DEPARTMENT OF
ECOLOGY
State of Washington

Standard Operating Procedure EAP078, Version 2.3

Collecting Groundwater Samples for Volatiles and Other Organic Compounds From Monitoring Wells.

April 2024

Publication 24-03-202

[Recertified 2023]

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.

Publication Information

This SOP is available on the Department of Ecology's website at https://apps.ecology.wa.gov/publications/SummaryPages/2403202.html.

Ecology's Activity Tracker Code for this SOP is 08-524.

***Recommended citation*:**
Marti, P.B. 2011 [Recertified 2023]. Standard Operating Procedure EAP078, Version 2.3: Collecting Groundwater Samples for Volatiles and Other Organic Compounds from Monitoring Wells. Publication 24-03-202. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2403202.html.

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Recertification Date – 7/3/2023

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SOP Revision History

Revision Date	Revision History	Summary of Changes	Sections	Reviser(s)
1/27/2014	2.0	Minor edits all sections, added Appendix B	All, added Append B	Pam Marti
12/01/2016	2.1	Minor editorial changes; no technical changes	All	Pam Marti
12/06/2016	2.1	Cover page, footer, recertification	All	Bill Kammin
12/20/2019	2.2	Minor editorial changes to all sections, accessibility updates	All	Pam Marti
4/15/2023	2.3	Minor editorial changes; no technical changes	All	Pam Marti

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for collecting groundwater samples for volatiles and other organic compounds from monitoring wells.

1.2 The goals of collecting groundwater samples from monitoring wells can include characterizing ambient conditions, defining the nature and extent of groundwater problems, identifying trends in contaminant concentrations, and determining compliance with regulatory standards.

1.3 To avoid bias in sampling results, groundwater measurements, and samples must 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.

1.4 When sampling wells that are not designed for groundwater monitoring, e.g., water supply wells or irrigation wells, see EAP077 Standard Operating Procedures for Collecting Groundwater Samples for Volatiles and Other Organic Compounds From Water Supply Wells (Marti 2020).

2.0 Applicability

2.1 This SOP provides general information to help guide EAP field staff in proper purging and sampling techniques for volatiles and other organic compounds. 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 general chemistry parameters or metals, see procedures described in separate SOPs, EAP099 for general chemistry (Carey 2018) and EAP100 for metals (Pitz 2019), on Ecology's web page: www.ecy.wa.gov/programs/eap/quality.html.

2.3 Documents such as the U.S. Geological Survey's (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 – An underground layer of saturated permeable/porous rock or sediments (e.g., gravel, sand, or silt) that is capable of storing and releasing 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) – 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 (MP) 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 Datasheets – 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 GPS - Global Positioning System

3.10 Measuring Point (MP) – A fixed and clearly marked point on a well casing from which depth-to-water/water level measurements are collected to ensure data comparability.

3.11 ORP – Oxidation-Reduction Potential. The electric potential required to transfer electrons from one compound or element (the oxidant) to another compound (the 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 how a study will be conducted and how its results will be assessed.

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 – 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 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 review 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 the principles and techniques of groundwater monitoring.

4.2 Field staff should have a detailed working understanding of the groundwater monitoring needs for the project described in the 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 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” and “Hazardous Waste Sites” (Ecology 2021).

5.0 Equipment, Reagents, and Supplies

5.1 Sample Measuring and Collecting Equipment

Field datasheet

Water level measuring equipment (e.g., calibrated electric water level meter, graduated steel tape)

Water quality meters and probes (e.g., pH, SC, DO, temperature, ORP)

Probe calibration standards/reagents

Field analytical devices (e.g., spectrophotometer, turbidimeter, etc.)

Flow cell

Pump (submersible, peristaltic, bladder)

Power supply (generator, battery)

Extension cord

Sample tubing and connectors

Sample containers/bottles

Sample preservatives

Sample filters/tubing adapters (analyte specific)

Laboratory-grade deionized water for quality assurance samples

Coolers with ice or ice packs

55-gallon barrels (to store and properly dispose of contaminated purge water)

5.2 Cleaning and Disinfecting Supplies

Deionized water

Laboratory grade soap (Liquinox®)

Dilute chlorine bleach solution

Cleaning solvents, if applicable

5.3 Safety Equipment

Nitrile gloves

Hearing protection

Safety goggles

Hard hat

First aid kit

Orange vest, Ecology issued

Traffic cones

Traffic signs, if applicable

5.4 Miscellaneous Equipment

Well location map

All applicable SOPs

Field paperwork: property owner contact information, field datasheets, sample bottle labels and tags, chain-of-custody sheets

Pencils, pens, etc.

Permanent marking pen or paint stick (for marking water level measuring point)

Calculator

Well keys, if applicable

Compass

GPS unit

Camera

Paper towels or clean rags

Plastic garbage bags

Plastic sheeting for ground cover

Buckets, plastic 5-gallon

1-liter container (to calibrate purge volume/rate)

Stopwatch

Field bag (containing rain gear, rubber boots, work gloves, etc.)

Hand cleaner

Product/Water interface probe, if applicable

5.5 Tools

Steel hand measuring tape (engineer scale)

Socket wrench set

Allen wrench set

Pipe wrenches

Crescent wrenches

Set of screwdrivers

File

Knife

Hammer

Pliers

Hack saw

Crowbar/manhole hook

Shovel

Machete/pruning shears

Whiskbroom

Spare well cover bolts/nuts

Spare well caps/plugs

Spare padlocks/keys

Wire brush

WD-40 (to be used away from the well head)

Bailing device (e.g., cooking baster, peristaltic pump with battery)

Flashlight

Spare batteries (e.g., electric tape, GPS, flashlight)

Tape (duct tape/electrical tape)

Well tagging equipment

6.0 Summary of Procedure

6.1 Project Planning

A QAPP must be completed and approved before water quality samples are collected 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 for standard field monitoring or measurement procedures. Non-standard procedures or deviations from SOPs should be described in detail in the QAPP.

Detailed information should be collected for each well location whenever practical, including well construction logs, water level data, site access agreements, and any other relevant information about the well.

Well location and construction information for sampled wells should be entered into Ecology’s Environmental Information Management (EIM) system database.

- If the well hasn’t been previously inventoried, use a GPS receiver when visiting the well to define a preliminary latitude and longitude coordinate. The field-collected coordinates can be refined using mapping tools in EIM when entering the well into the EIM database.
- If the well does not have a Department of Ecology unique well ID tag, then it should be tagged as described in SOP EAP081 (Daiber 2022). Well tags are available from Ecology’s Water Resources Program. Securely attach the tag to the well casing or other permanent, easily seen fixture of the well. Once a well is tagged, complete the well tag form and submit to Ecology's Water Resource Program along with a copy of the well log.

6.2 Sample Equipment Selection

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.

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.

Factors to consider when selecting sample equipment include:

- Analytes to be sampled.
- Type and location of 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.
- Groundwater chemistry.

Further details on choosing sampling equipment can be found in USGS (1997), Nielsen and Nielsen (2007), and in Appendix A.

To minimize sampling bias or error, all equipment surfaces that contact the sample should be made of inert material to the extent possible. Materials commonly used include high-quality stainless steel (pumps) and various forms of plastic (pumps, pump tubing and connectors). Organic compounds can be sensitive to sorption, desorption, and leaching of materials that might interfere with or bias analytical results. See USGS (1997) or Nielsen and Nielsen (2007) for material options.

Flexible tubing (e.g., silicone, polyvinyl chloride - Tygon®) is gas permeable and sorptive of organic compounds and is therefore not suitable for sampling organic analytes. More rigid tubing (e.g., polytetrafluorethylene (Teflon®), polyethylene, and propylene) offers greater performance over other materials for both organic and inorganic analytes. EAP projects involving organic analytes typically use rigid, high-density Teflon-lined polyethylene tubing that is dedicated to the well.

When sampling for organic analytes, sample equipment should be chosen to minimize changes in pressure, temperature, and atmospheric exposure of the water pulled from the aquifer. For this reason, these samples should be collected with positive pressure/displacement pumps. Positive pressure pumps most commonly used by EAP are stainless steel submersible or bladder pumps. In general, suction lift pumps are not recommended for sampling volatile organics because of the vacuum created at the intake to draw the sample to the land surface. The vacuum can result in the loss of volatile organics or other dissolved gases.

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).

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. Submersible or bladder pumps can be used for wells with water levels deeper than 20-25 feet. Bailers produce the least representative samples but can be used if pumps are not practical.

The pumping rate is an important consideration when selecting sample equipment. Sample rates should be high enough to fill sample containers efficiently and with minimal exposure to the atmosphere but low enough to minimize sample alteration by agitation or aeration. This is especially important for sensitive analytes, such as volatile organic compounds. Low-flow sampling procedures should be used at all wells.

6.3 Field Work Preparation

Inventory consumable field supplies several weeks before sampling to ensure adequate supplies of disposable gloves, calibration standards (pH, conductivity, ORP), tubing, filters, etc. Order necessary supplies, allowing ample time for delivery.

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.

Inventory sample bottles when they arrive to ensure the lab provided the correct type and number.

Establish the order in which the wells will be sampled. Sample order is either based 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.

Contact the property owner, property operator, or resident to confirm the sampling date and time and to discuss site access issues.

Prepare field datasheets for each well location before going into 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 the Manchester Labs Chain-of-Custody/Lab Analysis Required Form (LAR).

Inspect all equipment and verify that water quality field meters are in good working order, calibrated properly, and fully charged. Calibrate field water quality meters according to the manufacturer's instructions.

Field equipment, especially equipment being placed in a well, 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). 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.

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 the equipment is not reused immediately, it should be wrapped in clean plastic sheeting, a plastic bag, or aluminum foil. Equipment should never be placed on the bare ground prior to being used in a well.

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.

Down well equipment, such as a submersible or bladder pump, should be washed in a laboratory-grade soap (e.g., Liquinox) solution. Use a brush to scrub the exterior of the sampling equipment. Rinse the equipment with tap water, followed by a deionized water rinse. If the pump can be disassembled, wash the separate parts in the detergent solution with a brush, followed by a tap and deionized water rinse. Parts of the sampling equipment that are difficult to submerge while cleaning, like a pump's electrical cable, can be wiped down with a disinfectant-soaked towel and then rinsed thoroughly with deionized water.

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, methanol, isopropyl alcohol). Rinse the equipment with deionized water. Place the equipment on a clean surface to air dry.

Equipment that is difficult to clean, such as pump tubing, should be replaced between sample locations. Pump tubing has the potential to provide a source of error due to the amount of contact with the sampled water. To prevent possible cross-contamination, sample tubing should not be reused between sample locations. For long-term projects, the tubing may be dedicated to a well.

6.4 Purging and Sampling Procedures

Upon arriving at a well, set out safety equipment such as traffic cones and signs as needed.

Check the site for hazardous conditions, either physical or chemical.

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.

Before opening the well, spread clean plastic sheeting on the ground or a stable platform near the well to keep sample equipment clean. Set up field equipment: water level meter, field parameter meters, flow cell, and pump. If a gasoline-powered generator is used for the pump power supply, locate it as far from the wellhead or sample collection area as possible, preferably downwind.

Remove the well cover and compression cap. You will probably need a key to monitor wells on regulated facilities.

If the well has not been sampled before, establish and document a water level measuring point using the procedures described in SOP EAP052 (Marti 2018).

Measure the static water level according to SOP EAP052 (Marti 2018). The water level should be measured before inserting any other field equipment into the well. Take two measurements to confirm a stable and accurate reading. Record the water level value, date, and time on the well-specific field datasheet. If a stable measurement is not obtained after a few minutes, note this on the field datasheet and qualify the measurement.

If the well is suspected or known to have free floating product, the water level and product thickness should be measured with an interface probe.

If the well is equipped with a pressure transducer or other down well instrumentation, carefully note its position. Remove the instrumentation from the well according to SOP EAP074 (Sinclair and Pitz 2019). Note the removal time on the field datasheet.

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

Well volume: V = 0.041 x HD2 = ____ gallons, where

V is the volume of water in the well in gallons,

H is the height of the water column in the well (i.e., total well depth - measured depth to water) in feet and

D is the inside diameter of the well casing in inches

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 pump/tubing intake at the point of sample collection. If the well has been sampled before, the final intake should be placed at the same depth as used in previous sample events. Record the intake depth on the field datasheets. If the well has not been sampled before, position the intake at a depth prescribed by the project manager/field lead. The intake is typically positioned within the screened or open interval of the well. The final intake depth depends on the project objectives and should be specified in the QAPP.

Slowly lower the water level probe back into the well to measure water levels throughout purging. This is particularly important for low-yield wells. If the well has been sampled before, review past field datasheets for purge rates, total purge time, stabilized field parameter values, and amount of drawdown, if any, prior to sample collection.

Connect the pump tubing to the flow cell for field parameter measurements. Temperature, pH, conductivity, DO, and ORP should be measured in a closed atmosphere flow cell attached to the pump outflow. If it is not possible to use a flow cell, this should be noted on the field datasheet.

Start the pump and begin purging the well. Set the pump controller to the desired pumping rate (e.g., less than 0.5 liter/minute, USGS 1997). Use a graduated container and stopwatch to measure the pump rate and record it on the field datasheet.

Use water level measurements to help establish the optimum pump rate (which should not exceed 0.5 liter/minute). Purging should not cause a significant drawdown in the well. A significant drawdown is considered to be 5 percent of the total height of the water column or depth to the top of the screen. If an unacceptable drawdown occurs at the initial set pumping rate, gradually decrease the pump rate until the water level stabilizes at an acceptable level. Record the final pump rate on the field datasheet. If sampling a well that cannot sustain normal purging, see Part 6.5 for guidance on purging and sampling low-volume and poorly recovering wells.

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).

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.

When the purge flow is constant, begin recording field parameter values at regular intervals (e.g., 3-5 minutes). The frequency of measurements depends on the pump rate and the estimated time for the field parameters to stabilize. At a minimum, there should be a complete exchange of water in the flow cell between measurements.

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.).

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.

Field parameters are considered stable when 3 consecutive readings fall within the following stabilization criteria:

pH	± 0.1 standard units
Specific Conductance	± 10.0 µmhos/cm for values < 1000 µmhos/cm
Specific Conductance	± 20.0 µmhos/cm for values > 1000 µmhos/cm
Dissolved Oxygen	± 0.05 mg/L for values < 1 mg/L
Dissolved Oxygen	± 0.2 mg/L for values > 1 mg/L
Temperature	± 0.1° Celsius
ORP	± 10 millivolts

If sampling for metals in addition to organics, measure turbidity and review SOP EAP100 (Pitz 2019) for additional steps and considerations for sampling.

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, iron using a Chemetrics kit) as specified in the project QAPP.

Do not stop or significantly change the pumping rate during the final phase of purging or while sampling.

Change to clean, disposable, powder-free gloves and prepare for sample collection.

Collect samples in the order specified in the QAPP. Analytes most sensitive to change (e.g., organics) or most important for the study are usually collected first.

If samples are also being collected for general chemistry parameters and/or metals, see SOPs EAP099 (Carey 2018) and SOP EAP100 (Pitz 2019) for details of purging and sampling.

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.

Do not pre-rinse/field rinse organic bottles before sample collection.

Samples should be collected from the pump discharge tubing with as little disturbance as possible. When filling bottles for organics, tip the bottle at a slight angle and allow a slow, steady stream of water to run down the inner wall (Figure 1). This will minimize agitation, aeration, and volatilization while sampling. The discharge tube should be close to, but not touching, the sample container.

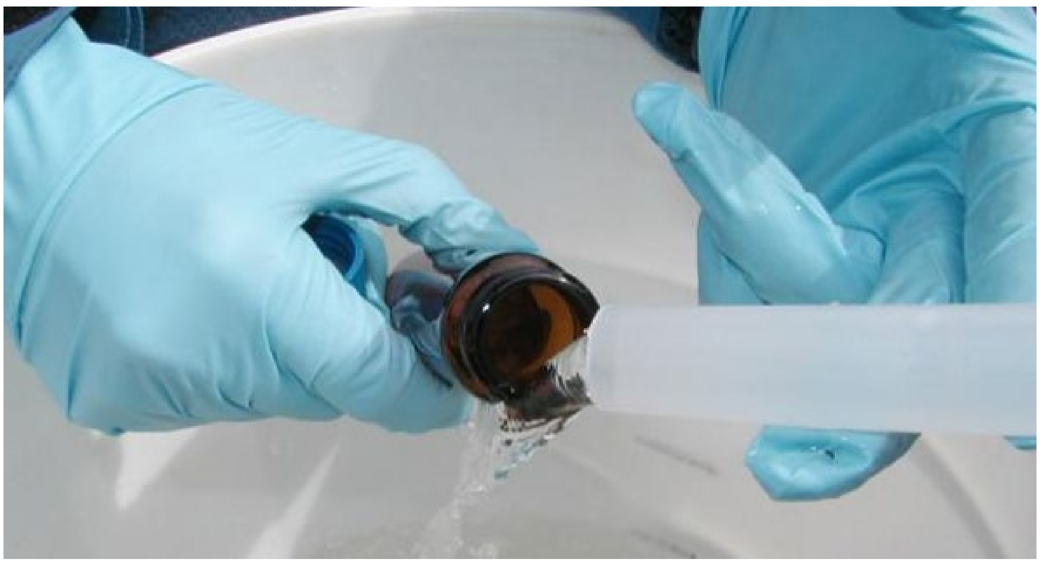

Figure 1: Filling an organics bottle.

Carefully fill the bottle to the recommended volume. For most organics, this would be to the shoulder of the bottle. VOA bottles require no headspace, so they should be filled up to just below the rim (Figure 2).

Figure 2: VOA bottle filled to the rim.

To achieve no headspace on a VOA bottle, fill the cap with water and add just enough to the bottle to form a positive meniscus. Take care not to over fill pre-preserved bottles (Figure 3).

Figure 3: Meniscus on VOA bottle.

Secure the cap. Invert the bottle and tap it lightly, then check for bubbles (Figure 4).

Figure 4: Checking a VOA bottle for bubbles.

If any bubbles are present, carefully remove the cap and add enough water to re-establish the meniscus. If bubbles are still present after recapping the bottle, set the sample aside. Collect a new sample using a clean bottle.

If, for some reason bubble-free samples cannot collected, save the three samples with the fewest bubbles to submit to the laboratory. Make a note on the field and laboratory forms indicating the samples contained bubbles.

Collect quality control (QC) samples, such as field replicates, as specified in the project QAPP. Field replicates are collected by alternating the sample stream between two of the same type of sample bottles.

After filling the sample bottles, attach pre-labeled tags. Note the sample date and time on the tag as well as the field sheet. Place the samples in an ice-filled cooler. Samples must remain at or below 6°C throughout handling, storage, and shipping.

Record any final observations or comments related to sample collection.

Remove sample equipment from the well (e.g., pumps, dedicated tubing). Clean all down-well equipment, such as pumps, as described in Part 6.3. Store the equipment for transport to the next sample location or at the conclusion of the field study. Rinse the dedicated sample tubing with deionized water and store it in clean plastic bags.

If down-well instrumentation was removed from the well during sampling, replace it to its previous position. Note the time the instrument(s) were re-installed on the field datasheet.

When all work at the well site is complete, close and secure the well.

Note any physical changes to the well on the field datasheets, such as erosion or cracks in the protective concrete pad or alteration to the well casing.

Collect any additional QC samples before leaving the site. These may include field blanks (e.g., equipment, transport, transfer). The types and numbers of quality control samples should be specified in the project QAPP.

Follow procedures outlined in the QAPP or Manchester Lab Manual for sample handling and management (e.g., chain of custody, sample courier service, or any special shipping requirements or restrictions). When planning for sample transport, take into account analytical holding times and minimize the time between sampling and delivery to the laboratory.

6.5 Low Volume and Poor Recovery Wells - Purging and Sampling Procedures

Some wells experience significant drawdown or in extreme cases may purge dry even with a low pumping rate. Slow recovering wells or wells that purge dry require extra care in order to be purged and sampled with minimal disturbance to the water column and fine materials in and around the well screen.

For low volume and poor recovery wells, review past field datasheets if available for previous purge rates, amounts of drawdown, and purge volume prior to sample collection.

Measure the well's water level as described in steps 6.4.6. to 6.4.7.

If you suspect the well may be low yielding, calculate the amount of standing water in one well volume as described in step 6.4.10.

If the well is not equipped with a dedicated sampling pump, install a decontaminated pump (e.g., bladder) or pump tubing (e.g., connected with a peristaltic pump). Slowly lower the equipment through the water column to avoid stirring up particulates. The final pump/tubing intake depth should be near the bottom of the screened interval. To prevent stirring up particulates, it is important not to touch the bottom of the well. Record the intake depth on the field datasheet.

Slowly lower the water level probe back into the well. It is important to measure the water level frequently throughout purging in low-volume or poor recovery wells to enable the pump rate to be adjusted downward if necessary.

Connect the pump tubing to the flow cell for field parameter measurements. If it is not possible to use a flow cell, this should be noted on the field datasheet.

Turn on the pump and begin purging the well at a rate less than 0.5 liter per minute. Use water level measurements to help establish the optimum pump rate. Purging should not cause a significant drawdown in the well. A significant drawdown is considered to be 5 percent of the total height of the water column or depth to the top of the screen. If an unacceptable drawdown occurs at the initial set pumping rate, gradually decrease the pump rate until the water level stabilizes at an acceptable level. Record the pump rate on the field datasheet.

At regular intervals, record field parameter values, water level, time of measurement, and amount of purge water discharged. Allow at least one complete exchange of water in the flow cell between measurements. Note and provide qualifying remarks if parameter readings are anomalous, the water level is dropping, or if, at some point, the water level stabilizes. Record observations during purging and sampling (e.g., purge water clarity, odor, etc.).

Continue purging until field parameters stabilize per section 6.4.22. Try to avoid purging low-yielding wells dry. If this is not possible, shut the pump off and allow the well to recover at least once before collecting samples. This generally constitutes an adequate purge, and the well can be sampled as soon as it has recovered enough water to fill the sample bottles. If time permits, purge the well a second time and allow it to recover before sampling. Samples should be collected within 24 hours of the final purge/recovery cycle.

- It should be noted that there can be significant alterations in groundwater chemistry when a well is purged dry and allowed to recover before sampling. Groundwater chemistry can change as formation water surrounding or entering the screened interval of the well is exposed to air which can affect volatile organics and redox sensitive analytes. Increased turbidity can also be an issue when sampling metals and some general chemistry parameters (Nielsen 2007).

Collect samples once field parameters stabilize and any end-of-purge analysis has been conducted.

- If the well has been purged dry and allowed to recover, field parameters should be measured after sample collection if there is an adequate volume of water.

Collect samples in the order specified in the QAPP. The sequence can be modified depending on the types of samples to be collected and on data objectives. The relative importance of each analyte should be evaluated by project. Samples for analytes of most interest may be collected first to ensure that a representative sample is obtained. This is particularly important when sampling low-yielding wells, which may not have a sufficient volume of water to fill all sample containers. Discuss with the lab the minimum volume of sample needed for each analyte.

Fill, preserve, label, and store sample bottles as described in steps 6.4.26 through 6.4.38. Follow analyte-specific sampling procedures for general chemistry parameters and metals as described in SOP EAP099 (Carey 2018) and SOP EAP100 (Pitz 2019).

Record any final observations or comments related to sample collection such as elapsed time for complete purge of the well and recovery rate of the well.

Follow procedures outlined in the QAPP or Manchester Lab Manual for sample handling and management (e.g., chain of custody, sample courier service, or any special shipping requirements or restrictions). Be conscious of analytical holding times and minimize the time between sampling and delivery to the laboratory.

Remove sample equipment from the well and continue with procedures as described in steps 6.4.40 through 6.4.44.

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 datasheets. 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 have 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 datasheets, 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 To ensure that good quality data are obtained throughout a project, a QAPP must be completed and approved before performing any field work. The QAPP details project goals, data quality objectives, quality assurance program procedures, sample handling requirements, and field and laboratory procedures.

8.2 Data collection, review, and analysis will follow the procedures specified in the project QAPP. Field staff should follow these general QA/QC procedures when collecting samples to minimize error.

8.3 Follow the project QAPP and any applicable SOP when collecting and handling samples.

8.4 Calibrate and maintain field water quality meters according to the manufacturer's instructions. Document the calibration in the field notes.

8.5 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 instructions, unless otherwise specified in the project QAPP.

8.6 Properly collect, handle, and store samples.

8.7 Collect the 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.

8.8 Follow the procedures in the project QAPP or Manchester Lab Manual for sample handling and management (e.g., chain of custody).

8.9 Document all data, observations, notes, deviations from project QAPP, etc., on the field datasheets and other project paperwork.

8.10 Properly clean, maintain, and store all field equipment after use.

8.11 Use consistent procedures from well to well.

9.0 Safety

9.1 Fieldwork should follow protocols described in the Environmental Assessment Program Safety Manual (Ecology 2021). A working knowledge of sections "Groundwater Sampling and Water-Level Measurements" and "Hazardous Waste Sites" in Chapter 2 is expected for all field staff. These protocols should be used to complement the judgment of an experienced field professional.

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 the possible chemical hazards, there are many 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 further guidance regarding working near traffic. Other physical hazards include slips, trips, heavy lifting, noise, electricity, steep, slippery, or uneven terrain, animals or 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 the 40-hour Hazardous Materials Safety & Health Training.

10.0 References

10.1 Carey, B. 2018. Standard Operating Procedure EAP099, Version 1.0: Collecting Groundwater Samples for General Chemistry Parameters from Monitoring Wells. Washington State Department of Ecology, Olympia

10.2 Daiber, E. 2022. Standard Operating Procedure EAP081, Version 1.2: Tagging Wells. Washington State Department of Ecology, Olympia

10.3 Ecology [Washington State Department of Ecology]. 2016. Manchester Environmental Laboratory - Lab Users Manual.10th edition. Washington State Department of Ecology, Olympia

10.4 Ecology [Washington State Department of Ecology]. 2021. Environmental Assessment Program Safety Plan. Washington State Department of Ecology, Olympia

10.5 Marti, P.B. 2018. Standard Operating Procedure EAP052, Version 1.2: Manual Well-Depth and Depth-to-Water Measurements. Washington State Department of Ecology, Olympia

10.6 Marti, P.B. 2020. Standard Operating Procedure EAP077, Version 2.2: Collecting Groundwater Samples for Volatiles and Other Organic Compounds from Water Supply Wells. Washington State Department of Ecology, Olympia

10.7 Nielsen, D.M. and G.L. Nielsen. 2007. The Essential Handbook of Ground-Water Sampling. CRC Press. 309 p.

10.8 Pitz, C. 2019. Standard Operating Procedure EAP100, Version 1.1: Collecting Groundwater Samples for Metals Analysis from Monitoring Wells. Washington State Department of Ecology, Olympia

10.9 Sinclair, K. and C. Pitz. 2019. Standard Operating Procedure EAP074, Version 1.2: Use of Submersible Pressure Transducers during Groundwater Studies. Washington State Department of Ecology, Olympia

10.10 USEPA [U.S. Environmental Protection Agency]. 2006. Guidance on Systematic Planning Using the Data Quality Objective Process. EPA QA/G-4.

10.11 USGS [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://pubs.water.usgs.gov/twri9A

11.0 Appendix A. Collecting Samples for Volatiles and Other Organic Compounds

11.1 This Appendix applies to EAP staff collecting and handling groundwater samples for volatile organic compounds (VOCs) and other organic compounds (e.g., semi-volatiles, total petroleum hydrocarbons, polynuclear aromatic hydrocarbons, pesticides, polychlorinated biphenyls).

It describes common procedures and practices that EAP staff use to collect these samples from wells without dedicated sampling pumps. General information is provided here and in Section 6.0 of this SOP to help guide field staff in the selection of proper sample equipment and sampling techniques. There are several documents that provide detailed information on this topic, including the USGS National Field Manual for the Collection of Water-Quality Data (USGS 1997) and The Essential Handbook of Ground-Water Sampling (Nielsen 2007).

11.2 Sample Equipment Selection

Selecting equipment for purging and sampling a well for VOCs and organics requires specific considerations, preparations, and precautions. To minimize sampling bias or error, all equipment surfaces that contact the sample should be made of inert material to the extent possible. The manner of sample equipment operation must be compatible with the characteristics of the well and the analytes being sampled to obtain data that will meet the project objectives and data quality requirements.

When sampling for volatile analytes sample equipment should be chosen to minimize changes in pressure, temperature and atmospheric exposure of the water pulled from the aquifer. For this reason these samples should be collected with positive pressure/displacement pumps. Positive pressure pumps most commonly used by EAP are stainless steel submersible or bladder pumps.

Although peristaltic pumps are regularly used to purge and sample monitoring wells, they are not recommended for sampling volatile analytes. Peristaltic pumps are negative pressure or suction lift pumps that create a vacuum in the intake line that draws the sample to the land surface. The vacuum can result in the loss of volatile analytes.

Following are some basic considerations for the most commonly used sample equipment.

11.2.1 Submersible and Bladder Pumps

Submersible and bladder pumps have similar operating requirements. Both are lowered into the well's water column. The pumps should be slowly lowered through the water column to avoid stirring up particulates or aerating the water in the well casing.

It is recommended that the intake depth of the pump and pumping rate for wells that are sampled repeatedly remain the same for all sample events. Typically the pump intake is placed at the midpoint or the lowest historical midpoint of the saturated screen length. The pump intake depth will be determined by the project manager.

Both submersible and bladder pumps need to be completely submerged to operate properly. Consult with the pump manufacturer to determine the minimum height of the water column above the pump so it can operate properly. This can range from 1 foot to more than 5 feet.

If possible the pump intake should be at least two feet above the bottom of the well, to minimize mobilization and uptake of particulates present in the well bottom.

Ideally, the pumping rate should be set so as not to cause a significant drawdown in the well. Wells should be pumped at a rate that is equal to or less than the natural flow conditions of the aquifer in the screened interval to avoid drawing the water level down.

Small-diameter bladder pumps are available for sampling small-diameter wells, which are becoming increasingly common in groundwater investigations.

Careful considerations should be given to placing pumps in wells that are excessively contaminated with free product (LNAPL or DNAPL) because it may be difficult to adequately decontaminate severely contaminated pumps in the field. When wells of this type are encountered, alternative sampling methods should be considered such as a peristaltic pump or bailer.

11.2.2 Peristaltic Pumps

Peristaltic pumps are generally not recommended for sampling volatile analytes because of the potential loss of analytes due to pump operation.

If a peristaltic pump is being considered to sample volatile analytes, the intended use of the data should be a primary consideration.

Use of the pump may be acceptable if the additional sample error that may be introduced by the negative pressure/vacuum created by the pumps operation does not affect any project decision making. For example, if contaminant concentrations are far above regulatory levels and groundwater monitoring will continue, then a peristaltic pump could be used. However, the data should only be used to qualitatively evaluate the presence of the contaminants.

A peristaltic pump should not be used if minor differences in the groundwater concentrations of volatile analytes could affect project decisions. For example, do not use a peristaltic pump when monitoring groundwater remediation to determine if cleanup goals have been achieved. In these cases sample equipment should be selected that will provide more accurate results.

Peristaltic pumps may be used to sample if the physical characteristics of the well limit other sample equipment options, such as when sampling smaller diameter wells. Small-diameter tubing used with a peristaltic pump is a possible option. However, the tubing used in the rotor head of the peristaltic pump should be less than a foot in length since it is found to be more gas-permeable and sorptive of organic compounds. This tubing should be replaced at each sample location. PharMed tubing is now recommended for use in the pump rotor head since it has been found to be less permeable to gas and vapors than other soft tubing options.

Peristaltic pumps may also be used in low-yielding wells that do not have sufficient water to operate submersible pumps.

11.2.3 Bailers

Even though bailers are not recommended for most groundwater sampling, they are useful in specific situations.

The use of bailers is discouraged because the repeated entry and removal of the bailer disturbs the water column and may mobilize sediment that is present in the well. The repeated disturbance to the water column can also aerate the water in the well casing.

However, in wells that are excessively contaminated with oily compounds, bailers can be an acceptable alternative to pumps. Bailers are easier to clean or can be disposable.

If a bailer is used to sample for volatile organic compounds, it should be a closed-top Teflon® bailer with a bottom-emptying sample device. The bailer should be lowered and raised smoothly at a constant rate and with as little disturbance to the water column as possible.

11.2.4 Passive Samplers

Although EAP does not have direct experience with passive samplers, the devices are an emerging technology for evaluating volatile organics and other analytes in groundwater.

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

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

11.3 Sampling Considerations

The following are general considerations when collecting samples for volatile analytes and other organics. Please refer to Section 6.0 of this SOP for instructions on basic monitoring well sampling procedures (e.g., water level measurement, well purging, and sampling methods).

Whenever possible, wells should be sampled in order of increasing chemical concentrations (known or anticipated). This minimizes the possibility of cross-contamination of sample equipment.

Protect the sample area from potential sources of airborne contaminants (e.g., dust, vapors from fuel cans, engine exhaust, etc.). Record on the field datasheets suspected but unavoidable extraneous VOC sources that are encountered when sampling.

While in the field try to keep unfilled sample bottles in a cool place (e.g., shade, ice-filled cooler). This will minimize the loss of volatile analytes when filling the sample bottles.

If samples are collected for multiple analytes, VOC samples (and other sensitive analytes) are typically collected first since these analytes are most sensitive to the sampling process. At low purge rates, direct sunlight and hot ambient air temperatures may cause groundwater in the tubing and flow cell to heat up. This may cause the groundwater to degas, which will result in the loss of volatile analytes. If possible, shade the equipment from sunlight.

Although the procedures used to fill sample bottles may seem a minor consideration, filling them improperly can jeopardize the careful work that went into properly purging a well to produce minimally-disturbed, representative samples. Improper sampling techniques can cause changes in sample composition due to agitation and exposure to air which can result in the loss of contaminants by volatilization or degassing.

The following table lists sample containers, preservation, and holding times for commonly sampled organics.

Table 1. Sample Containers, Preservation, and Holding Times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
VOCs	Water	40 mL, no headspace	(3) 40 mL vials with septum	1:1 HCl Cool to ≤6°C No headspace Ascorbic acid when chlorinated[1]	14 days
BNA (Semi-VOCs)	Water	1 gallon	1-gallon clear glass bottle	Cool to ≤6°C	7 days
TPH-G	Water	40 mL, no headspace	(3) 40 mL vials with septum	1:1 HCl Cool to ≤6°C	14 days
TPH-D	Water	1 L	1 L amber glass bottle	1:1 HCl Cool to ≤6°C	7 days unpreserved; 14 days preserved
PAH	Water	1 L	1 L amber glass bottle	Cool to ≤6°C	7 days
Herbicides	Water	1 L	1 L amber glass bottle	Cool to ≤6°C	7 days
Pesticides	Water	1 L	1 L amber glass bottle	Cool to ≤6°C	7 days
PCBs	Water	1 L	1 L amber glass bottle	Cool to ≤6°C	7 days
PBDEs	Water	1 L	1 L amber glass bottle	Cool to ≤6°C	7 days

[1]If sampling a municipal drinking water source, determine the presence of free chlorine using a field test kit. If free chlorine is present, preserve the VOC sample with 25 mg of ascorbic acid. The ascorbic acid is added to remove the free chlorine, which, if present, may cause the formation of trihalomethanes. Continue to preserve the sample with the 1:1 HCl.

12.0 Appendix B. General Reference Material

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12.4 Parker, L.V.1994. The Effects of Ground Water Sampling Devices on Water Quality: A Literature Review, Ground Water Monitoring Review, Vol. 14, No. 2, p. 130-141.

12.5 Puls, R.W. and C.J. Paul. 1995. Low-flow Purging and Sampling of Ground Water Monitoring Wells with Dedicated Systems, Ground Water Monitoring and Remediation; Vol. 15, N. 1, p. 116-123.

12.6 Puls, R.W., and M.J.Barcelona. 1996. Low-flow (minimal drawdown) Ground-Water Sampling Procedures, U.S. Environmental Protection Agency, Ground-Water Issue Paper EPA/540/S-95/504, 12 p.

12.7 USGS [U.S. Geological Survey]. 1995. Groundwater Data Collection Protocols and Procedures for the National Water Quality Assessment Program: Collection and Documentation of Water Quality Samples and Related Data, U.S. Geological Survey Report 95-399.
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