Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for the Collection and Analysis of pH Samples

Version 1.3

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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
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6/13/2007	1.3	Correct footer, title page	All	Bill Kammin

Environmental Assessment Program

Standard Operating Procedure for the Collection and Analysis of pH Samples

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP), Environmental Monitoring and Trends Section, Freshwater Monitoring Unit (FMU), Standard Operating Procedure (SOP) for the field collection and analysis of pH samples. The procedures cover meter calibration, sample collection, sample measurement, and quality assurance/quality control.

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 FEP – fluorinated ethylene propylene

3.5 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.

3.6 MQO's – Measurement Quality Objectives

3.7 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.

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

3.9 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.

3.10 Run – Scheduled sampling event (usually lasting 2-4 days).

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2006) such as 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 2006), 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 DO Sampler (based on design presented in Figure 4500-0:1 of the 20th Edition of Standard Methods).
5.2 Sampling ropes (1 @ 10 ft., 1 @ 35 ft. and 2 @ 55 ft.).
5.3 Extension pole with three prong clamp.
5.4 Field Logbook or Field Data Report Form (see attachment section for form).
5.5 pH meter capable of doing at least a two point calibration.
5.6 Refillable Star Probe.
5.7 pH 6.97 & 9.15 Low Ionic Strength Buffers (see attachment section for MSDS).
5.8 Dedicated 6.97 and 9.15 pH buffer calibration bottles (125 mL clear bottles).
5.9 pH probe filling solution.
5.10 pH probe storage solution.
5.11 Deionized water (DI water).
5.12 Meter Calibration Log Form (see attachment section for form).

6.0 Summary of Procedure

6.1 <u>Meter Calibration</u>.

6.1.1 Soak the pH probe in tap water for at least 30 minutes (overnight is better) before calibrating.

6.1.2 Rinse the pH probe filling solution chamber with deionized water (DI water). Then rinse and refill the probe chamber with probe filling solution. Note: This helps probe performance and probe life.

6.1.3 Empty and refill the dedicated 6.97 and 9.15 pH buffer calibration bottles with fresh buffer solution that are the same temperature and at least 8 °C.

6.1.4 Hold the cable end of the probe, rinse the other end of the probe with DI water, and flick the water off the probe with a quick downward jerking movement a few times. Note: avoid whacking the probe on the sink edge or counter.

6.1.5 Calibrate pH meter following the meter instruction manual for a two point calibration and store the probe in tap water.

6.1.6 Re-calibrate the pH meter after arriving at the first sample station also noting buffer temperature, slope[1], and the other calibration information on the Meter Calibration Log Form. The second calibration helps verify that the pH meter has warmed up and was calibrated properly.

6.2 Sample Collection.

6.2.1 DO 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.

6.2.1.1 Rinse a dedicated 1 L pH and conductivity grab sample bottle (marked with red permanent ink) with DI water and secure it in the DO sampler bottle holder location.

6.2.1.2 Put on a high visibility safety vest and carry the needed sampling gear to a well mixed location such as the main part of the channel where a representative stream sample may be collected.

6.2.1.3 Attach the sampling rope to the DO sampler, remove the bottle cap to the 1 L pH and conductivity grab sample bottle, and set the cap aside where it can remain clean.

6.2.1.4 Carefully lower the DO 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 lower the sampler about 0.5 meters to submerge it. *Note: This minimizes the sampling of surface film and any debris from the bottom of the sampler.*

6.2.1.5 Retrieve the sampler taking care not to dislodge bridge debris into it.

6.2.1.6 Replace the bottle cap.

6.2.1.7 Return to the van with all the sampling gear.

6.2.2 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).

[1] A slope of 102 or higher indicates a bad standard.

6.2.2.1 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 had been waded.*

6.2.2.2 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, and plunge the bottle into the water about 15 cm (6 inches), and then tip the bottle mouth up toward the water surface. Allow the bottle to fill and then take it out of the water. *Note: If sampling from a boat or in still water, plunge the bottle into the water, and move it away from the boat while tipping it to avoid contamination.*

6.2.3 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or when wading in a lake or slow moving stream.

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

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

6.2.3.3 Remove the cap from the bottle and place it where contamination can be avoided.

6.2.3.4 Position the bottle just over the desired sample location.

6.2.3.5 Invert the bottle and in one quick motion plunge the mouth of the bottle into the water about 15 cm (6 inches) and then tip the bottle mouth toward the water surface. Wait until the bottle has filled and then take it out of the water.

6.3 Sample Measurement Procedure.

6.3.1 Rinse the pH measurement cup and probe with DI or sample water.

6.3.2 Remove the cap from the pH and conductivity grab sample bottle and gently over fill the pH measurement cup with the sample water. *Note: excessive agitation of the sample water will affect pH.*

6.3.3 Turn on the pH[2] meter and allow it a few minutes to indicate a stable result.

6.3.4 If the pH meter has a stable reading, then verify it by moving the pH probe about an inch in the sample and by pushing the meter re-measure button. If the next stable reading is relatively unchanged from the initial stable reading (within 0.02 pH units), then record the result and the temperature of the sample on the Field Data Report Form.

[2] The pH meter should be set up to notify and hold (beep and display freezes) when it has a stable measurement (see the instrument manual for the meter).

Note: Always record the pH as soon as the meter has a verified stable result (sample pH changes with time).

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

6.3.6 If the pH result equals 6.5 or less or 8.5 or higher, then check calibration of the pH meter using the closest low ionic strength buffer (6.97 or 9.15). Record the calibration check result on the Field Data Report Form and if necessary, recalibrate meter, and re-measure the sample[3].

6.4 Troubleshooting Procedure. If the meter can not be calibrated or drifts during calibration, the calibration slope is greater than 101, fails consecutive calibration checks or gives an inaccurate or unexpected result, reading drifts or has a slow response time (takes more than three minutes) when measuring a sample; then check the meter calibration after doing one or more of the following steps.

6.4.1 Meter can not be calibrated or drifts during calibration:
6.4.1.1 Check to make sure the buffer temperatures are with in 2°C of each other.
6.4.1.2 Tap the side of the probe to eliminate any air bubbles from the electrode filling solution.
6.4.1.3 Change the battery.
6.4.1.4 Refer to meter instrument manual and perform self-test.
6.4.1.5 Alternately soak the probe in 10% HCl and household ammonia for a few minutes.
*Note: Household ammonia vapors can be a problem for the conductivity probe and can contaminate the Ammonia sample. This probe cleaning process **must** be done outside the van.*
6.4.1.6 Refer to meter instrument manual and perform self-test to identify and fix the problem.
6.4.1.7 Change the pH probe cable.
6.4.1.8 Replace the pH probe.

6.4.2. Meter calibration slope is greater than 101 (this usually indicates a bad buffer):
6.4.2.1 Empty and refill the dedicated 6.97 and 9.15 pH buffer calibration bottles with fresh buffer solution that are the same temperature and at least 8 °C.
6.4.2.2 Empty and refill the dedicated 6.97 and 9.15 pH buffer calibration bottles with fresh buffer solution from **unopened** buffer bottles. Make sure that the buffers are the same temperature and at least 8 °C.

6.4.3 Meter fails consecutive calibration checks or gives an inaccurate or unexpected result:
6.4.3.1 Change the battery and recalibrate the meter.
6.4.3.2 Empty and refill the dedicated 6.97 pH buffer calibration bottles with fresh buffer solution. These may have been diluted or contaminated.
6.4.3.3 Make sure the buffers are the same temperature (within 2°C of each other) and at least 8 °C when calibrating the meter.

[3] If the difference between the pH meter result and the standard is greater than or equal to 0.05 pH units then recalibrate the meter, if the difference between the pH meter result and the standard is greater than or equal to 0.10 pH units, then recalibrate the meter, re-read the sample, and "J" data since last calibration check.

6.4.4 Meter reading drifts or has a slow response time (takes more than three minutes) when measuring a sample:

6.4.4.1 Minimize changes in sample temperature by using the Van heating or cooling systems to keep the van inside air temperature as close to the water temperature as possible.

6.4.4.2 Alternately soak the probe in 10% HCl and household ammonia for a few minutes. *Note: Household ammonia vapors can be a problem for the conductivity probe and can contaminate the Ammonia sample. This probe cleaning process* ***must*** *be done outside the van.*

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

6.4.5 If you can not fix the meter, then turn it into the Operation Center Technician along with a completed Equipment Problem Report Form for repair.

6.5 QC Procedure.

6.5.1 Check the calibration of the pH meter after the first, middle, and last station of the day using the 6.97 low ionic strength buffer. Record the result on the Field Data Report Form and if necessary, recalibrate meter, and re-measure the last sample.

6.6 End of Day or Run Procedures.

6.6.1 If the meter and probe will be used on the next day, then store the probe in stream sample or tap water.

6.6.2 If the overnight air temperatures will be below 45 °F, then move the meter, probe, and standards into a heated room (hotel room, regional lab, or operation center).

6.6.3 If the meter and probe will not be used on the next day, then rinse the probe with DI water, plug the pH probe fill hole with the rubber plug, fill the probe storage cap with probe storage (or filling) solution, attach the cap to the probe, and store the meter and probe in a heated room.

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 organized in binders or in expanding files. After about six years, hardcopies are boxed and moved to EAP archives.

7.2 Data collected for Ecology's Ambient River and Stream Monitoring Program will be entered into our Access-based database, reviewed and verified following the Quality Control and Quality Assurance procedures (see 8.1 below), uploaded into EIM, and posted on our web page http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html .

7.3 Data collected for special project studies will be reviewed, verified, and stored based on the QAPP for the project.

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. Our QA program is described in detail in Hallock and Ehinger (2003).

8.2 The field QC sample is collected as a duplicate sequential field sample. This consists of the collection of an additional sample approximately 15-20 minutes after the initial sample collection at a station. This sample represents the total variability due to short-term, in-stream dynamics, sample collection and processing, and laboratory analysis.

8.3 A two-tiered system is used to evaluate data quality of individual results based on field QC. The first tier consists of an automated evaluation of the data. Results exceeding pre-set limits are flagged. The second tier QC evaluation is a manual review of the data flagged in the first tier. Data are then coded from 1 through 9 (1 = data meets all QA requirements, 9 = data are unusable). Criteria for assigning codes are discussed in more detail in Hallock and Ehinger (2003). We do not routinely use or distribute data with quality codes greater than 4.

8.4 The overall quality of data collected during the sampling year are evaluated in our annual reports (e.g., Hallock, 2006)

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 periodically to assist with these safety determinations.

10.0 References

10.1 Ecology, 2006. Environmental Assessment Program Safety Manual. Olympia, WA.

10.2 Ecology, 2006. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.

10.3 Hallock, D. and W. Ehinger, 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. 27pp. Publication No. 03-03-200. www.ecy.wa.gov/biblio/0303200.html

10.4 Hallock, D., 2006. River and Stream Water Quality Monitoring Report for Water Year 2005. Washington State Department of Ecology, Olympia, WA. 18pp. + appendices. Publication No. 06-03-032. http://www.ecy.wa.gov/biblio/0603032.html