



DEPARTMENT OF
ECOLOGY
State of Washington

Standard Operating Procedure EAP099, Version 1.2

Collecting Groundwater Samples: Purging and Sampling Monitoring Wells for General Chemistry Parameters

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Purpose of this Document

The Washington State Department of Ecology develops Standard Operating Procedures (SOPs) to document agency practices related to sampling, field and laboratory analysis, and other aspects of the agency's technical operations.

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The Washington State Department of Ecology's (Ecology's) Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

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Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Revision History	Summary of changes	Sections	Reviser(s)
8/2/2016	1.0	Initial publication	all	Carey, Kammin
8/28/2019	1.1	Format changes	all	Marti, Kaza
7/14/2023	1.2	Minor editorial changes.	all	Marti, P.B.

1.0 Purpose and Scope

- 1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for collecting samples for general chemistry parameters from monitoring wells.
- 1.2 For the purposes of this SOP, general chemistry includes nutrients (nitrogen and phosphorus), total dissolved solids, organic carbon, as well as cations and anions (to evaluate charge balance and describe hydrochemical grouping). Standard cations and anions include carbonate/bicarbonate (alkalinity analysis), calcium, magnesium, sodium, potassium, sulfate, and chloride. For iron and manganese standard sampling procedures, see EAP100 (Pitz, 2023).
- 1.3 Goals for collecting groundwater samples from monitoring wells can include characterizing ambient conditions, defining the nature and extent of groundwater problems, determining trends in contaminant concentrations, and evaluating compliance with groundwater standards or regulatory requirements.
- 1.4 Groundwater measurements and samples should be as representative of in situ conditions as possible. Factors that can alter groundwater chemistry during sampling include changes in temperature, pressure, and exposure to air. This SOP summarizes the general procedures and practices that EAP staff use to collect representative groundwater samples from monitoring wells, piezometers, or other wells that typically lack dedicated, in-place pumps.
- 1.5 When sampling wells that are not designed for groundwater monitoring, e.g., water supply wells or irrigation wells, see EAP Standard Operating Procedures for Collecting Groundwater Samples for General Chemistry Parameters from Water Supply Wells (Carey, 2023).

2.0 Applicability

- 2.1 This SOP provides general information to help guide EAP field staff in proper purging and sampling techniques for general chemistry parameters. Alternative procedures may be used if they provide scientifically valid and legally defensible groundwater data and are documented in the project Quality Assurance Project Plan (QAPP).
- 2.2 Field staff should be familiar with additional standard procedures related to activities described in this SOP. If samples are also being collected for organics or metals, see procedures described in separate SOPs, EAP078 for organics (Marti, 2023b) and EAP100 for metals (Pitz, 2023), on Ecology's web page: <http://www.ecy.wa.gov/programs/eap/quality.html>.
- 2.3 Documents such as the *USGS National Field Manual for the Collection of Water-Quality Data* (USGS, 1997) and the *Essential Handbook of Groundwater Sampling* (Nielsen, 2007) have additional detailed explanations of factors to consider when sampling monitoring wells.

3.0 Definitions

- 3.1 Aquifer – A formation, group of formations, or part of a formation that contains sufficient saturated permeable material to yield usable quantities of water to wells and springs.
- 3.2 Dissolved Oxygen – The concentration of oxygen that is dissolved or carried in water measured in mg/L or percent saturation.
- 3.3 Data Quality Objectives (DQOs) – Data Quality Objectives are qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).
- 3.4 Depth-to-Water - The distance between an established measuring point at the top of a well casing to the top of the water in the well. Also referred to in this SOP as water level measurement.
- 3.5 EAP – Environmental Assessment Program
- 3.6 Ecology – Washington State Department of Ecology
- 3.7 EIM – Environmental Information Management System. A searchable database of environmental monitoring data developed and maintained by the Washington State Department of Ecology.
- 3.8 Field Data Sheets – Weather-resistant sheets (“Rite in the Rain” ® writing paper) used to document all field activities, sample data, methods, and observations for each collection site.
- 3.9 General Chemistry Parameters—Analytes that require wet chemistry analysis, including alkalinity, total dissolved solids, nutrients (ammonium, nitrate, total nitrogen, ortho-phosphorus, and total phosphorus), organic carbon, chloride, calcium, magnesium, sodium, potassium, bicarbonate (alkalinity), sulfate, iron, manganese, and sulfate.
- 3.10 GPS - Global Positioning System
- 3.11 Oxidation-Reduction Potential (ORP)-The electric potential required to transfer electrons from one compound or element (oxidant) to another compound (reductant). Used as a qualitative measure of the state of oxidation in water.
- 3.12 pH – A measure of the acidity or alkalinity of water. A pH value of 0 to 7 indicates that an acidic condition is present, while a pH value of 7 to 14 indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.
- 3.13 Quality assurance project plan (QAPP) – A written plan that describes the goals, objectives, and details of how a study will be conducted and the results analyzed.

- 3.14 Specific Conductance (SC) – A measure of the water’s ability to conduct an electrical current. Specific conductance is related to the concentration and charge of dissolved ions in water.
- 3.15 Static water level (SWL) — The level to which water in a well naturally rises in the absence of external stresses such as the withdrawal or injection of water within the well or other nearby wells.
- 3.16 Water Level Measuring Point (MP) – An established (fixed) point on a well casing from which depth-to-water/water level measurements are made to ensure data comparability.
- 3.17 Water table elevation —The elevation of the top water surface of an unconfined aquifer with respect to a standard datum, e.g., the point where the pore water pressure equals atmospheric pressure in an unconfined aquifer.

4.0 Personnel Qualifications/Responsibilities

- 4.1 Staff new to groundwater sampling should become familiar with the most recent *USGS National Field Manual for the Collection of Water-Quality Data* (USGS, 1997); *The Essential Handbook of Ground-Water Sampling* (Nielsen, 2007), or an equivalent, for background information on principles and techniques of groundwater monitoring.
- 4.2 Monitoring staff should have a detailed working understanding of the groundwater monitoring needs for the project described in the Quality Assurance Project Plan (QAPP).
- 4.3 This document supplements, but does not replace, the need for on-the-job training. Field staff should be familiar with the sampling equipment and instruments being used. The field lead is responsible for ensuring that all field staff members adhere to prescribed sampling methods when conducting fieldwork.
- 4.4 EAP staff who sample groundwater are responsible for complying with this SOP and the requirements of the EAP safety manual - particularly Chapter 1 “General Field Work” and the following sections of Chapter 2: “Groundwater Sampling and Water-Level Measurements” (Ecology, 2019).

5.0 Equipment, Reagents, and Supplies

- 5.1 Sample Measuring and Collecting Equipment
- 5.1.1 Field data sheets
 - 5.1.2 Water level measuring equipment (calibrated electric water level meter, graduated steel tape)
 - 5.1.3 Water quality meters, multi-meters, and probes (e.g., temperature, pH, conductivity, dissolved oxygen (DO), and oxidation-reduction potential (ORP))
 - 5.1.4 Probe calibration standards/reagents
 - 5.1.5 Flow cell

- 5.1.6 Pump (submersible, peristaltic, bladder)
- 5.1.7 Power supply (generator, batteries)
- 5.1.8 Extension cord
- 5.1.9 Tubing and connectors
- 5.1.10 Sample containers/bottles (assuming that preservatives are added to sample bottles as appropriate by the lab)
- 5.1.11 Filters (45 µm)
- 5.1.12 Coolers with ice or ice packs
- 5.2 Cleaning and Disinfecting Supplies
 - 5.2.1 Deionized water
 - 5.2.2 Laboratory grade soap (Liquinox®)
 - 5.2.3 Dilute chlorine bleach solution
- 5.3 Safety Equipment
 - 5.3.1 Nitrile gloves
 - 5.3.2 Hearing protection
 - 5.3.3 Safety goggles
 - 5.3.4 Hard hat
 - 5.3.5 First aid kit
 - 5.3.6 Orange vest
 - 5.3.7 Traffic cones/signs, if applicable
- 5.4 Miscellaneous Equipment
 - 5.4.1 Well location map
 - 5.4.2 All applicable SOPs
 - 5.4.3 Field paperwork: property owner contact information, field data sheets, sample bottle labels and tags, chain-of-custody sheets
 - 5.4.4 Pencils, pens, etc.
 - 5.4.5 Permanent marking pen or paint stick (for marking measuring point)
 - 5.4.6 Calculator
 - 5.4.7 Well keys, if applicable
 - 5.4.8 Compass
 - 5.4.9 GPS unit
 - 5.4.10 Digital camera
 - 5.4.11 Paper towels or clean rags

- 5.4.12 Plastic garbage bags
- 5.4.13 Plastic sheeting for ground cover
- 5.4.14 Cart for transporting equipment
- 5.4.15 Buckets, plastic 5-gallon
- 5.4.16 1-liter container (to calibrate purge volume/rate)
- 5.4.17 Stopwatch
- 5.4.18 Field bag (containing rain gear, rubber boots, work gloves, etc.)
- 5.4.19 Hand cleaner/disinfectant
- 5.4.20 Tools
- 5.4.21 Steel hand measuring tape (engineer scale)
- 5.4.22 Socket wrench set
- 5.4.23 Allen wrench set
- 5.4.24 Pipe wrenches
- 5.4.25 Crescent wrenches
- 5.4.26 Set of screwdrivers
- 5.4.27 File
- 5.4.28 Knife
- 5.4.29 Hammer
- 5.4.30 Pliers
- 5.4.31 Hack saw
- 5.4.32 Crowbar/manhole hook
- 5.4.33 Shovel
- 5.4.34 Machete
- 5.4.35 Whiskbroom
- 5.4.36 Spare well cover bolts/nuts
- 5.4.37 Spare well caps/plugs
- 5.4.38 Spare padlocks/keys
- 5.4.39 Wire brush
- 5.4.40 WD-40 (to be used away from the well head)
- 5.4.41 Well monument bailing device (e.g., cooking baster, peristaltic pump with battery, small bottle)
- 5.4.42 Flashlight
- 5.4.43 Spare batteries (e.g., electric tape, GPS, flashlight)

- 5.4.44 Tape (duct tape/electrical tape)
- 5.4.45 Well tagging equipment

6.0 Summary of Procedure

6.1 Project Planning

- 6.1.1 A Quality Assurance Project Plan (QAPP) must be completed and approved before collecting water quality samples for analysis. The QAPP details project goals, data quality objectives, quality assurance program procedures, sample handling requirements (container requirements, preservation, holding times), and field and laboratory procedures. QAPPs may reference SOPs. Non-standard procedures or deviations from SOPs should be described in the QAPP.
- 6.1.2 Detailed information should be collected for each sampling well location whenever practical, including well construction logs, water level data, site access agreements, and any other relevant information about the well.
- 6.1.3 Well location and construction information for sampled wells should be entered into Ecology's Environmental Information Management (EIM) system database.
 - 6.1.3.1 If the well has not been previously inventoried, use a GPS receiver when visiting the well to define preliminary latitude and longitude coordinates. The field-collected coordinates can be refined using mapping tools in EIM when entering the well into the EIM database.
 - 6.1.3.2 If the well does not have a Department of Ecology unique well ID tag, then it should be tagged as described in EAP081 (Daiber, 2022). Well tags are available from Ecology's Water Resources Program. Securely attach the tag to the well casing or another permanent, easily-seen fixture of the well. Once the well is tagged, complete a well tag form and submit it to Ecology's Water Resources Program with a copy of the well log.

6.2 Sample Equipment Selection

- 6.2.1 The sampling equipment, materials, and method of sampling must be compatible with the well characteristics and analytes being evaluated. Selecting equipment for purging and sampling a well requires site- and project-specific considerations.
- 6.2.2 Groundwater chemistry can be altered by changes in temperature, pressure, and exposure to air that can occur during sampling. Therefore, it is imperative to select sample equipment and procedures that minimize these changes.
- 6.2.3 Factors to consider when selecting sample equipment include analytes to be sampled, type and location of the well, physical characteristics of the well (diameter and screen depth), depth to water, the amount of water to be purged before sampling, lithology adjacent to the screened interval and the groundwater chemistry. Further details on choosing sampling equipment can be found in U.S. Geological Survey (1997), Neilsen and Nielsen (2007), and in Appendix B.

- 6.2.4 To minimize sampling bias and error, all equipment surfaces that contact the sample should be made of inert material to the extent possible. Materials commonly used include various forms of plastic (pumps, pump tubing, and connectors) and stainless steel (pumps). General chemistry parameters are typically less sensitive than organics and trace metals to sorption, desorption, and leaching of materials that might interfere with or bias analytical results. See Nielsen and Nielsen (2007) for material options.
- 6.2.5 Flexible tubing (e.g., silicone, polyvinyl chloride - Tygon®) is gas permeable and sorptive of organic compounds but is suitable for sampling general chemistry parameters. More rigid tubing (e.g., polytetrafluorethylene (Teflon®), polyethylene, and propylene) offers superior performance over other materials for both inorganic and organic analytes. EAP projects involving general chemistry parameters typically use rigid, high-density polypropylene tubing that is dedicated to the well. When using a peristaltic pump, a small portion (~1.5 feet) of flexible tubing (silicone or Pharmed) must be attached to the polypropylene tubing to facilitate pump rotation.
- 6.2.6 The physical characteristics of a well may limit equipment selection. Small diameter wells (2-inch diameter and less) may dictate the equipment that can be used (e.g., peristaltic pump, submersible pump, small-diameter bladder pump).
- 6.2.7 Depth to water may also restrict sampling equipment selection. The lift capability of suction-based pumps (e.g., peristaltic and centrifugal pumps) is typically limited to less than 25 feet. For wells deeper than 20-25 feet, submersible or bladder pumps can be used. Bailers produce the least representative samples but can be used if pumps are not practical.
- 6.2.8 Pumping rate is important for general chemistry parameters, although usually not as critical as for volatile organics and trace metals. Low-flow sampling procedures should be used at all wells. Sampling rates should be less than 0.5 L/minute to minimize sample alteration by agitation or aeration. Dissolved forms of phosphorus are especially sensitive to aeration and can convert to particulate forms if transitioning from a low-DO to a high-DO environment. Low-flow sampling also means that purging continues until water quality parameters (temperature, pH, conductivity, DO, ORP) stabilize sufficiently.
- 6.3 Fieldwork preparation
- 6.3.1 Inventory consumable field supplies several weeks before sampling to ensure adequate supplies of disposable gloves, calibration standards (pH, conductivity), tubing, filters, etc. Order necessary supplies, allowing ample time for delivery.

- 6.3.2 Make arrangements with Ecology's Manchester Environmental Laboratory for sample analysis and transport before sampling. The Manchester Environmental Laboratory (MEL) Laboratory User's Manual (Ecology, 2016) contains detailed guidance on the planning steps necessary to request, track, ship, and analyze water quality samples collected in the field. To notify the lab submit a Pre-Sampling Notification Form and a Sample Container Request Form as early in the process as possible. Coordinate with the lab regarding any large projects, and projects that require special arrangements such as contract lab analysis, special courier, or sample delivery.
- 6.3.3 Inventory sample bottles when they arrive to ensure the lab provided the correct type and number.
- 6.3.4 Establish the order the wells will be sampled. Sample order is based either on logistics or the known or suspected water quality of a sample location. For contaminated sites, wells should be sampled in order of increasing chemical concentrations (known or anticipated). This minimizes the possibility of cross-contamination of the sample equipment.
- 6.3.5 Contact the property owner, property operator, or resident to confirm the sampling date and time and to discuss site access issues.
- 6.3.6 Prepare field data sheets for each well location before going in the field. It can be helpful to bring previous sample data for each well, such as water level, pump intake placement, pump rate, total purge time, stabilized field parameter values, etc. Other sample paperwork should also be filled out as much as possible, including bottle labels and tags and Manchester Labs Chain-of-Custody/Lab Analysis Required Form (LAR).
- 6.3.7 Inspect all equipment and verify that water-quality field meters are in good working order, calibrate properly, and are fully charged. Calibrate field water quality meters according to the manufacturer's instructions.
- 6.3.8 Equipment that is placed in a well and reused at other wells must be properly cleaned, disinfected, or decontaminated prior to and after use in each well. Cleaning procedures depend on the equipment (water level equipment, field parameter probes, down-well sample equipment, tubing for pumps). If possible, wells should be sampled in order from lowest to highest concentration of the highest priority analytes, although cleaning procedures should prevent cross-contamination.
- 6.3.9 Nitrile gloves should be worn when cleaning sample equipment. When not in use, sampling equipment should be placed on a clean surface, such as a clean plastic sheet. If equipment is not reused immediately, it should be wrapped in clean plastic sheeting or plastic bags. Equipment should never be placed on the bare ground prior to using it in a well.

- 6.3.10 Water level measuring equipment should be rinsed with deionized water between wells. If the well is suspected or known to be contaminated, the probe and any submerged tape should be wiped with a disinfectant-soaked towel or washed in a laboratory-grade soap (e.g., Liquinox) solution, followed by a tap water and deionized water rinse.
- 6.3.11 If a peristaltic pump is used, a new piece of silicone tubing at the pump head should be used for each well sampled. Each monitoring well should have dedicated tubing that extends to the bottom of the well. The dedicated tubing can be removed from the well between sampling events if not exposed to contamination.
- 6.3.12 If a submersible pump is used for general chemistry parameters, the pump should be washed in a laboratory-grade soap (e.g., Liquinox) solution. Use a brush to scrub the exterior of the sample equipment. Rinse the equipment with tap water, followed by a deionized water rinse. When sampling for organic carbon, extra rinsing with deionized water should be done when Liquinox is used for cleaning.
- 6.3.13 If sampling equipment is used in a contaminated well, additional cleaning may be required. Equipment may need a chemical rinse (e.g., acetone, nitric acid (unless nitrogen species are being sampled), methanol, isopropyl alcohol), especially if synthetic organics are a concern as described in EAP078 (Marti, 2023b). Rinse the equipment with deionized water.
- 6.4 Purging and Sampling Procedures
 - 6.4.1 Upon arriving at a well, set out safety equipment such as traffic cones and signs as needed.
 - 6.4.2 Check the site for hazardous conditions, either physical or chemical.
 - 6.4.3 Clean hands/dirty hands: One person should be designated to keep gloved hands clean for sample handling (clean hands), while the other person opens the well and conducts duties that involve potential contact with contaminants (dirty hands). The dirty hands do not touch the sampling bottles or tubing unless clean gloves are used.
 - 6.4.4 Before opening the well, set up a clean plastic sheet on the ground or a stable platform near the well to keep sample equipment clean (Figures 1 and 2). Set up field equipment: water level meter, field parameter meters, flow cell, and pump.
 - 6.4.5 Remove the well cover and cap. If there is a lock, unlock the compression cap.
 - 6.4.6 If the well has not been sampled before, establish and document a water level measuring point using the procedures described in SOP EAP052 (Marti, 2023a).

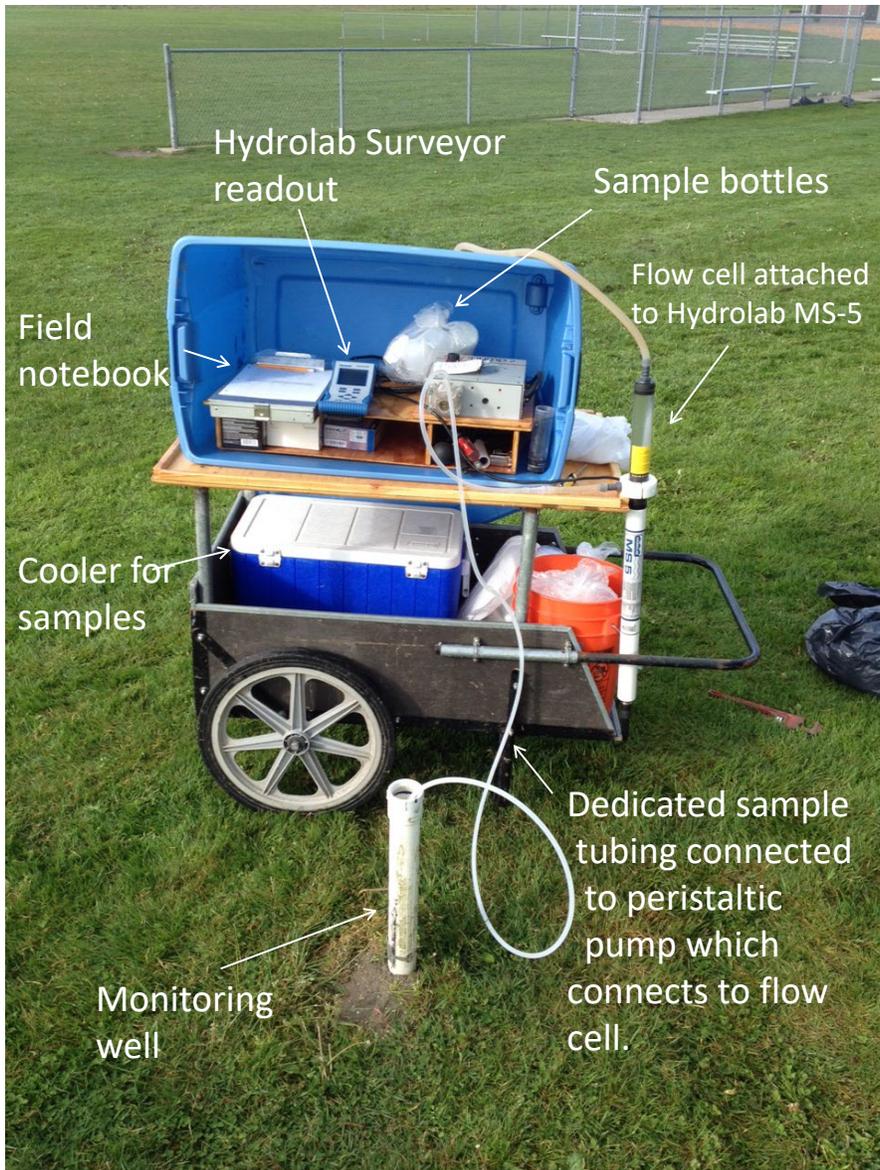


Figure 2. Mobile field sampling platform with convenient storage and weather protection.

- 6.4.9 Knowing the volume of standing water in a well is useful, particularly for projects where purge water must be properly managed and treated. Well volume can be calculated as follows:

$$\text{Well volume} = V = 0.041 \times HD^2 = \text{___} \text{ gallons}$$

Where V is the volume of water in the well, in gallons, the H is height of the water column (total depth – measured static water level) in feet, and D is the inside well casing diameter in inches.

- 6.4.10 If the well is not equipped with a dedicated sampling pump, install a decontaminated pump (e.g., submersible, bladder) or pump tubing (e.g., connected with a peristaltic pump). Slowly lower the equipment through the water column to avoid stirring up particulates. Place the tubing intake at the QAPP-prescribed final depth before starting to purge.
- 6.4.11 The final intake position should be set at the point of sample collection. If the well has been sampled before, the final pump intake should be placed at the same depth as used in previous sample events. Record the intake depth on the field data sheet. If the well has not been sampled before, position the pump intake at a depth prescribed by the project manager/field lead. The pump intake is typically positioned within the screened or open interval of the well and at least a few inches above the well bottom. The final intake depth depends on the project objectives and should be specified in the QAPP.
- 6.4.12 Slowly lower the water level probe back into the well to measure water levels throughout purging. This is particularly important for low yielding wells. If the well has been sampled before, review past field data sheets for purge rates, total purge time, stabilized field parameter values, and amount of drawdown, if any, prior to sample collection.
- 6.4.13 Connect the pump tubing to the flow cell for field parameter measurements. Temperature, pH, conductivity, DO, and ORP should be sampled in a closed atmosphere flow cell attached to the pump outflow, as shown in Figures 1 and 2. If it is not possible to use a flow cell, this should be noted on the field data sheet.
- 6.4.14 Turn on the pump, and begin purging the well. Set the pump controller to the desired pumping rate (e.g., less than 0.5 liter/minute, U.S. Geological Survey, 1997). Use a calibrated 1-liter bottle or graduated cylinder and stopwatch to measure the pump rate and record on the field data sheet.
- 6.4.15 If sampling a well that cannot sustain normal purging, see SOP EAP078 Part 6.5 (Marti, 2023b) for guidance on purging and sampling low volume and poorly recovering wells.
- 6.4.16 Purge water from wells that are not on regulated facilities or related to site cleanup may be discharged directly to the ground as long as the water is not contaminated. Direct the purge water away from the wellhead and work area. Purge water from wells associated with a regulated facility or cleanup site that is contaminated should be disposed of in accordance with Washington State regulations (Chapter 173-303-400 WAC).

- 6.4.17 The pump discharge should be a smooth solid stream of water with no air or gas bubbles in the tubing or flow cell. Tap and tilt the tubing or flow cell to remove bubbles. If necessary, gradually adjust the pumping rate to remove bubbles.
- 6.4.18 When the purge flow is constant, begin recording field parameter values (temperature, pH, conductivity, DO, and ORP) at regular intervals (e.g., 3-5 minutes). The frequency of measurements depends on the pump rate and the estimated time for field parameters to stabilize. At a minimum, there should be a complete exchange of water in the flow cell between measurements.
- 6.4.19 Record field parameter values, time of measurement, water level, and, if tracking, the amount of purge water discharged. Note and provide qualifying remarks if parameter readings are anomalous or unstable. Record observations during purging and sampling (e.g., purge water clarity, odor, etc.).
- 6.4.20 Continue purging and recording measurements uninterrupted until field parameters stabilize. At a minimum, five sets of field measurements should be recorded. Monitored field parameters for EAP studies include but are not limited to water temperature, pH, specific conductance, dissolved oxygen, and oxidation-reduction potential. Field parameters should be specified in the project QAPP.
- 6.4.21 Field parameters are considered stable when 3 consecutive readings fall within the following stabilization criteria:
- | | |
|----------------------------------|--|
| pH | ± 0.1 standard units |
| Specific Conductance
µmhos/cm | ± 10.0 µmhos/cm for values < 1000
± 20.0 µmhos/cm for values > 1000 |
| Dissolved Oxygen | ± 0.05 mg/L for values < 1 mg/L
± 0.2 mg/L for values > 1 mg/L |
| Temperature | ± 0.1° Celsius |
| ORP | ± 10 millivolts |
- 6.4.22 If sampling for metals or organics in addition to general chemistry parameters, measure turbidity and review SOP EAP100 (Pitz, 2023) and EAP078 (Marti, 2023b) for additional steps and considerations for sampling.
- 6.4.23 When field parameters have stabilized, disconnect the pump tubing from the flow cell and conduct any end-of-purge parameter field tests (e.g., low dissolved oxygen using a Chemetrics kit) as specified in the project QAPP.
- 6.4.24 Change to clean, disposable, powder-free gloves and prepare for sample collection. Samples should be collected in the order specified in the QAPP. Analytes most sensitive to change or most important for the study are usually collected first.

- 6.4.25 Keep sample containers capped until filling to avoid possible container contamination. Hold the cap while filling each sample bottle. If you have to set the cap down during filling, place the inside of the cap facing upward on a clean surface.
- 6.4.26 If samples are also being collected for organics, these samples should be collected first. See SOP EAP078, Marti (2023b) for details of purging and sampling for organics.
- 6.4.27 Collect samples that do NOT require filtration before those requiring filtration (e.g., bacteria, pathogens). All general chemistry parameters require filtering in the field.
- 6.4.28 Direct the pump discharge into laboratory-supplied bottles using clean hands. Fill containers directly from the discharge tubing. The discharge tube should be close to, but not touching, the sample container. Do not stop or significantly change the pumping rate during the final phase of purging or while sampling.
- 6.4.29 After collecting non-filtered samples, attach a new, disposable 0.45 µm in-line filter to the pump discharge tubing using a tubing connector. Do not stop the pump or adjust the pumping rate. Purge and discard at least 500 ml of well water through the filter before collecting the first sample.
- 6.4.30 Sample order should also take into account cross-contamination from preservatives. For example, sulfate samples should be collected before samples preserved with sulfuric acid (e.g., nitrogen series). This can prevent accidental contamination of an unpreserved sulfate sample with sulfuric acid preservative used for another sample. Likewise, samples for nitrogen compounds should be collected before samples preserved with nitric acid (e.g., total and dissolved metals).
- 6.4.31 When filtering samples for several parameters, the U.S. Geological Survey (1997) suggests the following sample sequence to account for reduced pore size as filtering progresses: trace metals, major cations, major anions, nutrients/alkalinity, and dissolved organic carbon.
- 6.4.32 Alkalinity should be analyzed using a field test kit immediately upon sample collection (Chemitrics Titrets Kit is currently used for EAP groundwater studies). Total alkalinity and pH values can be used to calculate bicarbonate concentration using Equation 1 from Standard Methods 4500-CO₂ D (*Standard Methods*, 20th Edition). Most of the total alkalinity will be bicarbonate when the pH is less than 8.3.¹
- HCO_3^- as mg CaCO₃/L = $(T - 5.0 \times 10^{(\text{pH}-10)}) / (1 + 0.94 \times 10^{(\text{pH}-10)})$ Equation 1
- where T = total alkalinity, mg CaCO₃/L
- 6.4.33 Most general chemistry bottles should be filled to the shoulder to allow for complete mixing by the lab analyst and to provide the correct preservative concentration for the sample (bottles from MEL contain preservative).
- 6.4.34 Bottles supplied by MEL are to be used for sample collection. Pre-preserved bottles will be supplied for nutrients and dissolved organic carbon.

- 6.4.35 Bottles for non-preserved general chemistry samples should be rinsed with about 100 ml of water discharging from the pump before collecting an actual sample (e.g., total dissolved solids, anions, and cations).
- 6.4.36 If the filter becomes clogged during sampling, which can occur due to high concentrations of fine particulates, replace it with a clean filter. Do not change the pump rate while replacing the filter. (Note: when a new filter is required to replace a clogged filter, remember to purge and discard the initial 500 ml of water before continuing with sample collection). High-capacity filters are recommended if fine particulates are present.
- 6.4.37 After filling sample bottles, attach pre-labeled tags to sample bottles. Note the sample date and time on the tag as well as the field sheet. All sample bottles from the same well should be placed in a plastic bag for transport to the lab. Bottles should be stored in an ice chest at 6° C.
- 6.4.38 Collect quality control (QC) samples, such as field replicates, as specified in the QAPP. Field replicates are collected by alternating the sample stream between two of the same type of sample container. A filter blank should be collected for all filtered analytes using deionized water from MEL. If sampling equipment is decontaminated between wells, a rinsate blank should be collected at least once/day for all analytes following the decontamination process.
- 6.4.39 Remove the dedicated sample tubing, if used, and rinse with deionized water unless the tubing will be cleaned in the laboratory. Store tubing in clean/dedicated plastic bags.
- 6.4.40 Down-well equipment, such as a submersible pump, should be washed in a laboratory-grade soap (e.g., Liquinox) solution. Use a brush to scrub the exterior of the sample equipment. Flush the equipment with the 0.1-0.2% soap solution, then with tap water. Rinse with deionized water. If the pump can be disassembled, wash the separate parts in the detergent solution with a brush, followed by a tap water and deionized water rinse. Parts of the sampling equipment that are difficult to submerge while cleaning, like a pump electrical cable, can be wiped down with a disinfectant-soaked towel and then rinsed thoroughly with deionized water.
- 6.4.41 Follow procedures outlined in the project QAPP or Manchester Lab Manual for sample handling and management (e.g., chain of custody, sample courier service for special shipping requirements).
- 6.4.42 When planning for sample transport, take into account analytical holding times as shown in Table 1, p. 30 of the *Manchester Environmental Laboratory (MEL) Laboratory User's Manual* (Ecology, 2016). Orthophosphate has a 48-hour holding time. Fecal and total coliform bacteria have a 24-hour holding time.
- 6.4.43 If down-well instrumentation was removed from the well during sampling, replace it to its previous position. Note the time that instrument(s) were re-installed on the datasheet.
- 6.4.44 Close and secure the well.

7.0 Records Management

- 7.1 Information about monitoring wells that EAP samples must be documented to enable their location, construction, and subsequent monitoring data to be archived in Ecology's Environmental Information Management (EIM) system and well log imaging databases. Consult the EIM help documents for a list of the well-specific metadata required by EIM.
- 7.2 Station information and monitoring notes should be documented during each site visit on site-specific field data sheets. All field entries should be neat and concise. The field lead is responsible for reviewing the form(s) for completeness before leaving a field site.
- 7.3 EAP staff has developed a number of data analysis spreadsheets, field forms, and other tools to standardize data collection and processing for groundwater monitoring projects. See the EAP Groundwater Assessment Sharepoint site for the most up-to-date version of these tools.
- 7.4 Field meter pre- and post-calibrations must be documented before and after each sampling event for pH, conductivity, and DO.
- 7.5 All hardcopy documentation, such as well reports and field data sheets, are kept and maintained by the project lead. At the completion of a project, hard copies are boxed and moved to EAP archives.

8.0 Quality Control and Quality Assurance

- 8.1 Data collection, review, and analysis will follow the procedures specified in the project QAPP, including following all SOPs, calibrating and maintaining instruments according to the manufacturer's recommendations, and documenting all procedures. Field staff should follow these general QA/QC procedures when collecting samples to minimize error:
- 8.2 Follow the project QAPP and any applicable standard operating procedures (SOP) when collecting and handling samples.
- 8.3 Calibrate and maintain field water quality meters according to the manufacturer's instructions. Document the calibration in the field notes.
- 8.4 Use equipment to purge and sample that is compatible with the characteristics of the well and analytes being sampled. Operate equipment in accordance with the manufacturer's instructions unless otherwise specified in the project QAPP.
- 8.5 Properly collect, handle, and store samples.
- 8.6 Collect appropriate quality control samples. These may include a field replicate and field blanks (e.g., filter, equipment, transport). The types and number of quality control samples should be specified in the project QAPP.
- 8.7 Follow the procedures in the project QAPP or Manchester Lab Manual for sample handling and management (e.g., chain of custody).
- 8.8 Document all data, observations, notes, deviations from project QAPP, etc., on the field data sheets and other project paperwork.

- 8.9 Properly clean, maintain, and store all field equipment after use.
- 8.10 Use consistent procedures from well to well.
- 8.11 Conduct a cation/anion charge balance to check the validity of water quality analyses. The sum of the cations should equal the sum of the anions. Cations include calcium, magnesium, sodium, potassium, iron, and manganese. Anions include bicarbonate (concentration calculated from alkalinity as shown in Equation 2 where pH is less than 10 (Murray and Wade, 1996)), chloride, and sulfate.

$$\left(\frac{\text{Alkalinity} \left(\frac{\text{mg}}{\text{L}}\right)}{50}\right) = \text{HCO}_3 \text{ (mg/L)} \quad \text{Equation 2}$$

(Murray and Wade, 1996)

The charge for each ion is calculated as follows:

$$\frac{\text{Charge}}{\text{L}} = \text{Ion concentration} \left(\frac{\text{mg}}{\text{L}}\right) \div \text{Atomic wt} \left(\frac{\text{mg}}{\text{mmole}}\right) \times \frac{\text{Charge}}{\text{L}} \quad \text{Equation 3}$$

Example: Na⁺: 55.0 mg/L in sample / 23.0 mg/mmole x 1⁺ (charge) = 3.30⁺

The difference between the sum of the cation charges and the sum of the anion charges divided by the total charges should be +/- 5% (*Standard Methods*, 1998, Method 1030 F).

9.0 Safety

- 9.1 Fieldwork should follow protocols specified in the Environmental Assessment Program Safety Manual (Ecology, 2019). A working knowledge of sections ‘Groundwater Sampling and Water-Level Measurement’ and ‘Hazardous Waste Sites’ in Chapter 2 is expected for all field staff. These protocols should be used to complement the judgment of experienced field professionals.
- 9.2 A Field Work Plan Form that documents field personnel, sampling locations, overnight lodging, planned itinerary, contact person(s), and emergency contacts must be completed for each sampling event. If a boat is used to access sites, an Ecology Float Plan must be completed.
- 9.3 Always assess the safety situation when sampling a monitoring well. In addition to possible chemical hazards, there are many possible physical hazards. Monitoring wells are often located near active business or industrial sites where hazards such as traffic and equipment are possible. Consult the EAP Safety Manual for guidance regarding working near traffic. Other physical hazards include slips, trips, heavy lifting, noise, electricity, steep, slippery, or uneven terrain, animals, insects, and foul weather.
- 9.4 All EAP field staff who work on hazardous waste sites are required to complete and maintain certification in First Aid/CPR and 40-hour Hazardous Materials Safety and Health Training.

10.0 References

- 10.1 ASTM, 2005. American Society of Testing and Material Standard D5521/D5521M-13. Standard Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers. www.astm.org/Standards/D5521.htm
- 10.2 Deutsch, W. J., 1997. Groundwater Geochemistry: Fundamentals and Applications to Contamination. CRC Press. 232 pp.
- 10.3 Ecology, Washington State Department of, 2019. Environmental Assessment Program, Safety Manual.
- 10.4 Ecology, Washington State Department of, 2016. Manchester Environmental Laboratory - Lab Users Manual. 10th edition.
- 10.5 Lombard, S. and C. Kirchmer, 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Environmental Assessment Program. <https://fortress.wa.gov/ecy/publications/summarypages/0403030.html>
- 10.6 Carey, B., 2023. Standard Operating Procedures EAP096, Version 1.2: Collecting Groundwater Samples for General Chemistry Parameters from Water Supply Wells. Washington State Department of Ecology, Environmental Assessment Program. 36 pp. In Publication.
- 10.7 Pitz, C., 2023. Standard Operating Procedure EAP100, Version 1.2: Collecting Groundwater Samples for Metals Analysis from Monitoring Wells. Washington State Department of Ecology, Olympia. In Publication
- 10.8 Marti, P.B. 2023a. Standard Operating Procedure EAP052, Version 1.4: Manual Well-Depth and Depth-to-Water Measurements. Publication 23-03-204. Washington State Department of Ecology, Olympia. <https://apps.ecology.wa.gov/publications/SummaryPages/2303204.html>.
- 10.9 Marti, P.B., 2023b. Standard Operating Procedure EAP078, Version 2.3: Purging and Sampling Monitoring Wells plus guidance on collecting samples for volatiles and other organic compounds. Washington State Department of Ecology, Environmental Assessment Program. 45 pp. In Publication.
- 10.10 Murray, K. and P. Wade, 1996. Checking anion-cation charge balance of water quality analyses: limitations of the traditional method for non-potable waters. Water SA, Vol. 22, pp. 27-32.
- 10.11 Nielsen, D.M. and G.L. Nielsen, 2007. The Essential Handbook of Ground-Water Sampling. CRC Press. 309 pp.
- 10.12 Ohio EPA, 2009. Technical Guidance Manual for Ground Water Investigations, Chapter 8: Monitoring Well Development, Maintenance, and Redevelopment, Division of Drinking and Groundwaters, Revision 2, 21 pp. www.epa.state.oh.us/Portals/28/documents/TGM-08_final2009W.pdf

- 10.13 Daiber, E., 2022. Standard Operating Procedure EAP081, Version 1.2: Tagging Wells. Publication No. 22-03-211. Washington State Department of Ecology, Olympia.
<https://apps.ecology.wa.gov/publications/UIPages/SummaryPages/2203211.html>
- 10.14 Sinclair, K. and C. Pitz, 2023. Standard Operating Procedure EAP074, Version 1.3: Use of Submersible Pressure Transducers During Groundwater Studies. Publication No. 19-03-205. Washington State Department of Ecology, Olympia. In Publication.
- 10.15 Puls, R. W. and M. J. Barcelona. 1989. Ground Water Sampling for Metals Analyses. U.S. EPA Superfund Ground Water Issue, EPA/540/4-89/001.
<http://nepis.epa.gov/Exec/ZyPURL.cgi?Dockey=10001KBH.txt>
- 10.16 Standard Methods, 1998. Standard Methods for the Examination of Water and Wastewater, 20th Edition. American Public Health Association.
- 10.17 U.S. EPA, 2006. Guidance on Systematic Planning Using the Data Quality Objective Process. EPA QA/G-4. <https://www.epa.gov/quality/guidance-systematic-planning-using-data-quality-objectives-process-epa-qag-4>
- 10.18 U.S. Geological Survey, 1997 to present, National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at <http://water.usgs.gov/owq/FieldManual/>

11.0 **Appendix A. Considerations when sampling for general chemistry parameters in monitoring wells.**

11.1 Well Selection Considerations

The design, construction, and development of a monitoring well can have a significant influence on the ability to obtain a groundwater sample that is representative of aquifer general chemistry.

EAP hydrogeologists do not always have control over how wells (and their associated filter packs and screens) are designed and installed. The primary aspects of a project that EAP staff will normally have control over include careful well selection and the use of proper sampling techniques.

The key criteria for selecting monitoring wells for general chemistry sampling include identifying wells that:

- Have low turbidity
- Are least likely to cause a significant change in the geochemical condition of the groundwater during sampling.

11.1.1 Considerations when selecting wells for general chemistry sampling include:

- Time elapsed since well construction and development

Newly constructed wells should be allowed to chemically equilibrate with the formation sediments before sampling for general chemistry parameters. Wells that have not been used for a long time may need to be redeveloped before using for water quality sampling.

- Well screen and filter pack design

Monitoring wells that were designed and constructed with a filter pack and screen that are sized appropriately for the aquifer matrix of interest are most likely to produce water that is representative of aquifer water quality. However, field-filtering of samples from other wells should remove particulates that would affect sample geochemistry.

- Design and integrity of the well annular seal

Monitoring wells that have leaky or improperly constructed grout seals may allow cross-contamination of samples by surface leakage and may produce water with altered pH or DO, which in turn can affect general chemistry parameters.

- Character of the aquifer matrix adjacent to the open interval

Monitoring wells screened in sediments that have a significant percentage of silt/clay may produce groundwater with an elevated turbidity level, even after redevelopment.

Purging monitoring wells screened in low permeability sediments may result in a large amount of water level drawdown or even pumping the well dry. This can lead to exposure of the well screen to the atmosphere, allowing groundwater entering the casing from the formation to be oxidized. Excessive drawdown can significantly bias the dissolved concentration and forms of phosphorus as well as the DO in samples from the well. If such wells are used for water quality sampling, purge rate and drawdown should be closely monitored to avoid drawdown below the top of the screened interval.

- Time elapsed since previous sampling

Discharge from monitoring wells that have not been sampled for an extended period of time tends to exhibit excess turbidity and often require re-development.

- Length of the well open interval

The objectives of your project and the site hydrogeology dictate the ideal length of the screened interval open to the adjacent aquifer. In many situations, shorter screen lengths (≤ 10 feet) are preferred for the most accurate measurement of in situ groundwater chemistry at a particular depth, although they may not represent the geochemistry at other depths. Longer screens, on the other hand, may dilute contamination that occurs in only part of the depth profile.

If the project goal requires the characterization of groundwater general chemistry across multiple water-bearing zones or in an aquifer with significant potential for vertical chemical stratification, consider adopting alternative monitoring approaches (e.g., sampling multiple short-screened wells constructed at different positions in the aquifer, use of multi-level samplers, use of packers to isolate particular portions of a longer screen).

- Water table position

If the top of the well screen lies above the water table, groundwater may experience atmospheric exposure and gas diffusion during sampling, potentially altering the geochemistry condition of the sample. The dissolved concentration or forms of phosphorus and dissolved oxygen are highly sensitive to exposure to the atmosphere. If monitoring wells are constructed in a manner that keeps the full length of the screened interval saturated under the full range of site water level conditions, then this is not a problem. However, if the objective of the study is to observe the effects of the most recent recharge, then the screened interval may be exposed to the atmosphere under low water table conditions. Atmospheric effects on water quality parameters should be taken into account for such situations, i.e., volatilization or mineralization of ammonium and precipitation of phosphorus.

If an existing well requires redevelopment (and permission is granted), conduct the redevelopment process a minimum of 48 hours prior to sample collection. Suggested practices for well redevelopment can be found in ASTM (2005) and Ohio EPA (2009).

11.2 Sampling Pump and Tubing Selection

The pump type selected for purging and sampling groundwater for general chemistry sampling can play an important role in the representativeness of samples. The key goal is to select a device that:

- Operates at a low enough flow rate to minimize suspension of normally immobile particles
- Does not cause aeration, degassing, or heating of the sample prior to collection

Bladder pumps, submersible and suction-lift (peristaltic and surface-centrifugal) pumps, and inertial lift (tubing check valve) pumps are acceptable for general chemistry sampling. Peristaltic are preferable to submersible pumps in low-yielding wells because they operate better at low flow than submersible pumps.

Bailers should not be used to sample monitoring wells for general chemistry parameters because they cannot produce as representative of a sample as a pump operating at low flow. Bailers are also open to the atmosphere, which can alter the geochemistry of water quality samples, including nitrogen and phosphorus species.

Sample delivery tubing should also be made from a material that is inert with respect to general chemistry parameters. High-density polyethylene tubing is the preferred tubing type for EAP studies for general chemistry.

11.3 Sampling Pump Placement

Care should always be taken when positioning a sampling pump (dedicated or non-dedicated) in a monitoring well to collect groundwater samples for general chemistry. The pump should be lowered slowly and smoothly into position to minimize disturbance of the water column. This helps limit mobilization of fine-grained material present in the formation adjacent to the open interval or at the bottom of the well casing.

The sampling intake depth should be specified in the project QAPP. The sampling pump intake should be positioned adjacent to the open interval of the well but should not be placed too close to the bottom of the well casing. Pumps placed near the base of the well may mobilize and capture sediments accumulated in the casing.

11.4 Control of pressure changes and atmospheric exposure of a groundwater sample

The concentration, phase, and mobility of phosphorus compounds can be highly sensitive to changes in the pressure or oxidation state of groundwater that can occur during sampling.

Bringing a groundwater sample to the surface and exposing it to the atmosphere can alter both the pH (due to a change in the partial pressure of CO₂) and the redox potential (Eh) of the water. This is particularly true if the sample is agitated or aerated during collection.

Changes in pH and Eh can result in a change in solubility for phosphorus and nitrogen and can lead to unwanted precipitation, sorption, or oxidation reactions that can alter dissolved concentrations and misrepresent the in-situ condition of the water. For example, exposing a groundwater sample to the atmosphere can result in a change from a reduced state to an oxidized state, causing phosphorus to precipitate out of solution and rapidly sorb onto solid particle surfaces, such as iron. If the metal particles bearing sorbed phosphorus are filtered from the sample before analysis, the resulting groundwater concentrations reported by the lab could be biased low.

Although some degree of change in pressure or exposure of the sample to the atmosphere is unavoidable, it is important to always take steps to minimize the impact of these changes on a sample. When sampling monitoring wells, the primary techniques for controlling these concerns are listed in Sections 6.2-6.8 of this SOP.

11.5 Passive samplers

Although EAP does not have direct experience with passive samplers, these are an emerging technology for evaluating some general chemistry parameters in groundwater.

Passive samplers are no-purge sampling devices designed to collect samples from a specific depth within a well that is in equilibrium with the adjacent groundwater. There are a variety of passive samplers, including devices that rely on sorption or diffusion onto or across the sampler medium to devices that recover grab samples at discrete depths.

When considering a passive sampling device for your project, consult with the product manufacturer to determine if the technology is compatible with the project goals and site condition.