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Quality Assurance Monitoring Plan

Continuous Monitoring for Oxygen, Temperature, pH, and Conductivity in Statewide Rivers and Streams

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Quality Assurance Monitoring Plan

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September 2009

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Signature: Date: September 2009
Gary Arnold, Section Manager, EOS, EAP

Signature: Date: September 2009
Bill Kammin, Ecology Quality Assurance Officer

Signatures are not available on the Internet version.

EIM	Environmental Information Management system.
FMU	Freshwater Monitoring Unit.
EAP	Environmental Assessment Program.
WOS	Western Operations Section.
SCS	Statewide Coordination Section.
EOS	Eastern Operations Section.

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Abstract

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Monitoring Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

The purpose of this program is to collect diel (24-hour) data for dissolved oxygen, temperature, pH, and conductivity in rivers and streams statewide. Data will be recorded at 15-minute intervals for several weeks to several months. Data will be collected during summer periods when oxygen concentrations, in particular, are expected to be lowest (as estimated from monthly grab sample data). Data may also be collected from the beginning and end of designated supplemental salmon and trout spawning seasons. Stations will generally be selected from among the Department of Ecology's statewide ambient monitoring stations.

The data may be used to (1) interpret data collected by monthly grab samples with diel components (primarily oxygen)[1], (2) support Total Maximum Daily Load (TMDL) studies, and (3) determine compliance with current and proposed water quality standards.

Background

Ambient Monitoring

Currently, the Washington State Department of Ecology (Ecology) Freshwater Monitoring Unit (FMU) collects monthly grab sample data at more than 80 stations statewide (Hallock, 2009). Sixty-two stations are "long-term" and sampled every year; the remaining stations change each water year (WY).[2] Samples are usually collected during daylight hours (0700 to 1700).

Temperature, oxygen, and pH all vary with a sinusoidal pattern throughout the 24-hour photoperiod. Temperature is affected directly by solar insolation and air temperature. pH and oxygen are affected by both temperature changes and light-driven photosynthesis.

A single result collected at some unknown point on a daily cycle is of limited usefulness. For temperature and pH, we know the daily maximum was at least as high as the grab sample result, and for oxygen the daily minimum was at least as low as the grab sample result.

[1] Continuous temperature is monitored under a different program.
[2] Water Year = October through September.

Diel Monitoring

The collection of diel stream data has several purposes:

- To identify areas with low oxygen concentrations, or high stream temperatures and pH, that mid-day grab samples might miss.
- To identify areas that are meeting water quality standards (WAC 173-201A). To remove a station from the 303(d) list for oxygen and temperature, diel data are required (Ecology, 2005). Grab data may be used only to assess *lack* of compliance.
- To enhance the interpretation of ambient monitoring monthly grab sample results. By knowing the diel pattern, it may be possible to determine where on the diel cycle the grab samples were collected and therefore model the full data series where diel data are not available. Similarly, continuous temperature data may improve modeled diel oxygen concentrations if the relationships between continuous temperature and continuous oxygen are understood. (Interpretations cannot be extrapolated beyond the time of day and seasons used to develop the model.)

Luminescence-based Technology Versus the Winkler Method

A relatively new technology for measuring dissolved oxygen allows for longer-term deployments than the usual Clark-cell sensor, which was subject to fouling and sensor drift. The technology uses the fact that the persistence of an induced luminescence in water is inversely proportional to the concentration of dissolved oxygen.

Although the Environmental Protection Agency (EPA) has recommended interim approval of a luminescent dissolved oxygen method (EPA, 2006), we conducted a pilot study in the fall of 2008 to test the technology for ourselves. We deployed a single Hydrolab MS5 sonde with a Luminescent Dissolved Oxygen (LDO) sensor in the Black River (station 23E060) from August 27 through November 7, 2009. We collected weekly grab oxygen samples analyzed by the modified Winkler method. LDO results were biased high relative to the Winkler results by 0.13 mg/L ($p=0.08$), possibly due to inaccuracies associated with air calibration. The average relative standard deviation between LDO and Winkler results was 1.4%. Winkler and LDO results matched remarkably well, with no discernable drift in the sensor during the 11-week deployment (Table 1 and Figure 1).

Table 1. Black River pilot study quality control results for oxygen. *Units are mg/L.*

Date and time (Year 2008)	Raw LDO	Adjusted LDO	Winkler	Difference	Relative Standard Deviation
08/28 10:30	7.88	7.75	7.62	0.13	2.37%
09/04 10:45	8.33	8.2	8.45	-0.25	1.01%
09/11 1:15	Power supply problem: No LDO result				
09/16 11:00	8.18	8.05	8.21	-0.16	0.26%
09/22 10:45	Power supply problem: No LDO result				
09/30 14:45	9.26	9.13	9.07	0.06	1.47%
10/09 14:45	9.58	9.45	9.5	-0.05	0.59%
10/21 8:45	8.82	8.69	8.65	0.04	1.38%
11/07 9:45	8.97	8.84	8.63	0.21	2.73%

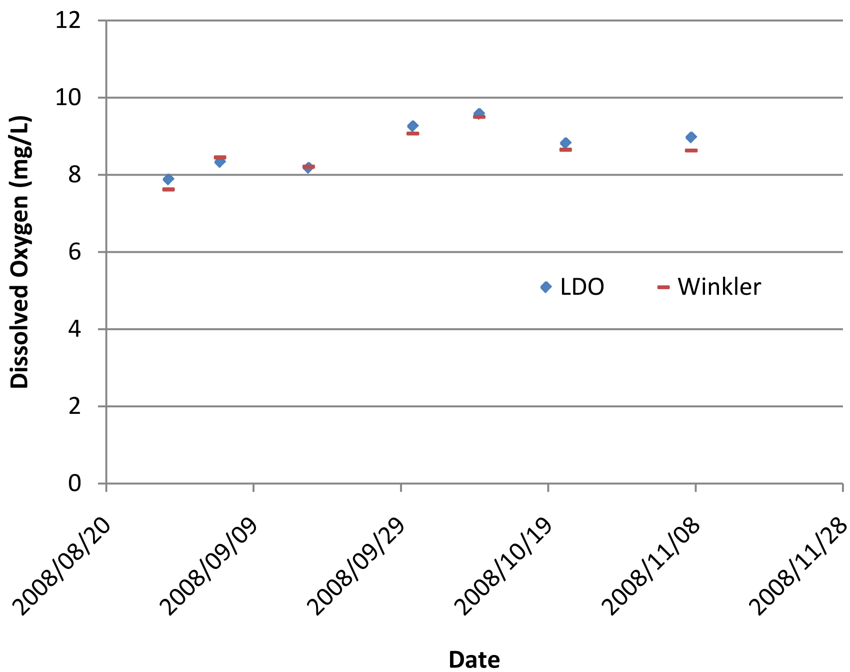

Figure 1. Black River pilot study quality control results for oxygen measured by the modified Winkler method and the LDO method.

Scope of QAMP

Both the luminescence-based technology for measuring dissolved oxygen and our deployment of long-term continuous water quality sensors (other than temperature sensors) are relatively new. Therefore, this program will initially be conducted on a small-scale local basis to expand on our earlier pilot project in order to further assess techniques (using and deploying instruments, and data management), feasibility, and reliability. Eventually, we expect to expand the program statewide.

This Quality Assurance Monitoring Plan is intended to address the collection of oxygen, temperature, pH, and conductivity data using deployed recording instruments. Although there are no water quality standards for conductivity, and conductivity does not typically vary greatly over the course of a day, conductivity may be related to streamflow and runoff events. In any case, the instruments we are likely to use include sensors for all four parameters.

Ecology's Freshwater Monitoring Unit already has a continuous temperature monitoring program that is far more extensive than this proposed program in terms of number of stations and length of time instruments are deployed (Ward, 2005). However, temperature is included here primarily because temperature data are useful for interpreting oxygen data.

Project Description

Goals

The project has two goals:

- Collect high-quality diel continuous data from as many of Ecology's ambient stream monitoring stations as resources permit. Make these data available, either complete or in summarized form, to internal and external users, including other state, federal, and local agencies; educational institutions; the private sector; and individuals.
- Help develop and evaluate Washington's Water Quality Standards (WAC 173-201A).

Objectives

Following are the project objectives:

- Establish continuous monitoring locations at as many ambient stream monitoring stations as resources permit.
- Store results in publicly accessible databases such as on Ecology's FMU web page and in Ecology's Environmental Information Management system (EIM) database.
- Evaluate and publish in our annual ambient monitoring report the deployed-period summary statistics, especially for oxygen concentration and temperature.
- Provide data for evaluating supplemental oxygen criteria.
- Provide data for conducting 303(d) assessments.

Organization and Schedule

Organization

The people in Table 2 are involved in this project. All are employees of the Washington State Department of Ecology, Environmental Assessment Program (EAP).

Table 2. Organization of project staff and responsibilities.

Staff (All are EAP staff)	Ecology Region	Title	Duties
Dave Hallock Freshwater Monitoring Unit, WOS Phone: (360) 407-6681	Statewide	Project Manager	Provides data management (Access), quality control, miscellaneous data validation, analysis, and reports. Enters data into EIM.
Brad Hopkins Freshwater Monitoring Unit, WOS Phone: (360) 407-6686		Unit Lead	Provides internal review of the QAMP, approves the budget, and approves the final QAMP. Manages sonde-telemetry station connectivity.
Don Watt Freshwater Monitoring Unit, WOS Phone: (360) 407-6818		Equipment Manager	Installs and maintains telemetry station infrastructure.
Chuck Springer Freshwater Monitoring Unit, WOS Phone: (360) 407.6997		Data Manager	Manages database (Hydstra or equivalent).
Bill Ward Freshwater Monitoring Unit, WOS Phone: (360) 407-6621	Southwest	Regional Staff Lead	Assists Project Manager.
Bruce Barbour Freshwater Monitoring Unit, WOS Phone: (360) 715-5215	Northwest		Assists Project Manager.
Troy Warnick Freshwater Monitoring Unit, WOS Phone: (360) 407-0294	Olympic Peninsula		Assists Project Manager.
Dan Sherratt Eastern Regional Office Phone: (509) 329-3420	Eastern		Assists Project Manager.
Chris Coffin Central Regional Office Phone: (509) 454-4257	Central		Assists Project Manager.
Robert F. Cusimano, WOS Phone: (360) 407-6596	Northwest and Southwest	Section Manager for the Project Manager	Provides internal review of the QAMP, approves the budget, and approves the final QAMP.
Gary Arnold, EOS Phone: (509) 454-4244	Eastern and Central	Section Manager for the Eastern Operations Section	Provides internal review of the QAMP and approves the final QAMP.
Will Kendra, SCS Phone: (360) 407-6698	Statewide	Section Manager for the Study Area	Provides internal review of the QAMP and approves the final QAMP.
William R. Kammin, Phone: (360) 407-6964	Statewide	Ecology Quality Assurance Officer	Reviews the draft QAMP and approves the final QAMP.

EIM Environmental Information Management system.
WOS Western Operations Section
SCS Statewide Coordination Section
EOS Eastern Operations Section.
QAMP Quality Assurance Monitoring Plan.

Schedule

There are two times of year when oxygen data may be needed to evaluate water quality criteria. All ambient stations have an assigned lowest 1-day minimum criterion below which the oxygen concentration should never fall at any time of year. The critical time of year, however, when oxygen concentrations are most likely to be their lowest, is early July through early September (Figure 2).

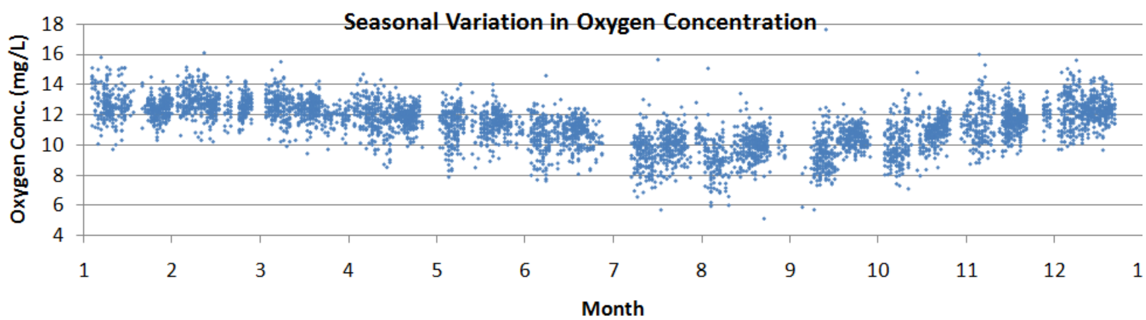

Figure 2. Oxygen concentrations by month from all ambient stations monitored between October 1, 2001 and May 6, 2009.

A second time of year for which continuous oxygen data may be useful is the beginning and ending of the supplemental salmon and trout spawning and incubation seasons that WAC 173-201A assigns to certain ambient stations. Currently, only temperature criteria apply to these seasons; however, assigning season-specific oxygen criteria is under consideration (Brown and Hallock, in draft). These seasons vary by location, but most start in the early fall and end in late spring. Oxygen is most like to be low at the beginning and especially at the end of these seasons.

We intend to schedule the deployment of continuous oxygen sensors to capture as much of the critical summer period as possible and, for stations with supplemental spawning seasons, at least the first two and last four weeks of the assigned season for each station. If a decision is made not to pursue supplemental oxygen criteria, we may drop deployments during supplemental spawning seasons.

Conductivity and pH are secondary parameters. They will be collected along with dissolved oxygen.

This is intended to be an ongoing project, though monitored stations will change from year to year. Data will be reported annually in conjunction with our grab sample and continuous temperature monitoring annual report (Table 3). Data will be loaded into EIM annually.

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	NA	Dave Hallock
Laboratory analyses completed	NA	
Environmental Information System (EIM) database		
EIM user study ID	AMS004	
Product	Due date	Lead staff
EIM data loaded	March - Annually	Dave Hallock
EIM QA	June - Annually	Dave Hallock
EIM complete	September - Annually	Dave Hallock
Annual final report		
Author lead	Dave Hallock	
Schedule		
Draft due to supervisor	March - Annually	
Draft due to client/peer reviewer	April - Annually	
Draft due to external reviewer(s)	NA	
Final (all reviews done) due to publications coordinator (Joan)	July - Annually	
Final report due on web	September - Annually	

Quality Objectives

The accuracy and instrument bias measurement quality objectives (MQOs) of each sonde and/or sensor is verified through post-deployment calibration checks following the procedures described in *Standard Operating Procedures for Hydrolab® DataSonde® and MiniSonde® Multiprobes* (Swanson, 2007). These SOPs will be modified as necessary in accordance with users manuals to account for luminescent-type oxygen probes.

In addition, deployment, mid-deployment, and retrieval grab-sample checks collected at the deployment location will be used to evaluate the accuracy criteria in Table 4. Note that the accuracy criteria also include errors associated with the grab sample results. Grab sample data may be used to first correct continuous data for linear drift or a constant offset. This will be done prior to evaluating accuracy and precision if the mean difference between grab sample and LDO results is greater than 2%.

Table 3. Accuracy, precision, and reporting limits.

Parameter	Accuracy	Precision (% relative standard deviation)	Reporting Limit
Oxygen	± 0.5 mg/L	10	NA
Temperature	± 0.4 ºC	10	NA
pH	± 0.3 standard units	10	NA
Conductivity	± 5 µS/cm or 10%, whichever is greater	10	NA

NA – not applicable.

Continuous data will be compared to post-calibration checks and grab sample results. Differences not meeting criteria in Table 4 may result in the affected data set being qualified or rejected, depending on the amount of difference and the number of checks that failed to meet the criterion.

Precision MQOs are to be compared against the average relative standard deviation of data pairs collected during a deployment (Mathieu, 2006).

Because sensors will frequently be deployed in association with stream-side flow monitoring equipment, there is a potential for sampling bias relative to average cross-section conditions. In addition to deployment location grab samples, we will collect grab samples from the thalweg in accordance with Ward (2007) upon deployment and retrieval of sensors. These data will not be used to correct for bias or drift, but they can be used to determine whether data from this program are comparable to grab sample data from Ecology's River and Stream Ambient Monitoring program (Hallock and Ehinger, 2003). If thalweg grab samples differ from deployment location grab samples by more than the criteria in Table 4, data may be qualified or rejected.

Sampling Process Design (Experimental Design)

Study Area

The continuous monitoring program may potentially monitor any surface water (river, stream, or lake) in the state, and even in bordering states and Canada for streams entering Washington. However, most stations are expected to be basin or long-term stations that are part of Ecology's statewide ambient stream monitoring program. In addition, the initial focus will be on stations with telemetered streamflow monitoring gages. This simplifies deployment of sensors, improves security, and allows us to monitor sensor performance in near real time.

In addition, we will focus initially on stations with supplemental salmon and trout spawning and incubation criteria (to support oxygen criteria development), and on stations where grab sample data indicate potential low oxygen concentrations.

When sensors are deployed independent of flow monitoring equipment, locations will be chosen that are:

- Well-mixed (representative of cross-section conditions).
- Off the streambed and away from tributary sources.
- Well hidden to prevent loss to vandalism or damage.
- Safe to access.

Representativeness

Continuous monitoring data collected through this program will not be representative of a watershed or of the state as a whole, but will be considered representative of the stream reach being sampled.

Comparability

All measurements and analytical procedures will be standardized and documented so that the data can be compared with samples collected and analyzed in a like manner.

Completeness

Completeness is a measure of the amount of valid data needed to meet the goals defined for the uses of the data. The goals for this program are to (1) collect high-quality data for multiple uses and (2) determine compliance with water quality standards (Chapter 173-201A-200(1)(c) WAC). In addition, an interim goal is to support the development of new water quality standards for oxygen.

There are no completeness requirements for the first goal.

The requirements of continuous monitoring data to evaluate compliance with water quality standards are described by Water Quality Program Policy 1-11 (Ecology, 2006). This policy requires that “continuous data” be collected at least hourly.

For a waterbody to be classified as *meeting tested criteria* (Category 1), continuous data are required that “cover the seasonal duration in which dissolved oxygen concentrations are expected to be lowest.” Therefore, we will consider our data set complete for Category 1 determination if we are confident that our data include the lowest 7-day average minimum in a given season. This will require no missing daily minima during that period and sufficient data before and after that period to be confident that the monitored period contained the lowest concentrations. If a more extensive temperature data set is available, temperature data may be used to help identify the expected low oxygen period.

Data requirements are less extensive to identify a waterbody as *impaired* (e.g., Category 5, the 303(d) list). For continuous data, Policy 1-11 requires that at least one 7-day average daily minimum fall below the criterion. Hence data from a single 7-day period at any point in the season may be considered complete provided there are no missing daily minima.

To support the development of new oxygen criteria, at least 7 days of continuous data from the first and last two weeks of the designated supplemental spawning season are required.

Completeness requirements for temperature are similar to those for oxygen. There are no completeness requirements for pH and conductivity.

Sampling Procedures

The sampling procedures will follow those described in *Standard Operating Procedures for Hydrolab® DataSonde® and MiniSonde® Multiprobes* (Swanson, 2007), modified as necessary in accordance with users manuals to account for luminescent-type oxygen probes. Grab-sample checks will follow procedures in Ward (2007).

Sondes may be deployed in the stream as described in Swanson (2007), but at some locations sondes or sensors will be deployed in a 2½ inch pipe married to pre-existing stage recording infrastructure (Figure 3). A basket at the end of the pipe secures the sonde but allows free exchange of water to the sensors. A standard sonde cable runs through the pipe and connects the sonde to an SDI-12 cable, which connects to a data logger. The data logger queries the sonde and processes data following procedures described in Butkus (2005).

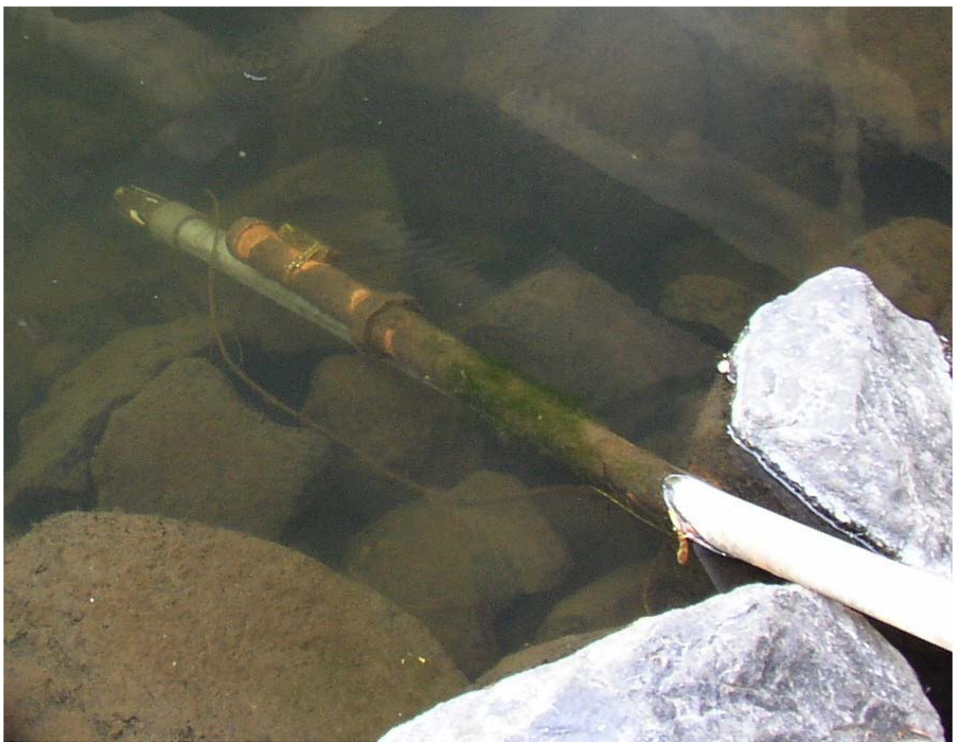

Figure 3. In-pipe sonde deployment.

The sonde is in the lower pipe; the upper pipe contains a stage height sensor.

Field work will follow procedures specified in *Standard Operating Procedure for Areas of Moderate Concern* to minimize the risk of spreading aquatic invasive species. If stations are located in Areas of Extreme Concern, we will follow procedures in *Standard Operating Procedures to Prevent Accidental Introductions of Aquatic Organisms from Areas of Extreme Concern Through Aquatic Plant Monitoring Activities* (Parsons, In Draft). If modifications are necessary, they will be reviewed and approved by Jenifer Parsons.

Measurement Procedures

Measurements will be collected using the methods described in Table 5.

Table 4. Measurement Methods and specifications.

Parameter	Method	Resolution[a]	Accuracy[a]
Oxygen	Hach LDO[tm] or other brand luminescent technology	0.01 mg/L	±0.2 mg/L at > 8 mg/L
Temperature	30K ohm thermistor	0.01 ° C	± 0.10 ° C
pH	Glass electrode with refillable reference	0.01 standard units	± 0.2 standard units
Conductivity	Graphic electrodes (four)	0.001	± 0.5 % + 1 µS/cm

[a] Resolution and accuracy as reported by Hydrolab©. If we use other sensors, they will have similar specifications.

Quality Control Procedures

The accuracy and instrument bias of each sensor will be verified through post-deployment calibration checks following the procedures described in Swanson (2007) and with deployment, retrieval, and monthly grab check samples collected as described in Ward (2007). Quality control associated with grab samples is described in Hallock and Ehinger (2003) and evaluated annually (e.g., Hallock, 2009).

If check samples and post-deployment calibrations indicate an offset or a linear drift, continuous data may be adjusted as necessary prior to evaluating against data quality objectives. If check samples and the post-deployment calibration are not consistent, or if data do not meet quality objectives after adjustments, then the data will be qualified or rejected.

Pre-deployment, post-deployment, and anomalous data will be deleted from the raw data set.

Data Management Procedures

See the *Quality Control Procedures* section for procedures for detecting and correcting errors.

Data will be reviewed and entered into one or more databases:

- An Access®-based database that we currently use to manage continuous temperature data is also capable of managing data from Hydrolab® sondes. This database includes additional customized quality control procedures, data summaries, and automated export of daily summaries to Ecology's EIM database (which is not designed to manage continuous data).
- Hydstra® is the database currently used to manage streamflow data collected by the same telemetry systems this project may use. This database will already be part of the work flow and, with some enhancements, it could manage continuous water quality data, as well.
- Ecology's Environmental Assessment Program is currently evaluating several databases specifically designed to manage continuous data. One of these may become standard for managing Ecology's continuous data and supplement EIM.

In addition, data will be provided either on Ecology's Stream Monitoring web page (www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html) or on Ecology's Flow Monitoring web page (www.ecy.wa.gov/programs/eap/flow/shu_main.html).

Data will not be obtained from existing databases or literature files; acceptance criteria are not applicable.

Data summaries may be loaded into EIM; however, EIM is not currently capable of storing continuous data.

Responsibilities for data management are listed in Table 2.

Audits and Reports

A summary of results, methods, and data quality evaluations will be included in our annual *River and Stream Water Quality* reports (e.g., Hallock, 2009).

Responsibilities for reports are listed in Table 2.

Data Verification and Validation

Verification procedures are summarized below:

- Calibration checks and field procedures will be documented on appropriate forms.
- Data will be checked for entry errors and completeness.
- Pre- and post-calibration check results and field measurements will be reviewed to ensure the data quality objectives were met.
- Results will be checked for reasonableness using data plots, field measurements, amount of change between sequential results, and, if necessary and available, independently collected data such as air temperatures and stage/flow data.
- Detected data errors will be corrected, flagged with data qualifiers, or rejected.

Responsibilities for data verification are listed in Table 2.

Data Quality (Usability) Assessment

Data that have met specified MQOs and passed data verification will be available to internal (Ecology) and external users. The data will be summarized and stored on the web for public access, and in one or more databases. The data will also be summarized and compared to state water quality standards in our annual *River and Stream Water Quality* reports (e.g., Hallock, 2009).

Project objectives will have been met if sufficient data are available after the quality review to meet the requirements in the *Completeness* section.

Data analysis consists primarily of comparing results to water quality standards. Procedures are defined in Ecology's Water Quality Program Policy 1-11 (www.ecy.wa.gov/programs/wq/303d/policy1-11Rev.html).

The sampling design will be considered successful if project objectives are met. If, for example, stream-side measurements are not representative of thalweg measurements, deployment procedures may need to be changed.

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Appendix. Glossary, Acronyms, and Abbreviations

Ambient monitoring: Background or away from point sources of contamination.

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.

Diel: A 24-hour period.

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

Grab sample: A discrete sample from a single point in the water column.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

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.

Reach: A specific portion or segment of a stream.

Sinusoidal: A wave the amplitude of which varies in proportion to the sine of time.

Sonde: Device for testing physical or chemical conditions.

Telemetry: Automatic recording and transmission of data.

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

Total Maximum Daily Load (TMDL): A water cleanup plan. A distribution of a substance in a waterbody designed to protect it from 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.

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.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FMU	Freshwater Monitoring Unit
LDO	Luminescent dissolved oxygen
MQO	Measurement quality objective
QA	Quality assurance
RSD	Relative standard deviation
SOP	Standard operating procedures
TMDL	(See Glossary above)
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
mg/L	milligrams per liter (parts per million)
s.u.	standard units
μS/cm	microsiemens per centimeter, a unit of conductivity