait for the pH meter to stabilize. It is better to be consistent with the wait time than to wait for the pH meter to stabilize, which might never happen.
2. Determine the sample volume and acid normality you will use (Table 11). 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 0.16*N* titrant, and adjust as necessary. 1.6*N* will only be used when alkalinity or ANC is greater than 4.0 meq/L, although it may not be necessary. Table 11 provides suggested sample volume and titrant normality, but should be adjusted as necessary per site. Following initial data analysis, we suggest using 150 mL of sample if measured value is < 1.0 meq/L.
3. Record sample titration normality on the Datasheet (RD[05]).

**Table 11.** 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 | 100 | 0.1600 | 150 |
| 1.0-4.0* | 50-200 | 50 | 0.1600 | 100 |
| 4.0-20 | 200-1000 | 100 | 1.600 | 150 |
| >20 | >1000 | 25 | 1.600 | 50 |

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

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

   b. Insert cartridge into the end slot of the titrator (Figure 27) and **rotate cartridge** one-quarter turn to lock into place.

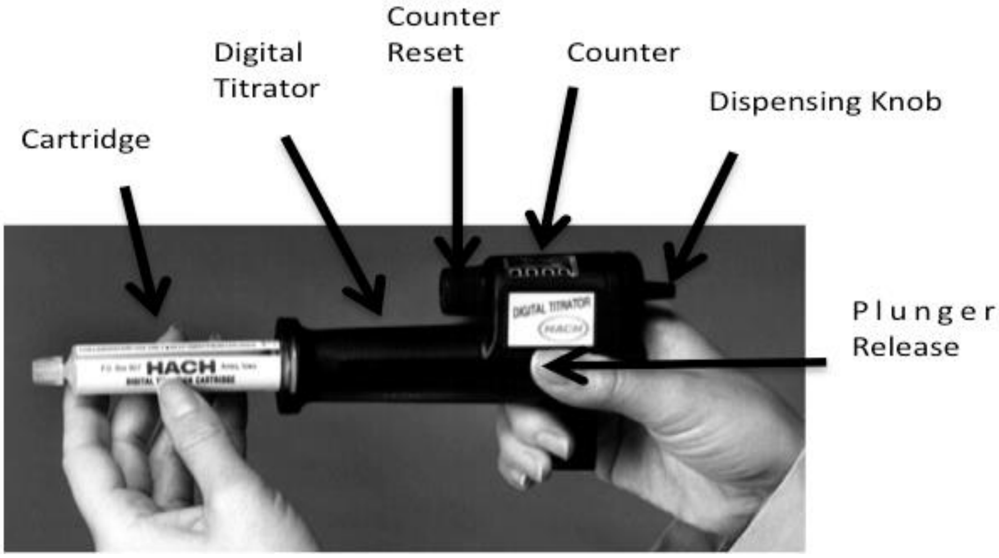


**Figure 27.** Inserting titrant cartridge into digital titrator. Photo from the Hach Digital titrator manual

   c. Depress plunger-release button and push plunger forward until it is touching inside of cartridge. If plunger will not engage with the cartridge, ensure that the cartridge has been rotated one-quarter turn and is locked into place.
   d. Attach titrator set up to titrator bracket on the mounting bracket.

5. While wearing gloves, remove cap on titration cartridge and insert a clean titration tube into the cartridge tip (Figure 27). 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.

**Figure 28.** Digital titrator with titrant cartridge and titration tube attached. Photo from the Hach Digital titrator manual.

6. Turn the delivery knob to expel a few drops of titrant into a discard/acid waste container (Figure 29). This should remove air bubbles from the tube.

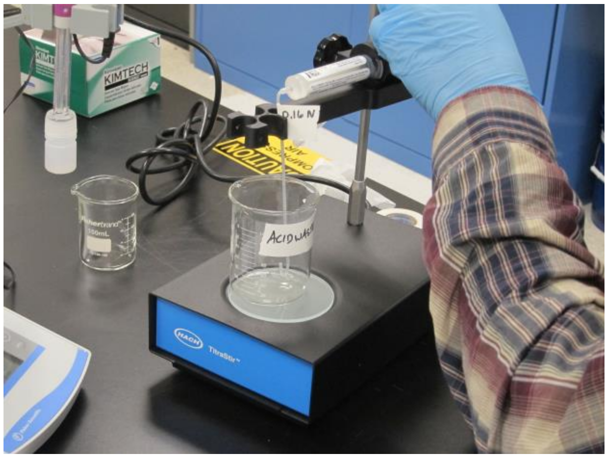


**Figure 29.** Diagram of procedure to expel acid from digital titrator set-up into a temporary acid waste container.

7. **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.
   b. Once the counter has been set to zero, do not turn the delivery knob.
8. If conductivity is greater than **100 µs/cm**, place a clean, small, magnetic stirrer into the appropriate sized beaker (Table 11). **Do not use a stir bar if conductivity is less than 100 µs/cm. Using a stir bar in low conductivity water will increase the diffusion of gases into the sample and alter the pH**
9. Shake sample bottle for 30 s to homogenize.
10. Using a clean **volumetric** pipette (for alkalinity, filtered sample) or a graduated cylinder (for ANC, unfiltered sample), measure out the appropriate volume of sample and transfer to appropriate glass beaker (Table 11). 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.
    a. A small amount of sample will remain in the pipette tip when dispensing the sample from the pipette to the beaker. Touch and hold the tip of the pipette to the beaker wall and allow pipette to drain. Once flow from pipette stops, hold tip against the beaker wall for 10 more seconds to remove the majority of sample. A small volume of sample will be retained in the pipette.
11. 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.

12. **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 sample to stabilize as long as your swirls are consistent. Do not swirl so fast that you create bubbles or a vortex in the sample.
13. Rinse pH meter and temperature sensor with deionized water. Be cautious not to rinse probes over sample.
14. 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 pH sensor bulb, sensor reference electrode and temperature sensor (Figure 30). 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.
15. **Record:** 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.
16. 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 30).

**Figure 30.** 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

17. **Add Titrant** (Table 12). 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 in a spreadsheet. Near equivalence points (pH ~10, 8.1 and 5), pH can change rapidly (Figure 31). **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 you 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 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.
    a. pH ≥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 the stirrer to homogenize the sample for 15 s. Record pH and counter reading on the Alkalinity/ANC laboratory data sheet (RD[05]).**
    b. pH <5.5 - <u>Bicarbonate equivalence point</u>. Cautiously and slowly add titrant in small (but do **NOT** add less than **<u>three counts</u>** 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 a computer program.**

**Table 12.** 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 |

18. When possible, enter data into computer spreadsheet and graph the titration curve (change in pH divided by change in titrant volume (y-axis) by volume of titrant added (X-axis) (Figure 31).
    a. If more than one inflection point occurs in proximity, the true inflection point has been missed, and a duplicate sample should be analyzed being sure to take precaution and add titrant in smaller increments around the inflection point.
    b. If more than one titration inflection point occurs at 2 or more points near the equivalence point and you have used the minimum number of counts, you do not need to redo the analysis.

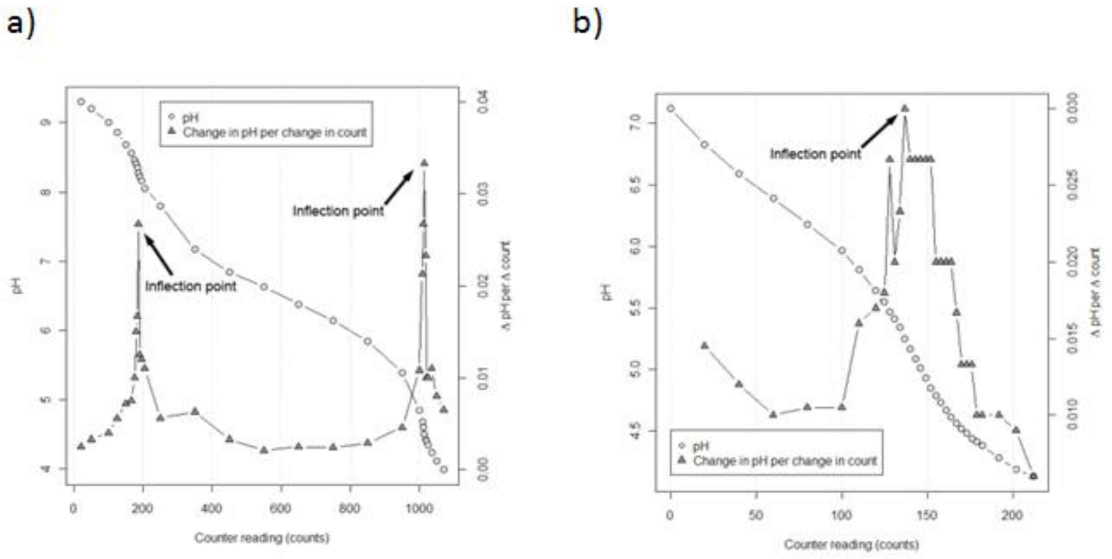


**Figure 31.** Example of inflection point titration using a digital titrator of a) a high alkalinity sample and b) a low alkalinity sample. Note difference in Y-axis scale. (Modified from USGS TWRI Book 9, Alkalinity, Version 3.0 7/2006).

19. 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.
20. Dispose of sample.
21. Repeat for all remaining samples at all stations.

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

## D.4 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. Refer to section 6.1.

### 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. However, to ensure that the titrator has maintained calibration, annually perform a calibration check, using a known sample, of the accuracy and precision of the digital titrator. This will be part of the Cal/Val equipment plan.
    a. Hach titrators have a lifetime warranty. Please contact the manufacturer for trouble shooting.

## 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. For detailed instructions on protocol specific data entry into mobile devices, see the NEON Internal Sampling Support Library (SSL). 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.

## SOP F Sample Shipment

Information included in this SOP conveys science-based packaging, shipping, and handling requirements, not lab-specific or logistical demands. For that information, reference the CLA shipping document on CLA's NEON intranet site.

Shipments are to have a hardcopy of the "per Sample" tab of the shipping inventory (RD[11]) sent in each box as well as an electronic shipping inventory that is emailed to the receiving laboratory and to the contact in NEON Collections and Laboratory Analysis at the time of shipment. ShipmentID (shipment tracking #) must be included in the electronic version of the shipping inventory, but is not necessary for the hard copy. Also include the shipment tracking # in the email.

Shipment files should be named: *DXX_SWC_ShippingInventory_YYYYMMDD*, where YYYYMMDD is the date shipped. If multiple shipments are sent on the same day: *DXX_sWC_ShippingInventory_YYYYMMDD_#of#*

### 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. Pack glass bottles in packing material for protection from breaking.
2. Place samples into the cooler (suggested: 9 -12 qt for 1 station, 12 qt for 2 stations, or 28 qt for 4 stations) and add ice or ice packs (**0˚C ice packs Do NOT use dry ice.**). Cooler sizing is site and season specific. Please adjust as necessary to ensure bottle arrive intact and at the appropriate temperature. **ALL** water chemistry samples should be surrounded by the ice or ice packs, including the filter(s) (wrapped in foil and placed in a resealable plastic bag). Water ice allows you to better surround each bottle and keep the samples cool.
    a. There should be at least an equal volume of ice and samples in the cooler.
    b. During summer months:
        a) Cool samples before shipping in ice in the field or refrigerator in the lab.
        b) Place fresh ice/ice packs in cooler before shipping, especially during summer months.
        c) Place more ice packs in cooler, since coolers may sit outside in the sun for several hours.
    c. If water ice is used, line cooler with a small trash bag and tie up to prevent water leakage if ice melts. Additionally, if ice is used, care must be taken to pack sample bottles securely, in case ice melts (e.g., attaching egg crate foam to the inside of the cooler and cooler lid, using foam to separate bottles (**Figure 32**), wrapping bottles in bubble wrap (note this keeps ice from sample and may not keep sample as cool in hot summer months, so use cautiously) and placing in a

resealable bag, or placing ice in resealable bags, so if the ice melt the water filled bag will still provide a cushion for the bottles).

**Figure 32.** One example of protective shipping using foam and ice packs.

3. Surround bottles with absorbent packing material.
4. Fill remaining space with regular packing material.
5. Prepare a shipping inventory detailing the contents of the shipment, using the protocol-specific templates found on CLA's NEON intranet site. Include a printed copy of the inventory in the shipment box. Place 'per sample' tab of AOS shipping inventory (RD[11]) in a resealable plastic bag and tape to the inside top of cooler. Include a return shipping label (F.6)
6. Tape the cooler shut and ship to appropriate address
7. Save the inventory with the following naming convention: "**DXX_MOD_ShippingInventory_YYYYMMDD**" ex) D02_SWC_ShippingInventory_20151015
    a) If multiple shipments are sent on the same day: *DXX_SWC_ShippingInventory_YYYYMMDD_#of#*
   b. Complete packing slip, address shipment, and ship ground to the destination(s) specified in the CLA "Shipping Information for External Facilities" document.
   c. Email an electronic copy of the shipping manifest and tracking number to the email addresses listed in the CLA "Shipping Information for External Facilities" document.
   d. Include the shipment tracking # (Shipment ID) in the email body, as well as the electronic copy of shipping manifest.

## 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.
2. Place return shipping label and the AOS sample shipping inventory (RD[11]) 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

Fill out the AOS Sample Shipping Inventory (RD[11]). Each box sent should have a copy of the ‘per sample’ tab of the shipping inventory of its contents. The ‘Shipment ID’ does not need to be filled out on the hardcopy. The electronic shipping inventory that includes ShipmentIDs and IDs of all samples shipped should be emailed to the appropriate contact at the receiving analytical laboratory as well as the NEON CLA contact on the day that samples ship. Include shipping IDs and estimated arrival date(s)/time(s) in the email as well.

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

See the CLA shipping document on CLA’s NEON intranet site.

## 8 REFERENCES

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

Nielsen, David M., and Gillian Nielsen, 2006. The essential handbook of ground-water sampling. CRC Press.

Nevers, M.B., and R.L. Whitman, 2007. United States Geological Survey, USGS Lake Monitoring Field Manual.

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

Puls, R.W. and Barcelona, M.J. 1996. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures: EPA Ground Water Issue. Report EPA/540/S-95/504.

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

Rounds, S.A., 2012, Alkalinity and acid neutralizing capacity (ver. 4.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., sec. 6.6, September 2012, accessed December 2, 2012, from http://pubs.water.usgs.gov/twri9A6/.

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

YSI Model 85 Calibration Instructions. http://www.aquaticeco.com/YSIManuals/85.pdf

## APPENDIX A DATASHEETS

The following datasheets are associated with this protocol:

**Table 13.** Datasheets associated with this protocol

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

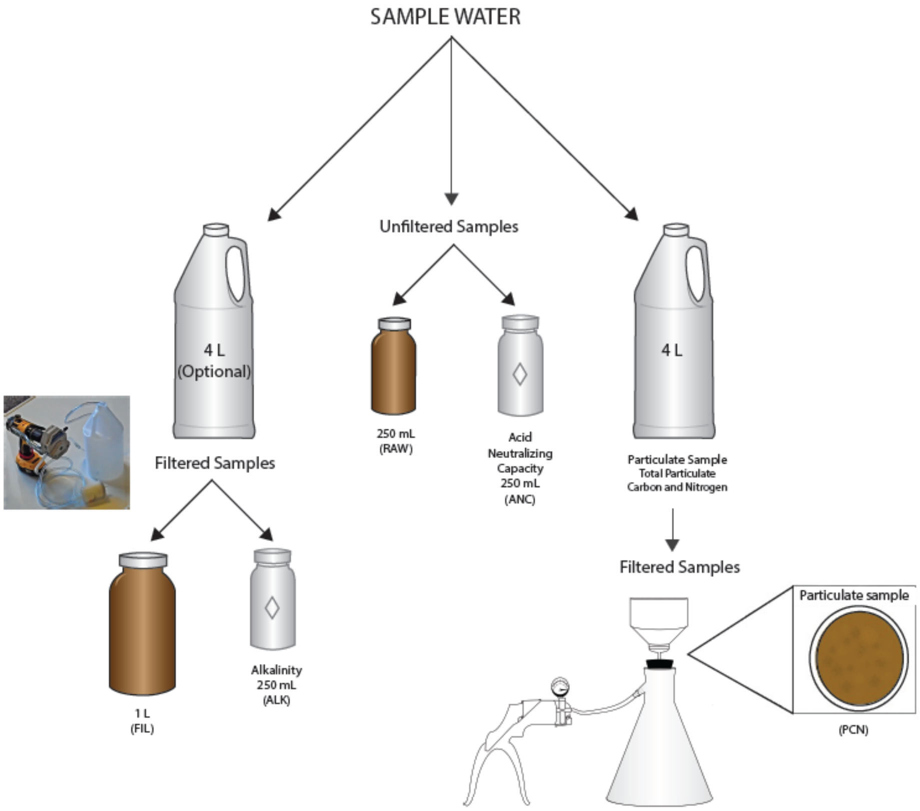
These datasheets can be found in Agile or the NEON Document Warehouse, user guides for mobile applications may be found in NEON's internal sampling support library.

# APPENDIX B QUICK REFERENCES

## B.1 Considerations for Implementation

Samples must be kept cool at all times (4°C ± 2°C). Samples should be processed (filtered and chilled) within 3 hours, but if logistical constraints make it difficult, processing samples within 6 hours is acceptable. The sooner the samples are processed, the better the data quality. If there is a problem with sample filtration and particulates can still be seen in the filtered samples, samples can be re-filtered, ONLY if it is within the 6-hour time window from collection.

## B.2 Flowchart of Sample Collection and Filtration

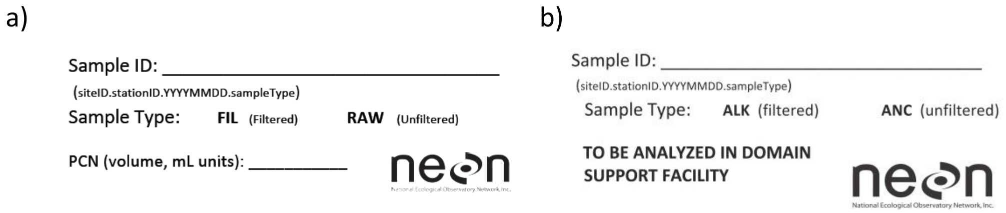


◊ Indicates sample bottles that will remain at the Domain Support Facility for analysis. Letters in parenthesis indicate the codes that correspond to the chemistry labels.

## A.3 Steps for Water Chemistry Sampling

**Step 1** – Check the water chemistry field sampling kit to make sure all supplies are packed.

**Step 2** – Prepare labels (2” * 4”).



a)

Sample ID: ___________________________

(siteID.stationID.YYYYMMDD.sampleType)

Sample Type: **FIL** (Filtered) **RAW** (Unfiltered)

PCN (volume, mL units): __________

b)

Sample ID: ___________________________

(siteID.stationID.YYYYMMDD.sampleType)

Sample Type: **ALK** (filtered) **ANC** (unfiltered)

**TO BE ANALYZED IN DOMAIN SUPPORT FACILITY**

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

**Step 3** – Ensure the General AQU Field Metadata Sheet (RD[07]) is completed per field site visit.

**Step 4** – Navigate to the sampling location or groundwater well. In lakes take a Secchi depth reading and determine thermal stratification.

**Step 5** – Rinse the collection bottles and caps with the appropriate sample water (i.e., use filtered water to rinse filtered samples).

**Step 6** – Collect samples

1. Filtered Samples: Fill ***FIL*** and ***ALK*** bottles completely to reduce any changes in $CO_2$ concentrations due to headspace:
    a. 1-L burned amber glass bottle for external lab – FILLED completely full (Code **FIL**)
    b. ANC - 250 mL wide-mouth, HDPE – FILLED completely full (Code **ALK**) *to be analyzed at the Domain Support Facility.
2. Unfiltered Samples: Fill ***RAW*** and ***ANC*** bottles completely to reduce any changes in chemistry due to headspace:
    a. 250 mL burned glass amber bottle – FILLED completely Full (Code **RAW**)
    b. Acid Neutralizing Capacity: 250 mL wide mouth HDPE – FILLED completely full (Code **ANC**) *to be analyzed at the Domain Support Facility.
    c. 4 L jug (for PCN and/or Filtered Sample)

**Step 7** – Filter for PCN particulate samples. Place filter grid side down/smooth side up.

**Step 8** – Ship samples overnight with ice packs within 24 hours of collection.

**Step 9** – Complete ALK and ANC titrations in Domain Facility.

# APPENDIX C REMINDERS

**Before heading into the field:** Make sure you…

- Collect and prepare all equipment including labels and filters.
- Pre-print labels on waterproof paper.
- Fill out the labels before they get wet.

**Sample collection:** Be sure to…

- Do not sample anywhere you or other field technicians have walked, or locations that appear recently disturbed. Wait for disturbance to pass.
- Use caution when sampling as items can easily fall into water while sampling.
- Fill bottles completely (no headspace).
- 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 water into the filter tower than you can filter.

**Sample titrations:** Be sure to…

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

## APPENDIX D ESTIMATED DATES FOR ONSET AND CESSATION OF SAMPLING

See the Site Specific Sampling Strategy Document on FOPS's NEON intranet site.

## APPENDIX E SITE-SPECIFIC INFORMATION

See the Site Specific Sampling Strategy Document on FOPS's NEON intranet site.