# Quality Assurance Project Plan

## City of Granite Falls
## Receiving Water Study

Prepared for:
City of Granite Falls

Prepared by:
Gray and Osborne

December 2023

# Publication Information

The plan describes the objectives of the study and the procedures to be followed to conduct a receiving water study for the City of Granite Falls.

# Contact Information

For more information contact:

Jay Swift, P.E.
Gray and Osborne
1130 Rainier Ave S.
Suite 300
Seattle, WA, 98144

*Phone*: (206) 284-0860

**COVER PHOTO**: Pilchuck River. PHOTO BY JAY SWIFT, GRAY AND OSBORNE.

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# City of Granite Falls
# Receiving Water Study

by Gray and Osborne

December 2023

**Approved by:**

| | |
|---|---|
| Signature: | Date: |
| Jay Swift, P.E., Gray and Osborne, Author<br><br>Signature: | Date: |
| Lyle Bjornson, City of Granite Falls<br><br>Signature: | Date: |
| Kevin Leung, NW Region Water Quality Program<br><br>Signature: | Date: |
| Chris Dudenhoeffer, Water Quality Program<br><br>Signature: | Date: |

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# 2.0 Abstract

The major goal of this study is to establish receiving water (Pilchuck River) alkalinity concentrations to support development of water quality based permit limits for the City's effluent. The current NPDES Permit Fact Sheet notes that "Ecology does not have sufficient information on the alkalinity of the receiving water to determine compliance with water quality criteria for pH. This information necessary to determine whether the effluent pH has a reasonable potential to cause a violation of the water quality standards." 25 receiving water samples will be collected and tested for alkalinity.

# 3.0 Background

## 3.1 Introduction and problem statement

The City of Granite Falls (City) owns, operates, and maintains an activated sludge wastewater treatment plant (WWTP). The WWTP discharges treated effluent to the Pilchuck River through the WWTP outfall. The Washington State Department of Ecology (Ecology) issued to the City a National Pollutant Discharge Elimination System Waste Discharge Permit (NPDES) WA0021130 on August 1, 2020. This Permit was modified on February 11, 2022 and expires on July 31, 2025. All discharges and activities authorized by this Permit must comply with the terms and conditions of the Permit. As a General Requirement (Section S.9), the Permit stipulates that the City must submit a Receiving Water Study Quality Assurance Project Plan (QAPP) by December 31, 2023, and then a Receiving Water Study Final Report (by December 31, 2024). The information in the Receiving Water Study Final Report is used by Ecology to determine if additional effluent limitations will be added to the City's NPDES Permit. As noted in the NPDES Permit Fact Sheet, "Ecology does not have sufficient information on the alkalinity of the receiving water to determine compliance with water quality criteria for pH."

The NPDES Permit states that the Quality Assurance Plan must be prepared in accordance with the guidelines provided in the Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies ("Ecology QAPP Guidance" Ecology Publication 04-03-030). Per the Permit, at least 25 receiving water samples must be collected, as close to possible in the critical period, outside the zone of influence of the effluent, using sampling station accuracy requirements of 20 meters, and tested for alkalinity, using the methods and the detection levels identified in Appendix A in the Permit.

As discussed in the TMDL Plam, Ecology collected continuous DO and pH data during two surveys in July and August of 2012, and one survey in August 2016. Observed DO minima consistently fell below water quality criterion during all three surveys. In general, DO was lowest between RM 12 and 2, in the downstream reaches; however, values below the criterion were observed at the upstream stations as well. Observed pH fell within the criteria during all surveys; however, PIL25.5 reached the upper limit of 8.5 on one day in July 2012. pH values were typically highest in the upstream reaches and lowest in the downstream reaches.

Secondary treated and disinfected effluent flows into the Pilchuck River through an outfall diffuser section buried approximately one foot below the bottom of the riverbed. The entire 18-foot section of the diffuser and all laterals were replaced in August 2009. The diffuser consists of an 18-foot section of ductile iron pipe with eighteen (18) 3-inch diffusers spaced 12 inches apart. The diffusers are buried and extend approximately 6 inches up from the riverbed with the discharge directed downstream.

## 3.2 Study area and surroundings

Figure 1 shows the study area.

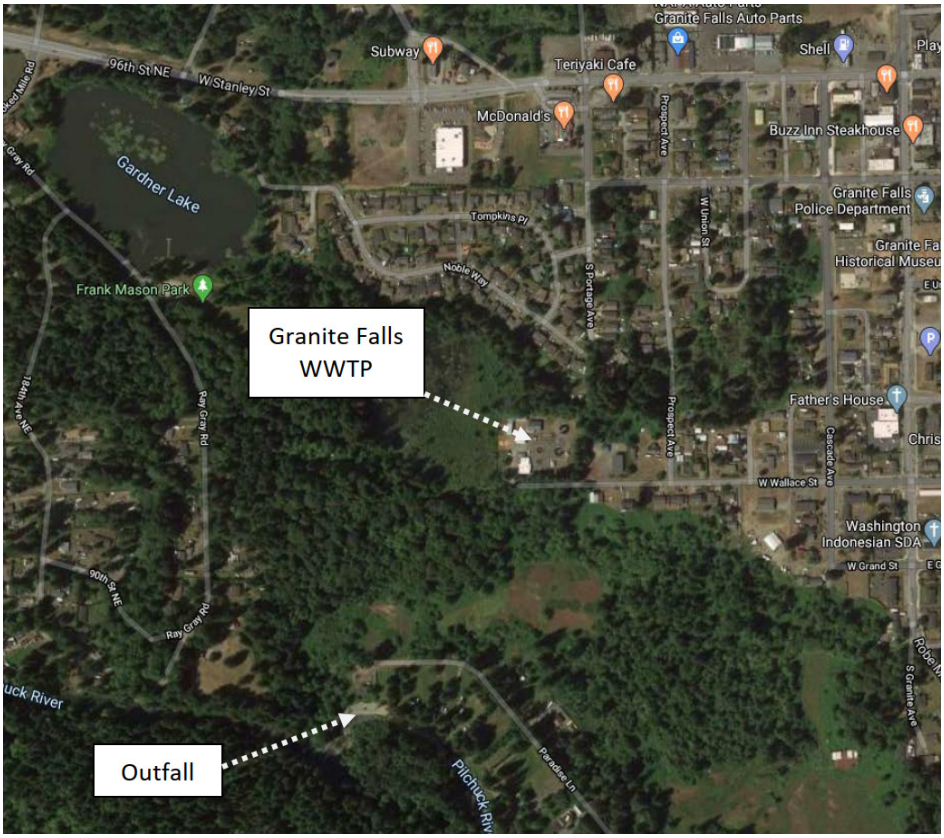
Granite Falls WWTP effluent discharges to the Pilchuck River. The Pilchuck River originates approximately 15 miles southeast of Granite Falls on the western slopes of the Cascade Mountains. The river flows northwesterly toward Granite Falls, then flows southwesterly to join the Snohomish River southeast of the City of Snohomish.

The climate of west central Snohomish County is dominated by marine influences bringing moist air into the interior of the County from Puget Sound and the Pacific Coast. The Cascade Mountains force the moisture-laden clouds upward with a resultant release of moisture. The mountains also act as a barrier against extreme continental influences which occur east of the Cascades. The prevailing winds are from the southwest in winter and the northwest in the summer and have a modifying effect on the climate. As a result of these conditions, the climate in the Granite Falls area is characterized by high rainfall and low evaporation rates in winter, while summers are cool and relatively dry.

Granite Falls is situated on a saddle between the Stillaguamish and the Pilchuck Rivers. The central downtown portion of the City is at approximately 400 feet above sea level. The easterly portion of the City exceeds 600 feet of elevation. The westerly portion of the City is at an elevation of approximately 340 to 320 feet. Elevation slopes both to the north and to the south in the direction of the two rivers with a general dip to the west

The landforms within Granite Falls result from both tectonic activity that created the Cascades and glaciation. The foothills of the Cascades begin in the eastern portion of the City. A large rock quarry operates immediately east of the City in Iron Mountain. The soils were deposited during glacial activity and are related to the Vashon Glaciation. The majority of the soils are composed of recessional outwash that was deposited as the glaciers receded from the area. The Soil Survey of Snohomish County Area, Washington shows soils within Granite Falls and southeast of it generally as Everett gravelly sandy loam (Soil Type 17). The Everett series consists of very deep, somewhat excessively drained soils on terraces and outwash plains. These soils formed in glacial outwash.

**Figure 1. Map of larger study area.**




## 3.2.1 History of study area

The area currently occupied by the City of Granite Falls began as an Indian trading cross point where tribes united from the Stillaguamish and Pilchuck Rivers to camp and trade goods. At the time, this was commonly known as Portage. By the 1890s, mineral and timber industries were the mainstay of the Granite Falls economy. In 1897, when President Grover Cleveland created the Washington Forest Reserve, the Town's affiliation with timber harvesting and the forest products industry was secured. Mineral veins discovered about 40 miles east of the City near Monte Cristo provided an equally strong influence on the economy. A railroad line connecting Everett to the mining town of Monte Cristo had a stop in Granite Falls and operated for about 40 years ending in about 1932. Once automobiles and roads made the area passable, the rail line was discontinued. Though brief, this period shaped the social and economic development of

Granite Falls. Even today, the City celebrates Railroad Days in honor of its history as a mining and timber town.

Granite Falls was incorporated in 1903 and began installing public infrastructure. A pressurized water supply and sewer collection system was installed in the City in 1914. The sewers discharged directly to the Pilchuck River. In 1980, the original sanitary sewer system was constructed which separated stormwater from wastewater.

In recent years, the City economy has shifted to a service-oriented economy serving recreational traffic on the Mountain Loop Highway. Seven quarries and a timber mill, all located in and around the City, provide jobs to the local economy as well. The City of Granite Falls, located in Snohomish County, provides sewer service within the City limits. The City owns, operates and maintains its wastewater facilities, which include a collection system and treatment plant, with treated effluent discharged via a diffuser to the Pilchuck River. The City is bounded on the south by the Pilchuck River, on the east by the Cascade foothills, to the north is the Stillaguamish River and to the west by unincorporated Snohomish County. Granite Falls was incorporated as a city in 1903. Since the fall of 1992, Granite Falls has been a Code City which operates under Title 35A RCW. The City and its UGA cover approximately 1,100 acres.

### 3.2.2 Summary of previous studies and existing data

There is a lack of current information about receiving water alkalinity. The current NPDES Permit Fact Sheet notes that "Ecology does not have sufficient information on the alkalinity of the receiving water to determine compliance with water quality criteria for pH. This information necessary to determine whether the effluent pH has a reasonable potential to cause a violation of the water quality standards." The Fact Sheet does note that the measured 90$^{th}$ percentile receiving water pH is 8.1, with a maximum of 8.2 and a minimum of 8.1.

### 3.2.3 Parameters of interest and potential sources

The key parameter of interest is alkalinity in the receiving water (Pilchuck River).

### 3.2.4 Regulatory criteria or standards

The key regulatory requirements are those listed in the City's NPDES Permit and the State Surface Water Quality Standards (WAC 173-201a). The pH in the receiving water must measure within the range of 6.5 to 8.5, with a human-caused variation within the above range of less than 0.2 units.

## 3.3 Water quality impairment studies

This is not a water quality impairment study per se; however, the information obtained in the study will be used to establish water quality based effluent permit limits to ensure compliance with water quality standards.

# 4.0 Project Description

## 4.1 Project goals

The major goal of this study is to establish receiving water (Pilchuck River) alkalinity concentrations to support development of water quality-based permit limits for the City's effluent.

## 4.2 Project objectives

The key objectives for this project are to

- Collect 25 receiving water samples and test them for alkalinity.
- Comply with all relevant QA/QC procedures including those listed in this QAPP.

## 4.3 Information needed and sources

The information needed is the new alkalinity and pH analytical data. The source of this information is the City's WWTP laboratory.

## 4.4 Tasks required

The tasks required for this study include the following:

- Preparation of sampling equipment
- Receiving water sampling
- Alkalinity measurement
- Quality Assurance
- Data Reporting

# 5.0 Organization and Schedule

## 5.1 Key individuals and their responsibilities

**Table 1. Organization of project staff and responsibilities.**

| Staff | Title | Responsibilities |
|---|---|---|
| **Chris Dudenhoeffer**<br>Dept. of Ecology | Ecology Water Quality Program Reviewer | Review QAPP |
| **Kevin Leung**<br>Dept. of Ecology | Ecology NW Region Water Quality Reviewer | Review QAPP |
| **Jay Swift**<br>Gray and Osborne<br>Phone: 206-284-0860 | Project Manager | Writes the QAPP. Conducts preliminary QA review of data, analyzes and interprets data. Writes the draft report and final report. |
| **Lyle Bjornson**<br>City of Granite Falls<br>Phone: (360) 691-7432 | Principal Investigator | Oversees and conducts field sampling, transportation of samples to the laboratory, and analysis. |
| **Nathan Stoneking**<br>City of Granite Falls<br>Phone: (360) 691-7432 | Laboratory Operator | Conducts field sampling, transportation of samples to the laboratory, and analysis. |
| **Darin Jackson**<br>City of Granite Falls<br>Phone: (360) 691-7432 | OIT | Assists with field sampling and transportation of samples |
| **Charles White**<br>City of Granite Falls<br>Phone: (360) 691-7432 | WWTP Assistant Operator | Assists with field sampling and transportation of samples |

EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan

## 5.2 Special training and certifications

Jay Swift has 11 years of analytical laboratory experience followed by 26 years as an environmental engineer. He has developed QAPPs for a number of effluent and receiving water studies, including plans for the Cities of Sumner and Puyallup, the 2021 City of Sultan Metals Receiving Water Study, and the 2006 Metals Receiving Water Study for the City of Granite Falls.

Lyle Bjornson, lead operator at the City of Granite Falls WWTF, has 22 years of experience in plant operation and management and analytical testing. The WWTF is accredited by the EAP for alkalinity.

## 5.3 Organization chart

Not Applicable - See Table 1".

## 5.4 Proposed project schedule

**Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.**

| Work type | Due date | Lead staff |
|---|---|---|
| **QAPP Approval** | | |
| QAPP submitted | December 6, 2023 | Jay Swift |
| QAPP comments received | December 15, 2023 | EAP and NW Regional Office |
| QAPP revisions provided | December 31, 2023 | Jay Swift |
| QAPP approved | January 30, 2023 | EAP and NW Regional Office |
| **Field and laboratory work** | | |
| Sampling and Analysis | May 1, 2024 – October 31, 2024 | Lyle Bjornson and Staff |
| **Environmental Information System (EIM) database** | | |
| EIM data loaded [1] | November 30, 2024 | Lyle Bjornson |
| EIM data entry review [2] | December 30, 2024 | Jay Swift |
| EIM complete [3] | December 30, 2024 | Jay Swift |
| **Final report** | | |
| Initial Report to Ecology | December 15, 2024 | Jay Swift |
| Final Report to Ecology | 3 weeks after receipt of comments | Jay Swift |

[1] All data entered into EIM by the lead person for this task.
[2] Data verified to be entered correctly by a different person; any data entry issues identified. Allow one month.
[3] All data entry issues identified in the previous step are fixed (usually by the original entry person); EIM Data Entry Review Form signed off and submitted to Melissa Peterson (who then enters the "EIM Completed" date into Activity Tracker). Allow one month for this step. Normally the final EIM completion date is no later than the final report publication date.

## 5.5 Budget and funding

This project is being funded by the City of Granite Falls out of normal Sewer Utility Funds.

# 6.0 Quality Objectives

## 6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect a minimum of 25 water samples representative of the Pilchuck River and to have them analyzed. The analysis will use standard methods to obtain alkalinity data that meet measurement quality objectives (MQOs) that are described below and that are comparable to previous study results.

## 6.2 Measurement quality objectives

MQOs are quantitative indicators of precision, bias, sensitivity, representativeness, comparability and completeness. Analytical method descriptions, standard operating procedures (SOPs), and participating laboratories are referenced for determining the MQOs for these indicators.

### 6.2.1 Targets for precision, bias, and sensitivity

The MQOs for project results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Table 3.

**Table 3. Measurement quality objectives**

| Parameter | Method | Control Standard | Replicate (RPD) | Expected Range | Detection Limit |
|---|---|---|---|---|---|
| Alkalinity | SM 2320B | +/- 20% | 20% | 20 – 100 mg/L as $CaCO_3$ | 5 mg/L as $CaCO_3$ |

#### 6.2.1.1 Precision

Precision is a measure of variability among replicate measurements due to random error. It is assessed using replicate field measurements or laboratory analysis of duplicate samples. Laboratory duplicates and field replicates for assessment of precision will be analyzed at the frequency listed in Table 4. The MQOs for acceptable precision of duplicates is listed in Table 3. Procedures for field replicate measurements and sample collection will follow the standard operating protocols and procedures listed in Section 8.2 and Section 10.1.

#### 6.2.1.2 Bias

Bias is the difference between the mean of control standard measurements and the true value. Bias is addressed by calibrating field and laboratory instruments and by analyzing lab control samples, matrix spikes, and/or standard reference materials. The MQOs for acceptable bias in terms of the difference from the control standard are listed in Table 3. Matrix spikes and internal standards are not used for measuring the parameters in this study.

#### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as a detection limit. In a regulatory setting, the method detection limit (MDL) is the lowest quantity of a physical or chemical parameter that is detectable (above background noise) by each field instrument or laboratory method, and is often used to describe sensitivity. The acceptable method detection limits of the field and laboratory measurements are listed in Table 3. Methods have been selected with detection limits below the expected range of concentrations to provide accurate results.

### 6.2.2 Targets for comparability, representativeness, and completeness

#### 6.2.2.1 Comparability

Standardized methods and protocols will be followed to ensure the consistency and comparability of results to those generated by other projects in the watershed.
The standard operating procedures (SOPs) that will be followed for sampling and measurement, and to ensure comparability between projects are listed in Section 8.2.

#### 6.2.2.2 Representativeness

The receiving water samples will be representative of existing conditions. The samples will be collected upstream of the outfall, outside the zone of influence of the effluent, and will be collected year-round and at varying times during the day. The monitoring locations will be located in an active and well-mixed location and the samples and measurements will be collected mid-depth. The monitoring frequency and duration will provide sufficient data to comply with the goals of this study described in Section 4.1.

#### 6.2.2.3 Completeness

Completeness as a measure of the amount of valid data necessary to meet the project objectives. It is expected that a completeness of 95% of the field measurements and samples taken and analyzed acceptably will be adequate to complete the study objectives.

## 6.3 Acceptance criteria for quality of existing data

Minimal existing data are available for alkalinity in the Pilchuck River. The data collected with this project must meet the quality objectives or the data will be rejected or qualified as appropriate.

## 6.4 Model quality objectives

Not applicable. The project does not involve environmental modeling.

# 7.0 Study Design

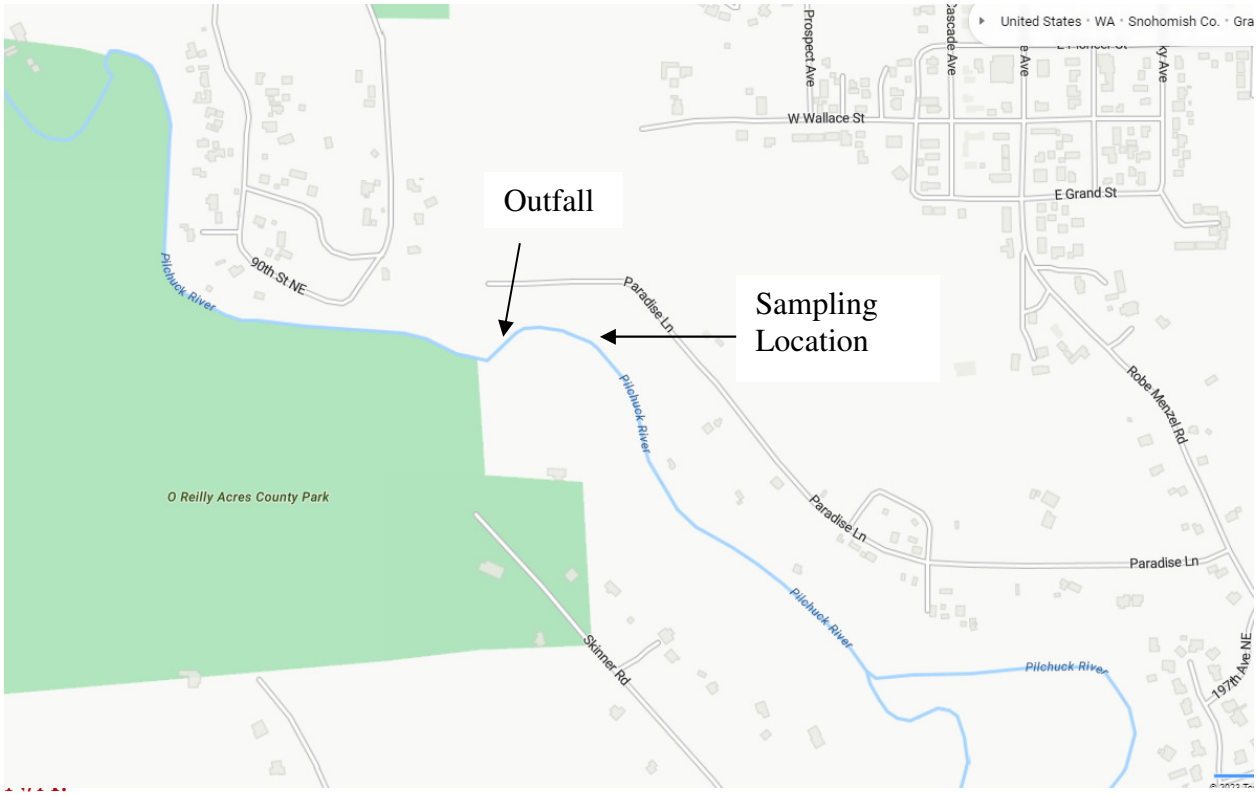
## 7.1 Study boundaries

Figure 1 shows a map of the study area and the discharge outfall in the river.

## 7.2 Field data collection

The proposed monitoring location is shown in Figure 2.

**Figure 2. Sampling Location**




## 7.4 Assumptions underlying design

The assumptions for the study design include the following:

- Sample collection and measurement frequency are sufficient for meeting the project goals described in Section 4.1.

- Collection of quality control (QC) samples (e.g., duplicates and replicates) sufficiently characterizes sampling and measurement variability.
- Calibration issues and measurement errors may cause data bias.
- Selected monitoring sites represent the ambient receiving water quality.

## 7.5 Possible challenges and contingencies

### 7.5.1 Logistical problems

Sample collection or field measurement times may need to be changed for any of the following reasons:

- Unsafe river access conditions (e.g., due to inclement weather, ice, flooding, etc.).
- Staff schedule conflicts.
- Field equipment failure.
- Sample delivery issues.
- Unforeseen circumstances

The City will develop procedures for rescheduling monitoring times and safely accessing the river during hazardous conditions.

### 7.5.2 Practical constraints

There are no known practical constraints that may limit the data collection.

### 7.5.3 Schedule limitations

The initiation of the field work will not begin prior to QAPP approval by Ecology. Once approved, it is not anticipated that the overall schedule will be affected by logistical issues because the City will be able to modify the specific days and times within each monitoring period for sample collection and field measurements.

# 8.0 Field Procedures

## 8.1 Invasive species evaluation

The Pilchuck River is not designated as an Area of Extreme or Moderate Concern for aquatic invasive species. Regardless, field staff will follow some of the procedures in SOP EAP070 (Parsons 2021) to minimize the spread of invasive species.

After conducting field work, staff will minimize the spread of invasive species by following these steps:

- Inspect all equipment and remove any visible soil, vegetation, vertebrates, invertebrates, plants, algae, or sediment. If necessary, use a scrub brush to loosen material and then rinse with clean or site water until all equipment is decontaminated.
- Drain all water from samplers or other equipment immersed in the stream before leaving the sampling site. If equipment is to be decontaminated at another location, field staff must ensure no soil, vegetation, vertebrates, invertebrates, plants, algae, or sediment is spread during transit or at the cleaning site.
- Where wading is necessary to complete field work, always swap to a clean set of waders, boots, and sampling equipment when moving between watersheds, or when moving any upstream distance within a watershed further than can be waded on foot.

## 8.2 Measurement and sampling procedures

The standard operating procedures (SOPs) that will be followed for sampling and measurement, and to ensure comparability between projects are listed below:

- Standard Operating Procedure, EAP015, Version 1.4, Manually Obtaining Surface Water Samples (Joy, J., 2021)
- Standard Operating Procedure, EAP031, Version 1.4, Collection and Analysis of pH Samples (Ward, W.J., 2018)
- Standard Operating Procedure, EAP034, Version 1.5, Collection, Processing, and Analysis of Stream Samples (Ward, W.J., 2017)
- Standard Operating Procedure, SOP EAP070, Version 2.3, Minimize the Spread of Invasive Species (Parsons, J. 2021)

In the dry season (low river flows), samples will be taken using hand-dip methods while wading in the river. In the wet season, an extension pole with a sampler attachment or hand-dip methods will be used to collect samples. Samples will be collected by quickly immersing the mouth of the bottles through the water surface to minimize the collection of floating contaminants. Samples will be processed immediately after sampling by placing in ice and delivering to the laboratory within the holding time requirements.

## 8.3 Containers, preservation methods, holding times

The table below lists the appropriate containers, preservation techniques, and holding times for samples in accordance with Title 40 Code of Federal Regulations, Part 136 (40 CFR 136).

**Table 4. Sample containers, preservation, and holding times.**

| Parameter | Matrix | Minimum Quantity | Container | Preservative | Holding Time |
|---|---|---|---|---|---|
| Alkalinity | Water | 500 mL no head space | 500 mL polyethylene bottle | Cool to 4°C ±2°C (1) | 14 days |

(1) Cooling will be done only if the sample is not tested the same day as sampled.

## 8.4 Equipment decontamination

Field gear will be cleaned in accordance with SOP EAP070 (Parsons 2021) to minimize the spread of invasive species. Sampling equipment will be rinsed thoroughly with de-ionized water after processing samples.

## 8.5 Sample ID

Each sample bottle will have a waterproof sample identification label or tag. Sample tags will be filled out completely with a waterproof pen. Tags or labels will be securely attached to sample bottles. Labels, tags, and forms will be completed prior to leaving for the field. Each sample bottle will be labeled “Rec Wat Samp” with the day’s date.

## 8.6 Chain of custody

Samples will be driven directly from the sampling location to the WWTP laboratory, about 5 minutes away, for analysis, which will be conducted the same day. No COC will be used, but a field log will be filled out each day.

## 8.7 Field log requirements

A field log will be used to record key information, including:

- Field personnel.
- Environmental conditions.
- Date, time, location ID, and description of each sample.
- Identity of QC samples collected.
- Any changes or deviations from the QAPP or SOPs.
- Unusual circumstances that might affect results.

Recommended field log practices include:

- Using permanent, waterproof ink for all entries.
- Making corrections with single line strikethroughs; initial and date corrections.

## 8.8 Other activities

Other activities to maintain sample collection, processing, and data consistency include:

- Briefings and trainings for field staff.
- Routine maintenance for sampling equipment.
- Lab notification for changes to sample schedules and bottle requirements.

# 9.0 Laboratory Procedures

## 9.1 Lab procedures table

The table below lists the measurement methods, frequency, expected range of results, and the detection limit for the parameters required for this study.

**Table 5. Measurement methods (laboratory).**

| Analyte | Sample Matrix | Samples (Number/ Arrival Date) | Expected Range of Results | Detection or Reporting Limit | Sample Prep Method | Analytical (Instrumental) Method |
|---|---|---|---|---|---|---|
| Alkalinity | Water | 4 to 5 / month May to October | 20 – 100 mg/L as CaCO3 | 5.0 mg/L (RL) | N/A | SM2320-B |

## 9.2 Sample preparation method(s)

Not applicable. No sample preparation techniques are required for this study.

## 9.3 Special method requirements

Not applicable. No special methods are required for this study.

## 9.4 Laboratories accredited for methods

The City's WWTP laboratory is accredited for alkalinity.

# 10.0 Quality Control Procedures

The project's quality control (QC) procedures consist of three parts:

1. Consistent pH meter calibration methods and schedules.
2. Adherence to the relevant SOP procedures and periodic evaluation of staff.
3. Collection of field QC measurements and samples during each sampling run.

These procedures are used to assess the quality of the collected data and to identify issues associated with data collection, processing, and analysis.

## 10.1 Table of field and laboratory quality control

**Table 6. Quality control samples, types, and frequency.**

| Parameter | Field | | Laboratory | | | |
|---|---|---|---|---|---|---|
| | Blanks | Replicates | Check Standards | Method Blanks | Analytical Duplicates | Matrix Spikes |
| Alkalinity | None | Once every 10 samples | Once every 5 batches | None | Once every 5 batches | None |

QC samples have MQOs associated with it (Section 6.2) that will be used to evaluate the quality and usability of the results.

Field blank samples will be collected as an additional sample by filling the sample bottle with laboratory deionized water and transporting and storing the sample following normal procedures. Field blank samples will be used to assess potential contamination from field and laboratory sources.

Field replicate samples or measurements will be collected as an additional sample or measurement after the initial collection at a monitoring location. This sample represents the total variability due to short-term, in-stream dynamics, sample collection and processing, and laboratory analysis.

Check standards will be used to evaluate the analytical system calibration bias. Laboratory duplicates will be used to provide an estimate of analytical precision. Laboratory method blanks will be used to check for sample contamination in the laboratory process.

## 10.2 Corrective action processes

Actions that will be taken if activities are found to be inconsistent with the QAPP, if analysis results do not meet MQOs or performance expectations, or if some other unforeseen problem arises. Such actions may include:

- Repeating quality performance checks and, if warranted, cleaning, servicing, maintaining, and re-calibrating field and lab instruments.
- Convening project personnel to decide on corrective actions.
- Verifying that field measurement, sampling methods, and analytical procedures are followed.
- Retraining staff on Standard Operating Procedures (SOPs).
- Collecting additional samples or field measurements using the methods in the QAPP.
- Reanalyzing samples within appropriate holding time requirements.
- Reanalyzing lab samples that do not meet QC criteria.
- Consulting with the lab to address a measurement or analytical problem.
- Qualifying results based on final-result confidence.

A persistent, consistent bias in the data may warrant corrective change in procedures. Potential bias from changes in analytical or sampling procedures are assessed by overlapping new and old procedures for several months before adopting the new method. The results are used to determine bias between methods and to ensure that the measurement quality objectives (MQOs) are met.

# 11.0 Data Management Procedures

## 11.1 Data recording and reporting requirements

Raw analytical results will be recorded in bound notebooks. The information will also be transferred to Excel spreadsheets.

## 11.2 Laboratory data package requirements

Analytical results and QA/QC data will be transferred to Excel spreadsheets. The Excel spreadsheets will be forwarded to Gray and Osborne for review and incorporation into the final report monthly.

## 11.3 Electronic transfer requirements

The Excel spreadsheets will be forwarded to Gray and Osborne for review and incorporation into the final report monthly.

## 11.4 EIM/STORET data upload procedures

This study is not funded by Ecology or the EPA, and therefore the data is not required to be submitted to EPA's Water Quality Exchange (WQX) or Ecology's Environmental Information Management (EIM) data system.

## 11.5 Model information management

This study is not funded by Ecology or the EPA, and therefore the data is not required to be submitted to EPA's Water Quality Exchange (WQX) or Ecology's Environmental Information Management (EIM) data system.

# 12.0 Audits and Reports

## 12.1 Field, laboratory, and other audits

Not applicable. There is no requirement for this study to be audited.

## 12.2 Responsible personnel

Not applicable.

## 12.3 Frequency and distribution of reports

A final report will be provided at the conclusion of the project per the project schedule.

## 12.4 Responsibility for reports

Gray and Osborne will author the final report.

# 13.0 Data Verification

Data verification is "the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements" (EPA, 2002).

## 13.1 Field data verification, requirements, and responsibilities

Field logs will be reviewed quarterly by Gray and Osborne to ensure adequate documentation of sampling conditions.

## 13.2 Laboratory data verification

Initial review of the analytical results and QA/QC will be performed by City staff. In addition, Gray and Osborne staff will provide independent review of the laboratory data upon receipt from the WWTP laboratory to determine if the results meet the MQOs for bias, precision, and accuracy for the study and to ensure that all required analyses were performed. Laboratory data will be reviewed to ensure any potential issues with data quality are identified and corrected prior to the next sampling event. QC results will be evaluated and compared to the quality objectives. Based on these assessments, the sample data will be accepted, accepted with appropriate qualifications, or rejected.

## 13.3 Validation requirements, if necessary

Gray and Osborne's review will serve as data validation for the project.

## 13.4 Model quality assessment

N/A

# 14.0 Data Quality (Usability) Assessment

Data assessment is "a statistical and scientific evaluation of the data set to determine the validity and performance of the data collection design and statistical test, and to determine the adequacy of the data set for its intended use" (EPA, 2002).

## 14.1 Process for determining project objectives were met

Gray and Osborne will determine if the project data meets DQOs outlined in Section 6.0. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

If data is accepted with appropriate qualifications or rejected, the following data qualifiers and definitions will be used:

- U - The analyte was not detected at or above the reported sample result.
- UJ - The analyte was not detected at or above the reported sample result. However, the reported sample result is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.
- J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample; the result is qualified as an estimate.
- R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be confirmed.
- B - An analyte was identified in an aqueous field blank as well as in the sample.

## 14.2 Treatment of non-detects

Any sample results that are non-detects will be included in the study analysis. Non-detect results will be reported as the MDL on the monthly DMR.

## 14.3 Data analysis and presentation methods

Field and laboratory data will be entered into a Microsoft Excel® spreadsheet and qualified. The calculations for precision, bias, and completeness will be performed within the spreadsheet.

Precision is calculated as the relative percent difference (RPD) of two replicate or duplicate

results. If there are more than 2 results, then precision is estimated by calculating the percent relative standard deviation (%RSD). The calculations for RPD and RSD are provided in the quality assurance glossary in Section 0.

Bias due to calibration error is calculated from the results of analyses of control standards and the true value of the control standard as defined in the quality assurance glossary in Section 0.

## 14.4 Sampling design evaluation

Representativeness will be evaluated by reviewing the actual monitoring locations and times and noting any discrepancies from the requirements specified in Section 0. Completeness will be calculated from the amount of valid measurements of each parameter obtained from the study compared to the planned amount and compared to the DQO. If representativeness is not achieved due to a problem with or change in the monitoring locations or schedule, or minimum acceptable completeness is not achieved within the proposed duration of the study, then the study schedule will be extended and additional measurements and/or samples will be collected.

## 14.5 Documentation of assessment

Documentation regarding the data usability assessment will be provided in the final report.

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# 16.0 Appendices

Appendices include:

- 16.1 Appendix A. Glossaries, Acronyms, and Abbreviations
- 16.2 Appendix B: Standard Operating Procedures

# Appendix 16.1
# Glossaries, Acronyms, and Abbreviations

**Alkalinity:** A measure of the capacity of water to neutralize acids (see pH description). Alkaline compounds in the water such as bicarbonates, carbonates, and hydroxides remove hydrogen ions and lower the acidity of the water.

**Ambient**: Background or away from point sources of contamination. Surrounding environmental condition.

**Anthropogenic**: Human-caused.

**Chronic critical effluent concentration:** The maximum concentration of effluent during critical conditions at the boundary of the mixing zone assigned in accordance with WAC 173-201A-100. The boundary may be based on distance or a percentage of flow. Where no mixing zone is allowed, the chronic critical effluent concentration shall be 100% effluent.

**Clean Water Act:** A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

**Conductivity:** A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

**Critical condition:** When the physical, chemical, and biological characteristics of the receiving water environment interact with the effluent to produce the greatest potential adverse impact on aquatic biota and existing or designated water uses. For steady-state discharges to riverine systems, the critical condition may be assumed to be equal to the 7Q10 flow event unless determined otherwise by the department.

**Designated uses:** Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained.

**Diel:** Of, or pertaining to, a 24-hour period.

**Dissolved oxygen (DO):** A measure of the amount of oxygen dissolved in water.

**Dilution factor:** The relative proportion of effluent to stream (receiving water) flows occurring at the edge of a mixing zone during critical discharge conditions as authorized in accordance with the state's mixing zone regulations at WAC 173-201A-100. http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A-020

**Diurnal:** Of, or pertaining to, a day or each day; daily. (1) Occurring during the daytime only, as different from nocturnal or crepuscular, or (2) Daily; related to actions which are completed in

the course of a calendar day, and which typically recur every calendar day (e.g., diurnal temperature rises during the day, and falls during the night).

**Effluent:** An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

**National Pollutant Discharge Elimination System (NPDES):** National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (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.

**Pollution:** Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

**Reasonable Potential Analysis (RPA):** Statistical calculation using effluent discharge monitoring data of the reasonable potential to violate aquatic life and human health water quality standards, based on mixing, effluent, and receiving water conditions.

**Streamflow:** Discharge of water in a surface stream (river or creek).

**Surface waters of the state:** Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

**Thalweg:** The deepest and fastest moving portion of a stream.

**Total Maximum Daily Load (TMDL):** A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

**Total suspended solids (TSS):** Portion of solids retained by a filter.

**Turbidity:** A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

**Wasteload allocation:** The portion of a receiving water's loading capacity allocated to existing or future point sources of pollution. Wasteload allocations constitute one type of water quality-based effluent limitation.

**Watershed:** A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

**7Q2 flow:** A typical low-flow condition. The 7Q2 is a statistical estimate of the lowest 7-day average flow that can be expected to occur once every other year on average. The 7Q2 flow is commonly used to represent the average low-flow condition in a water body and is typically calculated from long-term flow data collected in each basin. For temperature TMDL work, the 7Q2 is usually calculated for the months of July and August as these typically represent the critical months for temperature in our state.

**7Q10 flow:** A critical low-flow condition. The 7Q10 is a statistical estimate of the lowest 7-day average flow that can be expected to occur once every ten years on average. The 7Q10 flow is commonly used to represent the critical flow condition in a water body and is typically calculated from long-term flow data collected in each basin. For temperature TMDL work, the 7Q10 is usually calculated for the months of July and August as these typically represent the critical months for temperature in our state.

**90$^{th}$ percentile:** An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90$^{th}$ percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

## Acronyms and Abbreviations

| | |
|---|---|
| BMP | Best management practice |
| DO | (see Glossary above) |
| DOC | Dissolved organic carbon |
| e.g. | For example |
| Ecology | Washington State Department of Ecology |
| EIM | Environmental Information Management database |
| EPA | U.S. Environmental Protection Agency |
| et al. | And others |
| FC | (see Glossary above) |
| GIS | Geographic Information System software |
| GPS | Global Positioning System |
| i.e. | In other words |
| MEL | Manchester Environmental Laboratory |
| MQO | Measurement quality objective |
| NAF | New Approximation Flow |
| NPDES | (See Glossary above) |
| NSDZ | Near-stream disturbance zones |
| NTR | National Toxics Rule |
| PBDE | Polybrominated diphenyl ethers |
| PBT | Persistent, bioaccumulative, and toxic substance |

| | |
|---|---|
| PCB | Polychlorinated biphenyls |
| QA | Quality assurance |
| QC | Quality control |
| RM | River mile |
| RPD | Relative percent difference |
| RSD | Relative standard deviation |
| SOP | Standard operating procedures |
| SRM | Standard reference materials |
| TIR | Thermal infrared radiation |
| TMDL | (see Glossary above) |
| TOC | Total organic carbon |
| TSS | (see Glossary above) |
| USFS | United States Forest Service |
| USGS | United States Geological Survey |
| WAC | Washington Administrative Code |
| WDFW | Washington Department of Fish and Wildlife |
| WQA | Water Quality Assessment |
| WRIA | Water Resource Inventory Area |
| WSTMP | Washington State Toxics Monitoring Program |
| WWTP | Wastewater treatment plant |

## Units of Measurement

| | |
|---|---|
| °C | degrees centigrade |
| cfs | cubic feet per second |
| cfu | colony forming units |
| cms | cubic meters per second, a unit of flow |
| dw | dry weight |
| ft | feet |
| g | gram, a unit of mass |
| kcfs | 1000 cubic feet per second |
| kg | kilograms, a unit of mass equal to 1,000 grams |
| kg/d | kilograms per day |
| km | kilometer, a unit of length equal to 1,000 meters |
| l/s | liters per second (0.03531 cubic foot per second) |
| m | meter |
| mm | millimeter |
| mg | milligram |
| mgd | million gallons per day |
| mg/d | milligrams per day |
| mg/kg | milligrams per kilogram (parts per million) |
| mg/L | milligrams per liter (parts per million) |
| mg/L/hr | milligrams per liter per hour |
| mL | milliliter |
| mmol | millimole or one-thousandth of a mole |
| mole | an International System of Units (IS) unit of matter |
| ng/g | nanograms per gram (parts per billion) |

| | |
|---|---|
| ng/kg | nanograms per kilogram (parts per trillion) |
| ng/L | nanograms per liter (parts per trillion) |
| NTU | nephelometric turbidity units |
| pg/g | picograms per gram (parts per trillion) |
| pg/L | picograms per liter (parts per quadrillion) |
| psu | practical salinity units |
| s.u. | standard units |
| µg/g | micrograms per gram (parts per million) |
| µg/kg | micrograms per kilogram (parts per billion) |
| µg/L | micrograms per liter (parts per billion) |
| µm | micrometer |
| µM | micromolar (a chemistry unit) |
| µmhos/cm | micromhos per centimeter |
| µS/cm | microsiemens per centimeter, a unit of conductivity |
| ww | wet weight |

## Quality Assurance Glossary

**Accreditation:** A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

**Accuracy:** The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS, 1998).

**Analyte:** An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

**Bias:** The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

**Blank:** A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS, 1998).

**Calibration:** The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology, 2004).

**Check standard:** A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab

Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

**Comparability:** The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

**Completeness:** The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

**Continuing Calibration Verification Standard (CCV):** A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

**Control chart:** A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

**Control limits:** Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

**Data integrity:** A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

**Data quality indicators (DQI):** Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

**Data quality objectives (DQO):** 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).

**Data set:** A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

**Data validation:** An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.
- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

**Data verification:** Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology, 2004).

**Detection limit** (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

**Duplicate samples:** Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

**Field blank:** A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology, 2004).

**Initial Calibration Verification Standard (ICV):** A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

**Laboratory Control Sample (LCS):** A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

**Matrix spike:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology, 2004).

**Measurement Quality Objectives** (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

**Measurement result:** A value obtained by performing the procedure described in a method (Ecology, 2004).

**Method:** A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (EPA, 1997).

**Method blank:** A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology, 2004; Kammin, 2010).

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

**Percent Relative Standard Deviation (%RSD):** A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

**Parameter:** A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Ecology, 2004).

**Population:** The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

**Precision:** The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS, 1998).

**Quality assurance (QA):** A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

**Quality Assurance Project Plan (QAPP):** A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

**Quality control (QC):** The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

**Relative Percent Difference (RPD):** RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

**Replicate samples:** Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS, 1998).

**Representativeness:** The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS, 1998).

**Sample (field):** A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS, 1998).

**Sample (statistical):** A finite part or subset of a statistical population (USEPA, 1997).

**Sensitivity:** In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology, 2004).

**Spiked blank:** A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

**Spiked sample:** A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

**Split sample:** A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

**Standard Operating Procedure (SOP):** A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

**Surrogate:** For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

**Systematic planning:** A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

## References for QA Glossary


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# Appendix 16.2
# Standard Operating Procedures

DEPARTMENT OF ECOLOGY
State of Washington

# Standard Operating Procedure
# EAP015, Version 1.4

## Manually Obtaining Surface Water Samples

August 2021
Publication 21-03-028
[Recertified August 2019]

# 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/2103208.html.

Ecology's Activity Tracker Code for this SOP is 15-072.

***Recommended citation*:**
Joy, J. 2019. Standard Operating Procedure EAP015, Version 1.4: Manually Obtaining Surface Water Samples. Washington State Department of Ecology, Olympia.
https://apps.ecology.wa.gov /publications/SummaryPages/2103208.html.
[Approved or Recertified August 2019.]

# Contact Information

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology – https://ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Original Author – Joe Joy (retired)
Date – 10/24/2006

Original Reviewer – Trevor Swanson
Date – 6/26/2013

Reviewer – Eiko Urmos-Berry
Date – 07/18/2019

Current Reviewer – Arati Kaza
Date – 08/06/2019

QA Approval – Arati Kaza, Ecology Quality Assurance Officer

Recertification Date – 08/06/2019

SIGNATURES AVAILABLE UPON REQUEST

*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.*

*Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by Ecology.*

*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 | Revisers |
|---|---|---|---|---|
| 10/10/2006 | 1.0 | Formatting; signatories | All | Bill Kammin |
| 7/1/2010 | 1.1 | Three-year review | All | Kammin |
| 6/26/2013 | 1.2 | Three-year review | All | Trevor Swanson |
| 7/28/2016 | 1.3 | Three-year review/recertification. Made quite a few changes to update references and links to manuals, SOPs, and websites. | All | Eiko Urmos-Berry |
| 7/18/2019 | 1.4 | Converted SOP to new template, updated Figure 1 photo, added alt text to all figures and photos, updated references and links, and fixed minor grammatical errors. | All | Eiko Urmos-Berry |
| 8-9-2021 | 1.4 | Applied Accessibility standards | All | Joan LeTourneau |
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## 1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for manually obtaining surface water samples.

1.2 This includes procedures for collecting samples from lotic and lentic waterbodies, wastewater treatment plant access points, and outfalls, pipes, and drains. It also describes procedures for sampling while wading on beaches and from boats and bridges. This SOP does not describe the operation of unattended automated sampling devices, nor does it cover pelagic marine or groundwater sampling.

## 2.0 Applicability

2.1 This SOP should be followed when manually collecting samples from surface waters as described in section 1.2.

## 3.0 Definitions

3.1 Composite sample: A sample in one container comprised of discrete sub-samples collected spatially, temporally or both.

3.2 Grab sample: A sample collected during a very short time period at a single location.

3.3 Halocline: The depth where salinity increases rapidly over a relatively short depth interval in a manner similar to temperature in a thermocline.

3.4 Integrated sample: A sample comprised of continuously collected sub-samples from a water column or across a cross section of a waterbody - differentiated from a composite sample by the term ‘continuously collected.’

3.5 Intermediate sampling container: A temporary sampling container used to directly sample water and transfer it to the primary container. Often, 500 or 1000 mL polypropylene containers are used as intermediate containers to collect samples for transfer to smaller bottles, which often contain acids or other preservatives.

3.6 LAR: Laboratory Analysis Request form.

3.7 Lotic: Flowing water systems such as rivers and streams.

3.8 Lentic: Still water systems such as lakes and ponds.

3.9 MEL: Manchester Environmental Laboratory

3.10 Pelagic: Waters of open seas, oceans, or lakes that are not near the shore.

3.11 Thalweg: The line defining the points along the length of a river bed with the greatest volume of moving water.

3.12 Thermocline: A distinct layer in a waterbody in which temperature changes more rapidly with depth than it does in the layers above or below, usually at a rate of 1º C or more for each 1 meter of depth.

3.13 Thiosulfate: A chemical MEL puts into sampling containers to rapidly dechlorinate water samples, especially those taken at wastewater treatment facilities.

## 4.0 Personnel Qualifications/Responsibilities

4.1 All field staff must comply with the requirements of the EAP Safety Manual (Ecology, 2019). A full working knowledge of the procedures in Chapter 1 - General Field Work, especially the sections titled Working in Rivers and Streams, Working near Traffic and from Bridges, and Fall Protection, is expected. Sampling from a boat requires one person onboard to be a qualified boat operator and all persons onboard must be familiar with Chapter 3 of the EAP Safety Manual - Boating.

4.2 All field staff must be familiar with other standard procedures for sampling water quality parameters described in this SOP. Several water quality parameters have special sample pre-treatment, filtering, post-treatment, and collection procedures applicable to this SOP. If a vertically (depth) integrated sampler is to be used, field staff should read Isokinetic Depth-Integrated Sampling Methods, Chapter A4, section 4.1.3 (USGS, 2006).

4.3 The field lead directing sample collection must be knowledgeable of all aspects of the project's Quality Assurance Project Plan (QAPP) to ensure that credible and useable data are collected. All field staff should be briefed by the field lead or project manager on the sampling goals and objectives prior to arriving to the site.

4.4 All field staff must comply with EAP Procedure 1-15, *Minimizing the Spread of Aquatic Organisms* (EAP, 2010), found at:
http://teams/sites/EAP/EAPProcedures/01-15InvasiveSpecies.pdf
and SOP EAP070, *Minimizing the Spread of Aquatic Invasive Species* (Parsons et al, 2018) found at:
https://apps.ecology.wa.gov /publications/SummaryPages/1803201.html

4.5 This SOP pertains to all Natural Resource Scientists, Environmental Engineers, Environmental Specialists, Hydrogeologists, and Interns and Technicians in WA Department of Ecology's Environmental Assessment Program.

## 5.0 Equipment, Reagents, and Supplies

### *5.1 Equipment and Supplies*

5.1.1 Intermediate sampling containers and devices (e.g., 500 or 1000 mL bottles, syringe for field filtering, stainless or Teflon dipper, depth integrated sampler, Van Dorn or Kemmerer sampler, appropriate ropes/cables/rods, mobile bridge crane or davit) (Figure 1).

**Figure 1**
*Top (left to right):* **Weighted sampler with bottles and dissolved oxygen bucket for bridge sampling; Kemmerer bottle.**
*Bottom (left to right):* **Van Dorn sampler; DH-76 depth integrated sampler with bottle.**

5.1.2 Sampling extension pole with sampling container attachment.

5.1.3 Glass or polypropylene bottle supplied by the laboratory with appropriate preservatives and filtering devices (Figure 2).

5.1.4 Safety equipment appropriate for the sampling sites: safety vests and lines, personal floatation devices (PFDs), bridge traffic control signs and cones, or boating safety equipment.

5.1.5 Latex gloves for hygienic protection; leather gloves for handling ropes and cables.

5.1.6 Anti-bacterial hand sanitizer or soap.

5.1.7 Coolers.

5.1.8 Ice (Regular, blue, or dry – depending on shipping method).

5.1.9 Deionized water.

5.1.10 Sample tags with sample numbers assigned by MEL

5.1.11 LAR forms.

5.1.12 Field notebook and pens.

5.1.13 Disinfection solutions, brushes, or other equipment necessary to minimize the spread of invasive species from site to site. See EAP Policy 1-15 for more information.

5.1.14 Sampling containers

- The most common containers for sampling surface waters in EAP are made of polypropylene or glass. The MEL manual (MEL, 2016) describes the type of bottle and volume of sample necessary to complete the laboratory analysis. The containers usually come directly from MEL and some may have chemicals to stabilize or neutralize the sample.

**Figure 2: Sample containers commonly used for water samples.**

- Check bottles for loose lids. Damaged or leaking containers should be recycled or discarded.
- Containers left over from previous projects should be closely inspected before using. Bottles with old or discolored preservative should be sent back to MEL for proper disposal. Fecal coliform sampling bottles, 500 and 1000 mL polypropylene bottles, and 500 mL Teflon metal sampling bottles (and associated Teflon vials with nitric acid preservative) should also be sent back to MEL for reuse. Most other bottles can be recycled or discarded as necessary. Check with MEL if there is a question on whether a bottle can be reused.
- Holding times for sterilized microbiological sample bottles are 6 months. MEL does not guarantee that bottles are sterile after 6 months. Check the MEL manual (MEL, 2016).
- For efficiency, some parameters can be combined into one container. Check the MEL manual (MEL, 2016).

## 6.0 Summary of Procedure

### *6.1 Pre-sampling Preparation*

6.1.1 File an EAP Field Plan. This plan also includes a section to enter information pertaining to a Float Plan. Forms are available and should be posted on the EA Program SharePoint site at: http://teams/sites/EAP/Field%20Schedules/Forms/AllItems.aspx

6.1.2 Obtain proper sample bottles from the laboratory and arrange for sample analyses. MEL's sample container request and pre-sampling notification forms are available at http://teams/sites/EAP/manlab/LabUsers/SitePages/Home.aspx. MEL will provide lab sample numbers after forms are submitted.

6.1.3 Obtain ropes, extension poles, meters, and intermediate sampling devices through equipment check-out procedures.

6.1.4 Notify the laboratory at least two weeks prior to sampling, especially if special preparations are needed for your samples or the parameters have a short holding time.

6.1.5 Sampling on Thursday through Sunday must be pre-approved with the laboratory for bacteria and other analyses with short holding times.

6.1.6 If the range of concentrations can be estimated before sampling (from past samples or otherwise), inform the lab beforehand or write it on the sample tags so the proper set of dilutions can bracket the range.

6.1.7 If the water is extremely turbid (<25 mL can be filtered) the laboratory may need to modify its analytical method. Call the lab as soon as possible so they can prepare for adjustments.

6.1.8 Prior to collecting sample, prepare sample ID tags containing the project name, sample number, site, date, parameter, and space for time. Also, prepare a field lab book or page with similar information.

6.1.9 Pre-book air transportation for sample coolers if possible. For ground shipments, check on delivery times and last shipment times for the day.

## *6.2 General Considerations and Cautions*

6.2.1 Never compromise your personal safety or that of a field partner to collect a water sample. Always plan ahead to avoid falling and drowning hazards.

6.2.2 If only one sample is taken from a site in a lotic system, collect it in, or as close as safely possible, to the thalweg or predominant downstream current. Avoid back eddies and side channels that would not be representative of the water quality affecting downstream sites. If stratification is present, consider sampling the strata individually.

6.2.3 If collecting samples along a transect while wading, set-up a tag line for safety and to help keep a straight transect.

6.2.4 If only one sample is taken from a site in a lentic or estuarine system, determine the most representative site to safely sample and achieve the goal of the project. Determine if stratification is present with a thermistor, salinometer, or by other means. If stratification is present, consider sampling the strata individually. Note the depth of the halocline or thermocline in the field notebook and the depth where a sample was collected.

6.2.5 Do not rinse a sterilized sample container or one that contains preservative.

6.2.6 Collect water samples after performing other field tasks if they cannot immediately be stored in a cool, dark place.

6.2.7 Be careful not to disturb sediment from the stream bed, particularly in slower moving waters. If sample contamination from stirred sediment is an issue, collect samples from the bank using a sampling extension pole while avoiding touching the stream bottom.

6.2.8 If sampling from a bridge, find the thalweg and determine if the current is too strong for a weighted sampling device to sink and obtain a representative sample.

6.2.9 If sampling from a boat, avoid gas and oil contamination. Collect the sample from near the bow while the boat moves upstream or upwind.

6.2.10 Before leaving the sampling site, inspect and clean all equipment (sampling devices, ropes, boots, etc.) to the level required by EAP070 – Minimizing the Spread of Invasive Species.

### *6.3 Direct Sampling*

6.3.1 Remove stopper/lid from container just before sampling. Be careful not to contaminate the cap, neck, or the inside of the bottle with your fingers, wind-blown particles, or dripping water from your clothes, body, or overhanging structures.

6.3.2 If no preservative is present in the container, face upstream in lotic waters and upwind in lentic waters and proceed as follows:

6.3.3 Hold the container near its base, reach out in front of your body, and plunge it (mouth down) below the surface to about mid-water column. If the water is so shallow that this technique will disturb sediment and contaminate the sample, it may be necessary to collect a surface water sample. Make sure to note your change of methods, if any.

6.3.4 Fill the bottle to the appropriate level depending on the analyte to be tested.

6.3.5 Pour out a small volume if needed to create a headspace for mixing in the lab. Do not create a headspace for some analytes like volatile organics and alkalinity.

6.3.6 If an extension pole is used from a pier, dock, or from shore, securely attach the sample container (with its lid in place) to the holder with the clamps or bands. Remove the container lid, being careful not to contaminate the container, and follow the above procedure. Do not use this method for samples that already have preservative in the container; use methods outlined in 6.4 - Sampling with Intermediate Devices and Containers.

6.3.7 If preservative is present in the container and you can reach the water with your hand, use the following procedure:

6.3.8 Hold the container upright and place the lid over the mouth so that only a small area forms an opening (Figure 3).

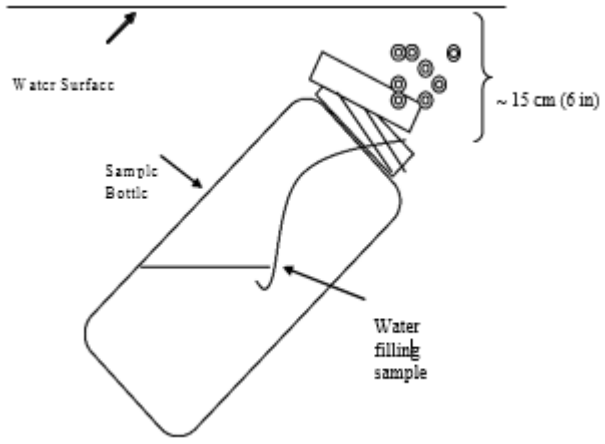


**Figure 3: Illustration of the cap position of a sample container that already contains a preservative while filling with a sample.**

6.3.9 Immerse the bottle about 15 cm (6 inches) under the water surface while holding the cap in position with your fingers as far away from the opening as possible.

6.3.10 Observe the rate the container is filling and remove it from the water before the headspace area is reached. If overfilling occurs, get a new sample container and repeat.

6.3.11 This procedure does not work well in fast moving, shallow water. Use procedures in section 6.4 if this is the case.

6.3.12 Sample free-falling water from drains, pipes, and outfalls by using an intermediate sampling device if necessary

6.3.13 Replace the lid of the container. Invert it several times to evenly mix any preservative with the sample.

6.3.14 Rinse any large amount of dirt or debris from the outside of the container.

6.3.15 Mark the time on the sample ID tag, and then attach it to the container. Place in appropriate storage.

### *6.4 Sampling with Intermediate Devices and Container*

6.4.1 Triple rinse an intermediate container (Figure 1) with site water and pour the rinsate away from or downstream of the sampling location. If used in a contaminated environment (e.g. wastewater treatment plant, stormwater drain), it should be washed with soap and water and rinsed off-site before use. Some organic and micronutrient sampling procedures require acid and deionized water rinses as well. For especially turbid sites, be sure to inspect and rinse out any sediment or organic debris that may have collected at the bottom of the container. If there is any doubt, use a new and clean container to sample.

6.4.2 Fill the intermediate container with water following the technique described in 6.4.1 as closely as possible. Submerge the container to a depth that does not disturb bottom sediments, but also avoids sampling the surface layer.

6.4.3 For vertically (depth) integrated samples, raise and lower the sampler at a constant rate. If the sample container is overfilled or underfilled, dump the sample and adjust the transit rate or try a different nozzle size (USGS, 2006).

6.4.4 Kemmerer or Van Dorn bottles should be lowered to an appropriate depth and triggered with a messenger. Be aware that messengers may not work if the messenger is too light for the transit depth to the bottle.

6.4.5 Sticks and leaves can be removed from the bucket or dipper if contamination of the sample can be avoided. Gently mix the water in the intermediate container by swirling before pouring it into the sample containers if using an open-top container, or slowly inverting three times if using a closed-top container. From the intermediate container, carefully fill the sample containers, leaving adequate headspace as needed. Do not overfill. Put a note in the field notebook if you suspect that sand or other heterogeneous materials were not adequately represented in the sample.

6.4.6 Release the first 50 - 100 mL from the Kemmerer or Van Dorn sampler outlet before beginning to fill sample containers. Avoid contaminating the sample with your hands or with the outlet extension tube.

6.4.7 Securely replace the stopper/lid of each sample container. Invert several times to evenly mix preservative with the sample.

6.4.8 Rinse any large amount of dirt or debris from the outside of the container.

6.4.9 Attach the ID tag. Place in appropriate storage.

### *6.5 Samples Collected from Bridges*

6.5.1 Follow the guidelines in the EAP Safety Manual chapter, Working near Traffic and from Bridges. Sample from the bridge only if all safety precautions are taken and the risk of injury is negligible.

6.5.2 Pick a spot on the downstream side of the bridge and observe the following:

- Make sure you are over the thalweg of the water body.
- Is the current too swift for the weight of your sampler? Do you have enough rope/rods/cables to break the water's surface and overcome the downstream current velocity? Will you be able to pull a weighted bucket up against the force of the current?

- Are debris moving downstream or is there boat traffic moving upstream or downstream? If conditions warrant, post an observer with a clear view of upstream and downstream conditions.
- If you do not know the depth of water at the site, roughly measure it. This is so the sampling device will not disturb bottom sediments when deployed.
- Clear any loose debris from the bridge railing and make sure the path from the railing to the water's surface is clear of obstructions.

6.5.3 If the DH-76 or other vertical (depth) integrated sampling device is being used, measure both depth and velocity at the transect points on the bridge. Mark transect points or stretch a tape along the bridge for easier reference.

6.5.4 Assemble, secure, and untangle the sampler with ropes/rods/cables and keep feet and legs clear of all ropes/rods/cables. Be aware of bridge traffic.

6.5.5 If the DH-76 or other integrated sampling device is being used, install the correct nozzle size for the depth and velocities at the site.

6.5.6 Place a clean intermediate container or sterilized bottle into the sampler and secure carefully.

6.5.7 Remove the stopper/lid just before lowering the sampler-with-bottle down on the rope, and set it somewhere free of dirt or other sources of contamination.

6.5.8 Wear heavy duty gloves to protect your hands from rope burns. Lower the sampler in such a manner so as not to contaminate the open bottle with dirt or dripping water.

6.5.9 When approaching the water surface, lower the sampler to where the bottom of the sampler is touching the water surface. This will clean any debris on the bottom the sampler. If the sampler has a fin on it, the sampler will position itself with the flow. Then lower the sampler quickly to submerge and collect a sample.

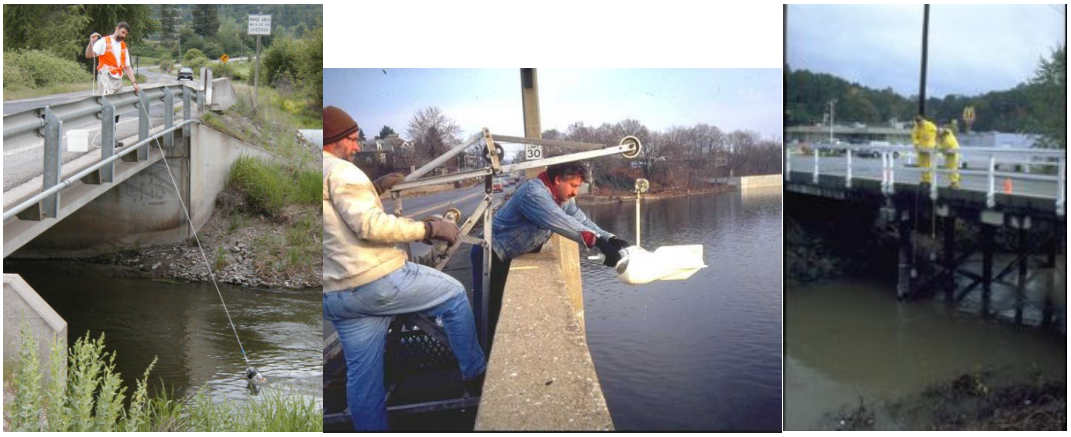

**Figure 4: Various methods of collecting water samples from bridges.**

6.5.10 Keep the bottle submerged long enough for the container or bucket to fill.

6.5.11 For vertically (depth) integrated samples, raise and lower the sampler at a constant rate. If the sample container is overfilled or underfilled, dump the sample and adjust the transit rate or try a different nozzle size (USGS, 2006).

6.5.12 Be aware that if Kemmerer and Van Dorn bottles are being used from bridges and the river current is swift, the messenger may not be able to trigger the closing mechanism.

6.5.13 Pull up the sampler and bottle; be careful not to contaminate the sample with dirt or water from either the rope or bridge, or other sources of contamination.

6.5.14 Pour out a small amount of the sample to allow for the air space needed for proper mixing at the lab (unless bottle contains preservative).

6.5.15 Replace the stopper/lid.

6.5.16 Rinse any large amount of dirt or debris from the outside of the container.

### *6.6 Samples Collected from Wastewater/Point Source Effluent*

6.6.1 Conduct a reconnaissance of potential sampling sites with assistance from facility personnel. Attend to all safety precautions. Avoid confined spaces.

6.6.2 Locate an appropriate sampling location representative of water being discharged to the receiving water body. In particular, the location should be below any chlorination or ultra-violet (UV) application.

6.6.3 Use a sampling extension pole or dipper (Figure 4) to collect samples without contacting the effluent with your hands. Wear protective clothing and gloves.


a)

b)

**Figure 5: a) Dipper and extension pole used from a streambank. b) Syringe and filter used for dissolved nutrient samples**

6.6.4 Note residual chlorine concentrations on lab sample tags.

6.6.5 If sampling bacteria at a facility that uses chlorine for disinfecting its effluent, order bottles with thiosulfate from MEL, to neutralize the chlorine

### *6.7 Samples Collected from Marine Water Bathing Beaches*

6.7.1 (Taken from the Beach Environmental Assessment, Communication and Health (BEACH) program guidance). More beach sampling information is available from the Quality Assurance Project Plan: BEACH Program (Sargeant, Lowe, 2014 and Ruffner, 2019).

6.7.2 Wade into roughly 2.5 feet of water.

6.7.3 Fill a water bottle at sampling sites by following procedures 6.3 or 6.4, as appropriate. If possible, use a sampling extension pole (Figure 4) to avoid collecting disturbed sediment.

### *6.8 Sample Labeling and Storage*

6.8.1 After collecting the sample, immediately loop the string attached to the proper sample tag over stopper/lid until secure. Make sure to attach sample tag beneath, not on top of, the aluminum foil cover of microbiology bottles, as the covers can be easily separated from the sample during transport and handling.

6.8.2 Check the tag to ensure accurate location and analytical information. Record the time the sample was collected on the tag and enter relevant data into the field notes. Use waterproof ink or pencil.

6.8.3 Place labeled sample bottle in a cooler with ice. It is important to cool most samples to 6˚C immediately and store them in the dark.

### *6.9 Sample Transport*

6.9.1 Samples transported from the EAP Operations Center (OC) by MEL courier.

6.9.2 Pack samples in regular cubed or crushed ice. Deliver samples to walk-in cooler at EAP OC and leave Lab Analysis Requested (LAR) forms in the "Out" box near the walk-in cooler. Make sure the LAR form contains the project name, station names, sample numbers, date, times, and parameters. The LAR form is available at: http://teams/sites/EAP/manlab/LabUsers/SitePages/Home.aspx. Carbon copy forms can be requested from the MEL courier.

6.9.3 Samples shipped via air or ground freight service

6.9.4 If glass containers are shipped to MEL, make sure they are adequately wrapped in "bubble" packing material to prevent breakage. Pack samples using blue ice. Cool to 4˚C and store in dark cooler. In warmer weather (80˚F and above), use ten to twelve blue ice packs per cooler. In cooler weather (below 80˚F) use six to eight blue ice packs, to avoid freezing samples. If you have access to dry ice, you may use it to ship **frozen** samples only. Be sure to contain the dry ice in newspaper or cardboard and to use packing materials around the sample containers. Also, use a well sealed container and include blue ice to keep the dry ice cold.

6.9.5 Put LAR form in a waterproof bag or tape it to the inside of the cooler lid and tape coolers shut after inspection. For air shipments, coolers must first be inspected by TSA. Make sure that coolers are taped shut after inspection.

## 7.0 Records Management

7.1 Specifically list forms to be used and locations of files.

7.2 Each sample collection will be fully described in the field notebook with waterproof ink (e.g., date, time, location identification, sample laboratory identification number, sample type, analyses to be performed, and ancillary data). Entries will be kept neat and concise. Measures will be taken to avoid losing the field notebook.

7.3 Sample locations will be described in enough detail to find on an Environmental Information Management (EIM) System map cover. Otherwise, a global positioning system (GPS) unit will be used to record an accurate location. Coordinates will be recorded as per EIM requirements.

7.4 Information for each laboratory sample will be entered onto a LAR form when the samples are submitted to MEL or other analytical facility.

## 8.0 Quality Control and Quality Assurance

8.1 QA/QC procedures will be addressed thoroughly on a project-by-project basis in the QAPP for the project.

## 9.0 Safety

9.1 Identify products, supplies, reagents, and activities that pose a safety hazard of any kind. Refer to EAP HQ Safety Manual when appropriate.

9.2 All field staff must comply with the requirements of the EAP Safety Manual, especially Chapter 1 - General Field Work, which includes special circumstances like fall protection, working on bridges, and working in rivers and streams. Sampling from a boat requires one person onboard to be a qualified boat operator and all persons onboard must be familiar with Chapter 3 of the EAP Safety Manual, Boating.

9.3 For further field health and safety measures refer to the EAP Safety Manual: http://teams/sites/EAP/safety/FieldOpsandSafetyManual.docx

9.4 Heavy duty gloves will protect hands from rope burns when lowering intermediate sampling equipment from bridges. Care is necessary on bridges to keep lines, ropes, and cables clear of other equipment, legs, and traffic.

9.5 Preferably, latex gloves should be worn to avoid bacterial or chemical exposure while performing direct sampling. If gloves are not worn, hands should be cleaned using anti-bacterial soap or hand sanitizer after each sampling station. Before ingesting food or drink, dirty over-clothes should be changed and hands should be washed.

## 10.0 References

10.1 Ecology, 2019. Environmental Assessment Program Safety Manual. Washington State Department of Ecology. Olympia, WA. http://teams/sites/EAP/safety/FieldOpsandSafetyManual.docx

10.2 Environmental Assessment Program, 2010. EAP Policy 1-15: Minimize the Spread of Aquatic Invasive Species. Washington State Department of Ecology. Olympia, WA. http://teams/sites/EAP/EAPProcedures/01-15InvasiveSpecies.pdf

10.3 MEL, 2016. Manchester Environmental Laboratory Lab Users Manual Tenth Edition Environmental Assessment Program. Washington State Department of Ecology. Manchester, WA.

10.4 Parsons, J. et al., 2018. Standard Operating Procedures EAP070, Version 2.2: Minimize the Spread of Invasive Species, Environmental Assessment Program, Olympia, WA. 33 pp. https://apps.ecology.wa.gov /publications/SummaryPages/1803201.html

10.5 Quality Assurance SharePoint site http://teams/sites/eap/qualityassurance/default.aspx

10.6 Quality Assurance internet site: https://ecology.wa.gov/About-us/How-we-operate/Scientific-services/Quality-assurance

10.7 Ruffner, J., 2018. Addendum to Quality Assurance Project Plan: Beach Environmental Assessment, Communication, and Health (BEACH) Program: Monitoring Washington State Marine Beaches. Environmental Assessment Program, Olympia, WA. 9 pp. https://apps.ecology.wa.gov /publications/SummaryPages/1803108.html

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10.9 U.S. Geological Survey, 2006. Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, Sept. 2006. http://pubs.water.usgs.gov/twri9A4/.

DEPARTMENT OF ECOLOGY
State of Washington

# Standard Operating Procedure EAP031, Version 1.4

# Collection and Analysis of pH Samples

December 2018
Publication 18-03-240

## 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://fortress.wa.gov/ecy/publications/SummaryPages/1803240.html.

Ecology's Activity Tracker Code for this SOP is xx.

## Contact information

For more information contact:

Communications Consultant

Environmental Assessment Program

P.O. Box 47600, Olympia, WA 98504-7600

Phone: 360-407-7680

Washington State Department of Ecology – ecology.wa.gov

| Location of Ecology Office | Phone |
|---|---|
| Headquarters, Lacey | 360-407-6000 |
| Northwest Regional Office, Bellevue | 425-649-7000 |
| Southwest Regional Office, Lacey | 360-407-6300 |
| Central Regional Office, Union Gap | 509-575-2490 |
| Eastern Regional Office, Spokane | 509-329-3400 |

Washington State Department of Ecology

Environmental Assessment Program

# Standard Operating Procedures for the Collection and Analysis of pH Samples

Version 1.1

Author - William J. Ward
Date -

Reviewers – Dan Dugger (2013), Casey Clishe (2007)
Date -

QA Approval - William R. Kammin, Ecology Quality Assurance Officer
Date – 8/13/14

EAP031

Originally Approved -- June 14, 2007

Signatures on File

*Please note that the Washington State Department of 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.*

*Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.*

*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 | Rev number | Summary of changes | Sections | Reviser(s) |
|---|---|---|---|---|
| 4/9/2007 | 1.1 | Editorial; formatting | All | Bill Ward |
| 4/17/2007 | | Comments | All | Dave Hallock |
| 4/27/2007 | 1.2 | Edits based on comments | All | Bill Ward |
| 5/15/2005 | | Editorial comments | All | Bill Kammin |
| 5/18/2007 | | Edits based on comments | All | Bill Ward |
| 6/7/07 | | Editorial | All | Casey Clishe |
| 6/7/07 | 1.3 | Edits based on comments | All | Bill Ward |
| 6/13/2007 | 1.3 | Correct footer, title page | All | Bill Kammin |
| 4/10/13 | | Added new chemical awareness and waste disposal language, and updated procedures. Attached MSDS sheets. Also made minor procedure updates | 5, 6, 9 | Bill Ward |
| 5/12/14 | | Editorial comments | All | Dan Dugger, Andy Bookter, Bill Kammin |
| 5/14/14 | 1.4 | Edits based on all comments | All | Bill Ward |
| 8/13/14 | 1.4 | Final edits | All | Olegre, Kammin |
| 6/29/17 | 1.4 | Recertification | All | Kammin |
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## 1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for the field collection and analysis of pH samples. The SOP covers meter calibration, sample collection, sample measurement, and quality assurance/quality control procedures to ensure we have the highest data quality. It is not a substitute for the electrode user manual: calibration, maintenance, storage, and troubleshooting recommendations, or the mandatory training.

## 2.0 Applicability

2.1 This SOP is intended for freshwater monitoring.

## 3.0 Definitions

3.1 Ecology – Washington State Department of Ecology.

3.2 EAP – Environmental Assessment Program.

3.3 EIM – Environmental Information Management System. A searchable database developed and maintained by the Washington State Department of Ecology.

3.4 Field Logbook – A weather resistant logbook containing "Rite in the Rain" ® writing paper used to document any and all field activities, sample data, methods and observations for each and all sample sites.

3.5 MQO's – Measurement Quality Objectives

3.6 MSDS – Material Safety Data Sheets provides both workers and emergency personnel with the proper procedures for handling or working with a particular substance. MSDS's include information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment and spill/leak procedures.

3.7 OC – Operations Center. The location of the program field equipment, boats, walk-in cooler and shop (where technicians repair or fabricate the equipment).

3.8 pH – A measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solutions, increasing with increasing alkalinity and decreasing with increasing acidity. The pH scale ranges from 0 to 14.

## 4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2012). The required trainings include: First Aid, CPR, and Defensive Driving.

4.2 Boat operations require that staff meet specific training requirements as described in EAP's Field Safety Manual, such as an EAP Boating Course and an approved Boating Safety Course.

4.3 Because the procedure requires the use of hazardous materials, training is required as per the Ecology Chemical Hygiene Plan and Hazardous Material Handling Plan (Section 1) (WA State Department of Ecology, 2011), which includes Laboratory Safety Orientation, Job-Specific Orientation and Chemical Safety Procedures. The Standard Operating Procedures in Section 16 of the Chemical Hygiene Plan and Hazardous Material Handling Plan for handling chemicals must also be followed.

## 5.0 Equipment, Reagents, and Supplies

5.1 Bridge Sampler.
5.2 Sampling ropes (1 @ 10 ft., 1 @ 35 ft. and 2 @ 55 ft.).
5.3 Extension pole with a bottle clamp.
5.4 Field Logbook or Field Data Report Form (See Attachment A for example form).
5.5 Refillable pH electrode that is capable of having at least a two point calibration. *Note: Non-refillable (gel-filled) electrodes are not considered reliable enough for our field measurements.*
5.6 QC 7 pH buffer that is from a different manufacturer than the pH 7 calibration buffer.
5.7 pH buffers that bracket the expected range of field measurements (See Attachment B for MSDS sheets). *Note: These buffers are not considered a health hazard.*
5.8 Dedicated pH buffer calibration bottles (125 mL clear bottles) or pouches.
5. 9 pH electrode filling and storage solution. (See Attachment C for MSDS sheet). *Caution: These solutions may cause eye irritation.*
5. 10 Deionized water (DI water) and squirt bottle.
5. 11 Meter Calibration Log Form (See Attachment D for example form).

## 6.0 Summary of Procedure

6.1 Meter Calibration. *Note: Always store the meter, electrode, pH buffers, and filled DI squirt bottle overnight in a heat-controlled room that is kept between 15-30 °C (59-86°F). Also, all pH electrode calibrations must be done using buffers that are above 15°C (but not warmer than 30°C). Further, always keep the electrode upright (sensor tip down) and the storage bottle about half-full of the filling and storage solution.*

6.1.1 Empty and refill the dedicated pH buffer calibration and QC check bottles with fresh solution at the beginning of each week or when considered contaminated.

6.2 Non-Hach PHC281 Electrode Calibrations.

6.2.1 Calibrate electrode following the meter instruction manual for a two- or three-point calibration. Buffers used for a two-point calibration must bracket the expected range of the field measurement results (e.g., 4 and 7 or 7 and 10).

6.2.2 Record the calibration information on the calibration sheet or field log. Then reattach the electrode storage bottle, plug the electrode filling-hole hole, and store the electrode upright.

6.2.3 Hach PHC281 Electrode Calibrations.

6.2.3.1 Clear the junction. Remove the filling-hole cap, and slowly pull the attached electrode soaker bottle down the electrode in half-inch increments until there is a noticeable drop in the volume of the electrode filling solution.

6.2.3.2 Remove the electrode storage bottle and top off the electrode fill chamber with filling solution.

6.2.3.3 Calibrate electrode following the meter instruction manual for a three-point calibration (Note: Hach 4, 7, and 10 buffers must be used).

6.2.3.4 Check the calibration accuracy by reading the QC7 buffer.

6.2.3.5 Record the calibration information on the calibration sheet or field log. Then reattach the electrode storage bottle and store the electrode upright.

6.3 Sample Collection.

6.3.1 Bridge Sampler Method. This method is typically used to collect stream samples from a bridge or from the stream bank through the use of a rope.

6.3.1.1 Rinse a dedicated 1 L pH and conductivity grab sample bottle with DI water and secure it in the Bridge Sampler.

6.3.1.2 Put on a high-visibility safety vest and carry the needed sampling gear to a well-mixed sampling location where a representative stream sample may be collected.

6.3.1.3 Attach the sampling rope to the Bridge Sampler, remove the bottle cap, and set the cap aside.

6.3.1.4 Carefully lower the Bridge Sampler to the water surface, taking care to not dislodge any bridge debris onto it. Allow the bottom of the sampler to touch the water surface, and then raise the sampler off the water for a few moments to allow any debris from the bottom of the sampler to drop off and float away. Then rapidly allow it to submerge about 0.5 meters. *Note: These steps help minimize the sampling of surface film and any debris from the bottom of the sampler.*

6.3.1.5 Retrieve the sampler taking care not to dislodge bridge debris onto it, replace the bottle cap, and return to the van with all the sampling gear.

6.3.2 Hand Dip Method. This method is typically used to collect samples within reach of the water surface (when standing in or near the stream or lake, or from small boat).

6.3.2.1 Move to a well-mixed location such as the deepest part of the active channel or another location where a representative sample may be collected. *Note: Do not contaminate the sample location by wading upstream of it or collect a sample from an eddy that has been waded.*

6.3.2.2 Hold the base of the pH and conductivity grab sample bottle with one hand, and remove the bottle cap. Then invert the bottle, reach upstream, plunge the bottle mouth into the water about 15 cm (6 inches), and then tip it up toward the water surface. Remove the filled bottle from the water, replace the cap, and return to the van. *Note: If sampling still water or from a boat, then plunge the bottle opening into the water, and move it upstream or away from the entry location while tipping it upright.*

6.3.3 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or lake shore, or slow moving stream.

6.3.3.1 Secure the pH and conductivity grab sample bottle in the extension pole clamp.

6.3.3.2 Move to a location where a representative sample may be reached with the pole.

6.3.3.3 Remove the cap from the bottle, and place it where contamination will be avoided.

6.3.3.4 Invert the bottle over the desired sample location, plunge the bottle mouth into the water about 15 cm (6 inches), and then tip it toward the water surface. Allow the bottle to fill, remove it from the water, replace the cap, and return to the van.

6.4 Sample Measurement Procedure. *Note: It takes a minimum of three to five minutes to obtain a repeatable and stable pH measurement from a grab sample. Also note: Avoid significant sample temperature changes by keeping the collected sample in the shade by the stream, or closing up the van and turning on air conditioner or heater. (Sample pH can change with temperature).*

6.4.1 Unplug the electrode filling-hole, and remove the electrode storage bottle. Rinse electrode and pH measurement cup with DI or sample water.

6.4.2 Gently fill and overfill the pH measurement cup with the sample water. *Note: excessive agitation of the sample water will affect pH.*

6.4.3 Insert the electrode into the sample, turn on the meter, and gently stir the sample with the electrode a few times during the first two minutes.

6.4.4 Then gently stir the sample with the electrode, push the measurement button, and

continue to stir the sample until a stable result is indicated.

6.4.5 Gently stir and re-measure the sample until obtaining consecutive stable readings at about 30 second intervals (within 0.02 pH units).

6.4.5.1 ***Note: If the Hach PHC281 electrode initial measurement is acidic and it becomes progressively more acidic with each measurement, then clear the junction and remeasure the sample. This ensures that the result was not from a plugged junction that caused the electrode to mostly read 6 pH unit filling solution.***

6.4.6 Record the pH result on the Field Data Report Form or Field Logbook.

6.4.7 If the pH result equals 6.5 or less or 8.5 or higher, then check calibration of the pH meter using the closest buffer (e.g., 7 or 10). Record the calibration check result on the Field Data Report Form and, if necessary, recalibrate meter, and remeasure the sample.

6.4.8 Rinse electrode with DI water, carefully re-attach the half-filled electrode soaker bottle, plug the filling-hole, and store the electrode upright.

6.5 Troubleshooting Procedure. *Note: Most electrode calibration, calibration drift, field drift, or inaccurate field measurement issues can be caused by a plugged or contaminated electrode junction, cold or low battery, or worn out electrode. If none of the following steps work, then reference the electrode manual*.

6.5.1 Non-Hach PHC281 electrodes.

6.5.1.1 Refer to meter instrument manual and review the troubleshooting section and if necessary perform self-test to identify and fix the problem.

6.5.1.2 Alternately soak the electrode in 10% HCl and household ammonia for a few minutes (**This is not an accepted practice for the Hach electrode**). *Note: Household ammonia vapors can be a problem for the conductivity electrode and can contaminate the Ammonia sample. This electrode cleaning process* ***must*** *be done outside the van.*

6.5.1.3 If you cannot fix the electrode issue, then consult with a more experienced coworker to help resolve the problem.

6.5.2 Hach PHC 281 electrode.

6.5.2.1 If the calibration slope is greater than 101 or lower than 97 (usually indicates a bad buffer), then empty and refill one or all the dedicated pH buffer calibration bottles with fresh buffer solution that are the same temperature and at least 15 °C. Return to the calibration procedure (6.2).

6.5.3.2 Electrode cannot be easily calibrated or drifts during field measurements.

6.5.3.2.1 Make sure the electrode filling-hole is open. If it is not, then open it, and return to the calibration or field measurement procedure (6.2 or 6.4).

6.5.3.2.2 If the electrode filling-hole is open, then clear the junction. Remove the filling-hole cap, reattach the electrode soaker bottle, and slowly pull the bottle down the electrode in half-inch increments until there is a noticeable drop in the volume of the electrode filling solution.

6.5.3.2.3 Remove the electrode storage bottle, top off the electrode fill chamber with filling solution, and return to the calibration or field measurement procedure (6.2 or 6.4).

6.6 QC Procedure.

6.6.1 Check the calibration of the pH meter after the first, middle, and last station of the day using the 7 QC buffer and record the result on the Field Data Report Form.

6.6.1.1 If the difference between the pH calibration check result and the true QC buffer value is greater than or equal to 0.10 pH units, then recalibrate the meter.

6.6.1.2 If the difference between the pH meter result and the standard is greater than or equal to 0.15 pH units, then recalibrate the meter, re-read the sample, and "J" the data since last calibration check.

6.7 End of Day or Run Procedures.

6.7.1 Plug the electrode filling-hole hole, rinse it with DI water, replace the bottle cap, put the nearly half-filled electrode soaker bottle against the bottom of the electrode, slide the bottle cap down until it contacts the bottle threads, grasp the bottle cap and electrode to keep them from moving, and screw on the soaker bottle (goal is to prevent pushing air bubbles from entering the fill chamber through the junction).

6.7.2 Store the meter, electrode (tip down), calibration buffers, and a filled DI water squirt bottle into a heated room (hotel room, regional lab, or operation center).

## 7.0 Records Management

7.1 All hardcopy documentation of the data, such as completed Field Logbook and Field Data Report Forms are kept and maintained by the project lead. These documents are typically organized in binders or in expanding files. After about six years, hardcopies are boxed and moved to EAP archives.

## 8.0 Quality Control and Quality Assurance Section

8.1 The data QA program for field sampling consists of three parts: (1) adherence to the SOP procedures for sample/data collection and periodic evaluation of sampling personnel, (2) consistent instrument calibration methods and schedules, and (3) the collection of a field quality control (QC) sample during each sampling run.

8.2 Further data quality control and quality assurance procedures will be addressed thoroughly in each study Quality Assurance Project Plan.

## 9.0 Safety

9.1 Safety is the primary concern when collecting samples. Since most sample sites are located on highway bridges, road and pass conditions should always be checked before departure (especially in winter). If roadside hazards, weather, accidents, construction, etc. make sample collection dangerous, then skip that station. Note the reason on the Field Data Report Form and notify your supervisor of the hazard when you return to the office. If the hazard is a permanent condition, relocation of the station may be necessary. Review Ecology's Safety Program Manual (Ecology, 2017) periodically to assist with these safety determinations.

9.2 Waste disposal. Rinse the used pH buffers and the electrode filling/storage solution down the drain with water to reduce any impact on the wastewater treatment system.

## 10.0 References

10.1 Ecology, 2017. Environmental Assessment Program Safety Manual. Olympia, WA.

10.2 Ecology, 2011. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.