

# **Quality Assurance Project Plan**

# Lake Spokane Nutrient Monitoring

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# **Quality Assurance Project Plan**

# Lake Spokane Nutrient Monitoring

October 2010

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FRO: Eastern Regional Office	

EIM: Environmental Information Management system

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## Abstract

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

During 2010, Ecology submitted the *Spokane River and Lake Spokane Dissolved Oxygen Total Maximum Daily Load (TMDL): Water Quality Improvement Report* to the U.S. Environmental Protection Agency (EPA) for approval.

The most recent data collection effort on Lake Spokane occurred in 2001. As the 2010 TMDL moves from development to implementation, nutrient, productivity, and dissolved oxygen data will be needed to verify the baseline condition of Lake Spokane. This condition will be used for comparison to future effectiveness monitoring data.

During 2010 and 2011, Ecology and Avista Utilities will conduct regular critical-period (May to October) sampling on Lake Spokane, the Spokane River, and the Little Spokane River. Sampling will be for nutrients, dissolved oxygen, and measures of productivity. Data will be compiled and used to verify the baseline condition of Lake Spokane.

# Background

Toxic algae blooms, occurring in Lake Spokane in the 1970s, resulted in the court-ordered establishment of a phosphorus total maximum daily load (TMDL) because phosphorus was identified as the nutrient causing eutrophication. This resulted in the development of the existing phosphorus TMDL for Lake Spokane, which was originally adopted as a Phosphorus Management Plan in 1989. The existing phosphorus TMDL focused on preventing toxic blue-green algae blooms by requiring the city of Spokane, and other local entities that discharge to the river, to reduce the levels of phosphorus in their effluent at the time by 85%.

Subsequent years of excessive algae blooms in Lake Spokane, as well as violations of water quality standards for dissolved oxygen and phosphorus, demonstrated that the existing phosphorus TMDL does not adequately protect water quality. As a result, several waterbody segments of the Spokane River were included on Washington State Department of Ecology's (Ecology's) 1996, 1998 and 2004 303(d) lists of impaired waterbodies, which require that a TMDL be developed.

Ecology began TMDL development in 1998, with data collection focused during 2001. Since 2004, TMDL development has centered around the Spokane River TMDL Collaboration, a dialogue including Ecology, wastewater dischargers, local governments, the Idaho Department of Environmental Quality, the U.S. Environmental Protection Agency (EPA), the Spokane Tribe of Indians, environmental groups, and Avista Utilities. During 2010, Ecology submitted the TMDL (Moore and Ross, 2010) to EPA for approval.

In 2005, the Spokane River TMDL Collaboration's Monitoring Workgroup recommended nine categories of monitoring along the Spokane River and Lake Spokane (Spokane River TMDL Collaboration, 2005). One of these recommendations was to add six sites on the Spokane River to the ongoing ambient monitoring conducted by the Freshwater Monitoring Unit of Ecology's Environmental Assessment Program. The Freshwater Monitoring Unit added these monitoring sites to its program in 2007.

In addition, the Monitoring Workgroup recommended status and trends monitoring of nutrients, productivity, and dissolved oxygen on Lake Spokane as TMDL implementation begins and progresses. Implementation is expected to begin in the next few years. In order to measure improvements resulting from TMDL implementation actions, it is necessary to have accurate data describing the pre-implementation baseline condition. The last major nutrient/dissolved oxygen monitoring effort on Lake Spokane occurred in 2001. More up-to-date data is needed to verify the baseline condition recorded and modeled in 2001 and to account for any changes that may have taken place in the last 9 years.

The previous dataset was collected during a low-flow year. It appears that 2010 will also be a low-flow year; as of April 1, SNOTEL<sup>1</sup> sites in the Lake Coeur d'Alene watershed show snowpack between 36% and 57% of normal. This year should provide a good opportunity to

<sup>&</sup>lt;sup>1</sup> SNOTEL: An automated system of snowpack and related weather sensors operated by the U.S. Department of Agriculture.

verify/update the 2001 baseline condition under similar flow conditions. New Federal Energy Regulatory Commission minimum flows may mean that low flows will be slightly higher in 2010 than in 2001, creating a new low-flow baseline condition.

Because the loading targets in the Spokane River and Lake Spokane TMDL are based on data from the Spokane River at Nine Mile Bridge and the Little Spokane River at Mouth, these two sites are included in this project. Together, these two river sites effectively describe the water entering the upstream end of Lake Spokane.

This Quality Assurance (QA) Project Plan describes the procedures that will be used to accomplish the above monitoring activities. A field crew from Ecology's Freshwater Monitoring Unit and Avista Utilities will conduct the study.

# **Waterbody Description**

From its source at Lake Coeur d'Alene, the Spokane River flows west across the Idaho / Washington state line to the city of Spokane. From Spokane, the river flows northwesterly through the Lake Spokane reservoir, over Long Lake Dam, and through the Spokane Tribe of Indian's reservation to its confluence with the Franklin D. Roosevelt Lake impoundment of the Columbia River (Figure 1).

The river, including the Lake Coeur d'Alene catchment, drains an area of about 6,640 square miles in two states. Approximately 2,295 square miles are within eastern Washington with the remainder of the watershed in Idaho. Most residents in the watershed live in the Spokane metropolitan area. However, the incorporated area of Liberty Lake, east of Spokane, and the cities of Coeur d'Alene and Post Falls in Idaho are experiencing rapid growth.

The study area includes the lower Spokane River Water Resource Inventory Area (WRIA) 54 and the mouth of the Little Spokane River, which is in WRIA 55. The lower Spokane River extends 70 miles from the confluence of Hangman Creek to the Spokane Arm of the Columbia River (Lake Roosevelt). The lower 34 miles within the Spokane Tribe's reservation are outside the study area. Spokane Tribe water quality regulations apply to this section of the river.

There are seven hydroelectric dams downstream from the outlet of Lake Coeur d'Alene which significantly influence the dynamics of the Spokane River. The six Washington dams are run-of-the river (flow-through) types except for Long Lake Dam, which creates Lake Spokane, a 24-mile long reservoir.

There are seven wastewater discharges to the mainstem of the Spokane River between Lake Spokane and Lake Coeur d'Alene. These discharge a summer average of approximately 75 million gallons of treated wastewater per day. In Washington, beginning at Spokane and moving upstream, these discharges include the Spokane Wastewater Treatment Plant, Inland Empire Paper, Kaiser Aluminum, and Liberty Lake Sewer and Water District. Discharges in Idaho include the Post Falls Wastewater Treatment Plant, Hayden Sewer District, and the city of Coeur d'Alene Advanced Wastewater Treatment Plant.

Each discharger has a National Pollutant Discharge Elimination System (NPDES) permit which sets limits on the amount of pollutants that can be discharged to the river. NPDES permits set limits at levels protective of water quality. In Washington State, Ecology issues NPDES permits; in Idaho, EPA issues these permits.

Table 1 lists the water quality criteria for dissolved oxygen that apply to the Spokane River and Lake Spokane

In addition, the Spokane River has the following specific water quality criteria, per WAC 173-201A-130, from Long Lake Dam (RM 33.9) to Nine Mile Bridge (RM 58.0). Special conditions:

(a) The average euphotic zone concentration of total phosphorus (as P) shall not exceed  $25 \mu g/L$  during the period of June 1 to October 31.



Figure 1. Spokane River basin.

Portion of Study Area	Aquatic Life Uses	Dissolved Oxygen Criterion
Spokane River (from Nine Mile Bridge to the Idaho border)	Migration/ Rearing/ Spawning	Dissolved oxygen shall exceed 8.0 mg/L. If "natural conditions" <sup>a</sup> are less than the criteria, the natural conditions shall constitute the water quality criteria.
Lake Spokane (from Long Lake Dam to Nine Mile Bridge)	Core Summer Habitat	No measurable (0.2 mg/L) decrease from natural conditions.
Spokane Arm of Lake Roosevelt (from confluence of Columbia River and Spokane River to Little Falls Dam – outside of TMDL compliance point)	N/A	Dissolved oxygen shall not be less than 8.0 mg/L. <sup>b</sup>

Table 1. Designated aquatic life uses and dissolved oxygen criteria protected by this TMDL as defined in the 2006 water quality standards.

a Washington water quality standards (WAC 173-201A-020) define "natural conditions" or "natural background levels" as "surface water quality that was present before any human-caused pollution. When estimating natural conditions in the headwaters of a disturbed watershed, it may be necessary to use the less disturbed conditions of a neighboring or similar watershed as a reference condition."

b Spokane Tribe of Indians Surface Water Quality Standards (Resolution 2003-259).

# **Project Description**

The goal of this project is to collect baseline monitoring data on Lake Spokane to be used for comparison with past and future monitoring efforts.

To meet this goal, the following objectives need to be accomplished:

- For each year sampling is planned, collect bi-weekly (every other week) samples during the critical season<sup>2</sup> at the same well-established locations on Lake Spokane that were sampled during the 2001 TMDL data collection effort as well as one site each at Nine Mile Dam and the mouth of the Little Spokane River.
- Ensure field crews consistently follow the methods and procedures discussed herein to collect data that can be used in trend analysis with past and future data collected in a similar manner.
- Ensure that, if desired, collected data can be used with the CE-QUAL-W2 model.
- Investigate dissolved oxygen concentrations in the hypolimnion.
- Investigate nutrient concentrations in the euphotic zone.
- Write an annual data summary report of the results covering the following:
  - Summary table of chemical and physical data, as well as pertinent field notes.
  - Discussion of data quality and significance of problems encountered.
  - Comparison of sample results with Washington State water quality standards.
  - $\circ$   $\;$  Evaluation of significant findings and recommendations for further action.

<sup>&</sup>lt;sup>2</sup> The critical season for this study is May through October.

# **Organization and Schedule**

Table 2 lists the people involved in this project.

Table 2	Organization	of proj	iect staff	and res	nonsibilities
1 able 2.	Organization	or proj	ECT STAIL	and res	ponsionnies.

Staff All are EAP unless noted otherwise	Title	Responsibilities
David Moore Water Quality Program Eastern Regional Office Phone: 509-329-3541	Client	Clarifies scopes of the project, provides internal review of the QAPP, and approves the final QAPP.
Jim Ross Eastern Operations Section Phone: 509-329-3425	Project Manager	Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft and final data summary reports.
Tighe Stuart Eastern Operations Section Phone: 509-329-3476	Principal Investigator	Writes the QAPP, helps collect samples, and records field information.
Daniel Sherratt Eastern Operations Section Phone: 509-329-3420	Field Assistant	Writes the QAPP, helps collect samples, and records field information.
Gary Arnold Eastern Operations Section Phone: 509-454-4244	Section Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP. Reviews the project scope and budget, tracks progress.
Stuart Magoon Manchester Laboratory Phone: 360-871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.
Meghan Lunney Avista Utilities Phone: 509-495-4643	Aquatic Resource Specialist	Coordinates with Ecology and contractor for lake sampling and analysis.

EAP: Environmental Assessment Program.

EIM: Environmental Information Management database.

QAPP: Quality Assurance Project Plan.

Field and laboratory work	Due date	Lead staff		
Field work completed	11/2011	Jim Ross		
Laboratory analyses completed	12/2011			
Environmental Information System (EIM)	) database			
EIM user study ID	JROS0020	JROS0020		
Product	Due date	Lead staff		
EIM data loaded	2/2012	Dan Sherratt		
EIM quality assurance	3/2012	Jim Ross		
EIM complete	4/2012	Dan Sherratt		
Final report				
Author lead / Support staff	Jim Ross			
Schedule				
Draft due to supervisor	4/2012			
Draft due to client/peer reviewer	er 5/2012			
Draft due to external reviewer(s)	6/2012			
Final (all reviews done) due to publications coordinator (Joan)	7/2012			
Final report due on web	8/2012			

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

# **Quality Objectives**

#### Bias

Bias is defined as the difference between the population mean and the true value of the parameter being measured (Lombard and Kirchmer, 2004). Bias attributed to sampling and field measurement techniques will be minimized by following appropriate protocol and standard operating procedures (SOPs) discussed and referenced to in this QA Project Plan. Procedures provided in this QA Project Plan are used to collect representative samples and field measurements of the highest quality possible. The issue of sample bias is largely investigated at Manchester Environmental Laboratory (MEL), where standard analytical techniques are applied.

#### Precision

Precision is the measure of the variability in the results of replicate measurements due to random error (Lombard and Kirchmer, 2004). This random error is inherently associated with field sampling and laboratory analysis. Field and laboratory errors are minimized by adhering to strict protocols for sampling and analysis. Precision will be expressed as percent relative standard deviation (%RSD) between sets of duplicate field samples (Mathieu et al., 2007).

#### **Measurement Quality Objectives**

EPA defines measurement quality objectives (MQOs) as "acceptance criteria' for the quality attributes measured by project data quality indicators. [They are] quantitative measures of performance..." (EPA, 2002).

In practice, these are often the precision, bias, and accuracy guidelines against which laboratory (and some field) quality control results are compared. Precision may be assessed by the analysis of laboratory duplicates or check standard replicates, and bias by comparing the mean of blank and check standard results to known values (Hallock and Ehinger, 2003).

Analysis	Method	Expected Range of Values	Duplicate Samples RSD	Method Reporting Limits and/or Resolution				
Field	Field							
Water Temperature	Hydrolab MiniSonde® <sup>3</sup>	1.0 - 30° C	+/- 0.1° C <sup>1</sup>	0.01° C				
Specific Conductivity	Hydrolab MiniSonde® <sup>3</sup>	50 – 500 umhos/cm	+/- 0.5% <sup>2</sup>	0.1 umhos/cm				
рН	Hydrolab MiniSonde® <sup>3</sup>	6.0 – 9.0 SU	$0.05 \mathrm{~SU}^1$	1 to 14 SU				
Dissolved Oxygen	Hydrolab MiniSonde® <sup>3</sup>	1.0 – 12 mg/L	5% RSD	0.1 - 15 mg/L				
Laboratory								
Dissolved Oxygen	SM 4500OC	1.0 – 12 mg/L	+/- 0.1 mg/L <sup>1</sup>	0.01 mg/L				
Chloride	EPA 300.0	0.3 – 100 mg/L	5% RSD	0.1 mg/L				
Total Dissolved Solids	SM 2540C	1 – 10,000 mg/L	10% RSD	1 mg/L				
Alkalinity	SM 2320	20 – 200 mg/L as CaCO <sub>3</sub>	10% RSD	10 mg/L				
Ammonia	SM 4500-NH <sub>3</sub> H	<0.01 - 30  mg/L	10% RSD	0.01 mg/L				
Dissolved Organic Carbon	SM 5310B	<1 - 20 mg/L	10% RSD	1 mg/L				
Dissolved Nitrate/Nitrite	4500-NO <sub>3</sub> I	<0.01 - 30  mg/L	10% RSD	0.01 mg/L				
Total Persulfate Nitrogen	SM 4500-NO <sub>3</sub> B	0.5-50 mg/L	10% RSD	0.025 mg/L				
Dissolved Orthophosphate	SM 4500-P G	0.01 - 5.0  mg/L	10% RSD	0.003 mg/L				
Total Phosphorous	SM 4500-P F	0.01 - 10  mg/L	10% RSD	0.005 mg/L				
Total Organic Carbon	SM 5310B	<1 - 20 mg/L	10% RSD	1 mg/L				
Chlorophyll a	SM 10300	$1 - 1000 \text{ mg/m}^2$	25% RSD	2 mg/L				

Table 4. Summary of measurement quality objectives for field and laboratory parameters.

RSD: Relative standard deviation. <sup>1</sup> As units of measurement, not percentages. <sup>2</sup> As percentage of reading, not RSD. <sup>3</sup> Same for both the MiniSonde and DataSonde style of meters.

SM: Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition (APHA et al., 1998). EPA: EPA Method Code.

# **Sampling Process Design (Experimental Design)**

### Schedule

Ecology and Avista will conduct a two-year baseline sample collection effort from May 2010 through October 2011. Monthly sampling will occur during May and October, and sampling will increase to bi-weekly (every other week) between June and September. Sampling in future years should be planned in coordination with the five-year NPDES permit cycle required for all wastewater dischargers.

### **Field Crew**

A one-team field crew, consisting of three to four people, will collect water samples and field measurements at all lake sampling sites. When sampling is conducted by Ecology, either the project manager or the principal investigator will lead the crew to ensure proper techniques are applied. Ideally, all potential samplers from Ecology and Avista will be present during the first sampling event to become familiar with the area, the equipment, and the procedures discussed in this QA Project Plan. Ideally, once the Avista field crew has been adequately trained, it will not be necessary for Ecology personnel to be present when Avista conducts sampling.

### **Sampling Sites**

Water samples and field measurement profiles will be collected at six sites on Lake Spokane. The proposed lake sampling sites are shown in Figure 2. These are established sites from previous sampling studies on Lake Spokane and described in Table 5. Samples will also be collected at the Spokane River at Nine Mile Bridge (Ecology site 54A090) and the Little Spokane River near Mouth (Ecology site 55B070) in coordination with lake sampling efforts. These latter two locations are key control points for total phosphorus loading calculations.

Site ID	Description		Longitude	Latitude
LL0	Lake Spokane @ Station 0 (near Long Lake dam)	32.66	-117.83381	47.83400
LL1	Lake Spokane @ Station 1	37.62	-117.76001	47.83060
LL2	Lake Spokane @ Station 2	42.06	-117.70030	47.86374
LL3	Lake Spokane @ Station 3	46.42	-117.66569	47.86416
LL4	Lake Spokane @ Station 4	51.47	-117.60955	47.81382
LL5	Lake Spokane @ Station 5	54.20	-117.56812	47.79866
54A090	Spokane River @ Nine Mile Bridge	58.00	-117.54480	47.77670
55B070	Little Spokane River near Mouth		-117.53050	47.78290

Table 5. Sampling sites to be used in this study.

Sampling at the Spokane River at Nine Mile Bridge, and the Little Spokane River near Mouth sites will be done by an Ecology employee who has been trained on the ambient monitoring protocol discussed in the *Sampling Procedures* section of this document.

Field crews will ensure they are sampling at the correct locations on the lake by verifying the coordinates using a handheld Global Positioning System (GPS) unit. Horizontal accuracy measurements will be recorded in the field notes during each visit to a site to provide a range in which the measured coordinate values may deviate from the actual values. Notes on environmental conditions that may affect GPS accuracy, such as cloudy or overcast conditions, will be recorded in the field notes as well.



Figure 2. Proposed sampling locations on Lake Spokane.

#### **Parameters**

MEL will analyze water samples for ammonia, nitrate plus nitrite, total persulfate nitrogen, orthophosphorus, total phosphorus, alkalinity, chloride, dissolved organic carbon, total organic carbon, total dissolved solids, and chlorophyll *a*. Composite samples will be taken at each lake sampling location. One composite will be taken from each of three zones present in Lake Spokane (euphotic, interflow, hypolimnion). Table 6 specifies the make-up of each composite sample. Samples collected from the Spokane River at Nine Mile Bridge and the Little Spokane River near Mouth will be collected as surface grab samples from bridges at those locations.

Field staff will measure water temperature, dissolved oxygen, pH, and conductivity in Lake Spokane *in situ* by lowering a Hydrolab® multi-parameter water quality meter from a boat and recording values at predetermined intervals through the water column (see *Measurement Procedures* section). The water quality meter will be calibrated according to the manufacturer's directions and following standard measurement procedures (APHA et al., 1992).

### Layers (Zones) in Lake Spokane

Lake Spokane can be described in terms of three zones: euphotic, interflow, and hypolimnion.

The euphotic zone is defined by light penetration; the bottom of the euphotic zone is defined as the depth at which 1% of the light intensity measured at the surface remains. The interflow zone is an area of more quickly traveling, newer water being drawn at mid-depth through the lake toward the penstocks of Long Lake Dam, which are at a depth of 10-13 meters. The euphotic zone and the interflow zone often have considerable overlap. The upper boundary of the interflow zone is considered to be at a depth of 10 meters near Long Lake Dam, but varies shallower in the upper portion of the reservoir (above about RM 48). The lower boundary of the interflow zone is considered to be a depth of 20 meters.

The hypolimnion in Lake Spokane is defined as the portion of the lake below the interflow zone (i.e., below a depth of 20 meters).

The depth of the euphotic zone will be determined at each site by measuring light attenuation down through the water column using a light meter to measure light intensity. The depth where light intensity falls to 1% of the light intensity at the surface will be set as the total depth of the euphotic zone.

# **Sampling Procedures**

Field sampling and measurement protocols will follow those listed in an Environmental Assessment Program protocols manual (Ecology, 1993).

Samples collected by Ecology and by Avista will be collected into pre-cleaned containers supplied by MEL and described in the MEL *Lab Users Manual* (MEL, 2008).

Safety procedures detailed in the Environmental Assessment Program's Safety Manual (Ecology, 2006) will be followed for all sampling, including bridge and boat sampling.

River samples will be taken at Spokane River at Nine Mile and Little Spokane River at Mouth following the procedures used for ambient sampling by Ecology's Freshwater Monitoring Unit. This Unit will collect all stream samples.

Lake samples will be taken using a Kemmerer sampler with a graduated rope to ensure that samples are taken from the correct depth. The Kemmerer sampler will be triple-cleaned with deionized water between each station. The process of lowering the open sampler to depth will also provide a local-water rinse prior to sample collection.

During the original 2001 data collection, samples were collected every three meters from the surface of the lake to the bottom. Because the variation in nutrient concentrations with depth in Lake Spokane is well established (URS, 1981; Patmont, 1987; Wagstaff and Soltero, 1982; Cusimano, 2003), it is not necessary to duplicate this level of resolution. Furthermore, TMDL compliance as implementation progresses will be based on averages of large portions of the lake (Moore and Ross, 2010).

Three composite samples will be collected at each sampling station, each representing one of the layers of the lake. Each composite sample will consist of discrete samples taken at the depths shown in Table 6.

Discrete samples will be collected with a Kemmerer sampler and then emptied into a pre-cleaned carboy to form the composite sample. The carboy will then be well mixed, and sample bottles will be filled from it. Ecology and Avista will collect lake samples on an alternating schedule.

Sample parameters, containers, volumes, preservation requirements, and holding times are listed in Table 7. Chlorophyll *a* samples will not be field filtered; instead sample containers will be delivered to MEL within the 24-hour holding time for unfiltered samples. All samples for laboratory analysis will be stored on ice and delivered to MEL within the holding time listed in Table 7. Deliveries to MEL will be via Horizon/Alaska Air and Ecology courier.

Site	Euphotic Zone	Interflow Zone	Hypolimnion
LL0	1m, 3m, 6m, 9m*	12m, 15m, 18m	21m, 27m, 33m, 39m, 45m
LL1	1m, 3m, 6m, 9m*	12m, 15m, 18m	21m, 27m, 33m
LL2	1m, 3m, 6m*	12m, 15m, 18m	21m, 27m
LL3	1m, 3m, 6m*	12m, 15m, 18m	
LL4	1m, 3m, 6m*	9m	
LL5	1m, 3m*	Possibly near bottom**	

Table 6. Sample collection depths (meters) to be used for composites at each lake site.

\* The lower euphotic zone boundary will be determined before collecting samples; the euphotic zone composite will not include depths that are below that boundary.

\*\* If the euphotic zone at LL5 extends all the way to the bottom, then the interflow composite will be omitted. Note that there can be overlap between the euphotic zone and the interflow zone.

Table 7. Containers, preservation requirements, and holding times for samples collected (MEL, 2008).

Parameter	Sample Matrix	Container	Preservative	Holding Time
Chloride	Surface water	500 mL poly	Cool to 4°C	28 days
Total Dissolved Solids	Surface water	500 mL poly	Cool to 4°C	7 days
Alkalinity	Surface water	500 mL poly - no headspaceCool to 4°C; Fill bottle <i>completely</i> ; Don't agitate sample		14 days
Ammonia	Surface water	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 4°C	28 days
Dissolved Organic Carbon	Surface water	60 mL poly with Whatman Puradisc <sup>™</sup> 25PP 0.45um filters	Filter in field with 0.45um filter; 1:1 HCl to pH<2; Cool to 4°C	28 days
Nitrate/Nitrite	Surface water	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 4°C	28 days
Total Persulfate Nitrogen	Surface water	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 4°C	28 days
Orthophosphate	Surface water	125 mL amber poly with Whatman Puradisc <sup>™</sup> 25PP 0.45um filters	Filter in field with 0.45um pore size filter; Cool to 4°C	48 hours
Total Phosphorous	Surface water	125 mL clear poly	1:1 HCl to pH<2; Cool to 4°C	28 days
Total Organic Carbon	Surface water	125 mL clear poly	1:1 HCl to pH<2; Cool to 4°C	28 days
Chlorophyll a	Surface water	1000 mL amber polyCool to 4°C; 24 hrs to filtration		28 days after filtering

# **Measurement Procedures**

#### Field

Field measurements will follow approved Environmental Assessment Program SOPs (Ecology, 2010):

- EAP034 Collection, Processing, and Analysis of Stream Samples
- EAP013 Determining Global Positioning System Coordinates.
- EAP011 Instantaneous Measurement of Temperature in Water.
- EAP023 Winkler Determination of Dissolved Oxygen.
- EAP031 Measurement of pH in Freshwater.
- EAP032 Measurement of Conductivity in Freshwater.
- EAP033 Hydrolab® DataSonde and MiniSonde Multiprobes.
- EAP035 Measurement of Dissolved Oxygen in Surface Water.

EPA 360.1 Dissolved Oxygen: Use section 3.2 for collection of dissolved oxygen samples for Winkler titration at depths of over 5 feet.

Sampling sites will be located on maps, and deviations will be recorded in field notes. Deviations farther than 100 yards will be given a new site number. If the site location does not have easily recognizable landmarks, a GPS reading will be taken to obtain accurate latitude and longitude. Reading will follow Environmental Assessment Program SOPs.

At riverine sites (Spokane River at Nine Mile and Little Spokane River at Mouth), field measurements will be taken in accordance with the procedures used for ambient sampling. Conductivity and pH will be measured using ThermoOrion® single probes, temperature will be measured using a long line thermistor, and Winkler titrations will be used to determine dissolved oxygen.

At lake sites, conductivity, temperature, pH, and dissolved oxygen will be profiled using a Hydrolab® multi-probe. The profile will consist of discrete measurements taken at the following depths:

- 0.5 meter
- 1 meter
- 2 meters
- 3 meters
- 4 meters
- 5 meters
- 6 meters
- 7 meters
- 8 meters

- 9 meters
- 10 meters
- 12 meters
- 15 meters
- 18 meters
- 21 meters
- 24 meters
- Continuing at 3-meter intervals to bottom of lake

Last measurement should be taken one meter from bottom of lake.

Methods and targets for various field parameters are summarized in Table 4. Hydrolab® Multi-probe meters require daily calibration or daily checks (for deployed DataSondes) to meet precision targets. Care should be taken when using multi-probe meters in shallow water that sediment is not disturbed and that probes are completely submerged. Slow velocities also usually require a longer probe equilibration period. During high flows, a look-out for debris may be needed to prevent damage to meters.

Secchi disk depths will be recorded at each lake sampling site as a measure of lake clarity.

Euphotic zone determinations will be made using a submersible light meter. The euphotic zone boundary will be defined as the depth at which 1% of the light observed at the surface occurs. Light intensity will be profiled through the euphotic zone by taking measurements at the following depth intervals:

- At the surface (0 meters).
- One-meter intervals until the point at which <10% of the surface light is observed.
- Half-meter intervals until the point at which <1% of the surface light is observed.

#### Laboratory

Samples will undergo MEL standard analytical techniques (Table 4) with standard laboratory quality control procedures (MEL, 2006).

# **Field and Laboratory Quality Control Procedures**

Continuous or instantaneous Hydrolab and Thermo Orion meter measurements collected at each sampling event will conform to the quality control parameters in Table 8. Quality control measurements will be taken at intervals summarized in Table 9. Meter dissolved oxygen/ conductivity/pH/ temperature profiles will not be replicated in their entirety because of time constraints. Instead, every 10<sup>th</sup> measurement making up these profiles will be replicated by allowing the sonde to sit in place for two minutes after the initial measurement is taken and then taking a replicate set of measurements.

Parameter	Replicate Samples	Field Calibration Check Standards	Calibration Drift End Check	
Dissolved Oxygen	$RPD \le 20\%$	N/A	$\pm 4\%$	
Temperature	$\pm$ 0.3 $^{\circ}$ C	N/A	N/A	
Conductivity	$RPD \le 10\%$	$\pm$ 10 %	± 10%	
pН	$\pm 0.2$ pH units	$\pm$ 0.2 pH units	$\pm 0.2$ pH units	
Orion <sup>®</sup> Conductivity	$RPD \le 10\%$	$\pm$ 5 $\mu$ s/cm	$\pm$ 5 $\mu$ s/cm	
Orion <sup>®</sup> pH	± 0.2 pH units	± 0.1 pH units	$\pm 0.1$ pH units	

Table 8. Hydrolab® and Thermo Orion® equipment individual probe quality control requirements.

Secchi disk measurements will be duplicated at one site per sample event.

Meter dissolved oxygen measurements will be compared to Winkler samples. Enough Winklers will be taken during each sampling event to adequately assess dissolved oxygen meter accuracy or correct results, typically four or five Winklers. Winklers will be taken using the Kemmerer sampler at depths corresponding to particular Hydrolab readings, simultaneously with those readings. Typically this will mean some upper, middle, and lower depths to capture a range of dissolved oxygen readings. Winkler bottles will be filled by attaching a length of surgical tubing to the nozzle of the Kemmerer sampler and flushing the Winkler bottle from the bottom with three times the volume of the bottle, similar to the use of a standard dissolved oxygen funnel.

Conductivity and pH data will be verified using pre- and post-deployment calibration checks, which will be recorded and kept with field data.

Total variability for laboratory analysis will be assessed by collecting replicate samples. Sample precision will be assessed by collecting replicates for 10-20% of samples in each survey (Table 9). For lake sites, this will be accomplished by replicating all the samples taken at one site during each sampling run. At stream sites, a set of replicate samples will be taken at one of the two sites once every five runs. MEL routinely duplicates sample analyses in the laboratory (lab duplicate) to determine laboratory precision. The difference between field variability and lab variability is an estimate of the sample field variability.

Field blanks and filter blanks will be submitted with each sampling run to assess some areas of bias. Field blanks will be made by transferring deionized water from the Kemmerer sampler to the compounding carboy to the sample containers to ensure that secondary-container transfers are not causing sample contamination. The procedures used for collecting the stream samples are well established; a set of blanks for the stream samples will be submitted once per field season.

MEL will inform the project manager or principle investigator as soon as possible if any sample is lost, damaged, has a lost tag, or gives an unusual result.

Analysis	Field Replicates	Check Standard	Method Blank	Duplicate	Matrix Spikes	
Field Measurements						
Water Temperature	1/10 samples	N/A	N/A	N/A	N/A	
Dissolved Oxygen	1/10 samples	N/A	N/A	N/A	N/A	
Specific Conductivity	1/10 samples	1/run	N/A	N/A	N/A	
рН	1/10 samples	1/10 samples	N/A	N/A	N/A	
Secchi Disk	1/10 samples	N/A	N/A	N/A	N/A	
Laboratory Analyses						
Dissolved Oxygen (Winkler)	1/10 samples	N/A	N/A	N/A	N/A	
Chloride	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Total Organic Carbon	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Dissolved Organic Carbon	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Alkalinity	1/10 samples	1/batch	N/A	1/20 samples	N/A	
Total Nitrogen	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Ammonia Nitrogen	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Nitrate + Nitrite Nitrogen	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Orthophosphate	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Total Phosphorus	1/10 samples	1/batch	1/batch	1/20 samples	1/20 samples	
Total Dissolved Solids	1/10 samples	1/batch	1/batch	1/20 samples	N/A	
Chlorophyll <i>a</i>	1/10 samples	N/A	N/A	1/10 samples	N/A	

Table 9. Summary of field and laboratory quality control samples and intervals.

# Laboratory Budget

The lab budget estimate (Table 10) for the project is based on sampling six lake sites and two river sites, plus appropriate field duplicates, ten times a year. The lab costs are estimated to be \$7,955 for chlorophyll, \$37,670 for nutrients, and \$54,428 for the chemistry parameters. That equates to a total project lab cost of \$100,053.

Parameter	May	June	July	August	September	October	Totals
2010							
Chlorophyll	385	770	800	800	800	400	3955
Nutrients	1824	3648	3788	3788	3788	1894	18730
Chemistry	2616	5232	5480	5480	5480	2740	27028
2011							
Chlorophyll	400	800	800	800	800	400	4000
Nutrients	1894	3788	3788	3788	3788	1894	18940
Chemistry	2740	5480	5480	5480	5480	2740	27400

Table 10. Monthly project laboratory costs.

Nutrients are nitrate-nitrite, ammonia nitrogen, orthophosphate, total phosphorus, and total persulfate nitrogen. Chemistry is total organic carbon, dissolved organic carbon, total dissolved solids, alkalinity, and chloride.

Lab costs include 50% discount for Manchester Laboratory.

# **Data Management Procedures**

Field measurement data will be entered into a field book with waterproof paper in the field and then entered into EXCEL<sup>®</sup> spreadsheets (Microsoft, 2001) as soon as practical after returning from the field. This database will be used for preliminary analysis and to create a table to upload data into Ecology's Environmental Information Management (EIM) System.

Sample result data received from MEL by Ecology's Laboratory Information Management System (LIMS) will be loaded into EIM, then exported and added to a cumulative spreadsheet for laboratory results. This spreadsheet will be used to informally review and analyze data during the course of the project.

An EIM user study (JROS0020) has been created for this TMDL study and all monitoring data will be available via the internet. The Uniform Resource Locator address for this geospatial database is: <u>apps.ecy.wa.gov/eimreporting</u>. Ecology's EIM data engineer will upload all data to EIM.

All spreadsheet files, paper field notes, and Geographic Information System (GIS)products created as part of the data analysis and model building will be kept with the project data files.

# **Audits and Reports**

The project manager will prepare and submit a data summary of the findings of this study to the client annually.

This summary will contain at a minimum:

- Map and photos of sampling locations.
- Summary table of chemical and physical data, as well as pertinent field notes.
- Discussion of data quality and significance of problems encountered.
- Comparison of sample results with Washington State water quality standards.
- Evaluation of significant findings and recommendations for further action.

# **Data Verification and Validation**

Laboratory-generated data reduction, review, and reporting will follow the procedures outlined in the MEL *Lab Users Manual* (MEL, 2008). Lab results will be checked for missing and improbable data. Variability in lab duplicates also will be quantified using the procedures outlined in the *Lab Users Manual*. Any estimated results will be qualified and their use restricted as appropriate. MEL will send a standard case narrative of laboratory quality assurance/quality control results for each set of samples to the project manager.

Field staff will check field notebooks for missing or improbable measurements before leaving each site. The EXCEL® Workbook file containing field data will be labeled DRAFT until data verification is complete. Data entry will be checked against the field notebook data for errors and omissions. Missing or unusual data will be brought to the attention of the project manager for consultation. Valid data will be moved to a separate file labeled FINAL.

The field lead will check data received from LIMS for omissions against the Request for Analysis forms. Data can be in EXCEL® spreadsheets (Microsoft, 2007) or downloaded tables from EIM. These tables and spreadsheets will be located in a file labeled DRAFT until data verification is completed. Field replicate sample results will be compared to quality objectives in Table 4. The project manager will review data requiring additional qualifiers.

After data verification and data entry tasks are completed, all field, laboratory, and flow data will be entered into a file labeled FINAL and then into the EIM system. Another field assistant will independently review EIM data for errors at an initial 10% frequency. If significant entry errors are discovered, a more intensive review will be undertaken.

# Data Quality (Usability) Assessment

The field lead will verify that all field and laboratory measurements have met the appropriate quality objective. If results fall outside the quality objective, then the field lead will make the decision of whether to qualify or reject the data. If the data are qualified, then the field lead will determine how to use that data for analysis.

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# Appendix. Glossary, Acronyms, and Abbreviations

### Glossary

**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.

**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.

**Eutrophication:** An increase in productivity resulting from nutrient loads from human conditions such as fertilizer runoff and leaky septic systems.

**Hypolimnion:** The deepest layer of water in a lake where water temperature changes less than  $1^{\circ}$  C per one meter of depth.

**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.

**Nutrient:** Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

**Parameter:** Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

**Pollution:** Such 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.

**Total Maximum Daily Load (TMDL):** 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.

# Acronyms and Abbreviations

Avista	Avista Utilities Corp.
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GPS	Global Positioning System
MEL	Manchester Environmental Laboratory
N/A	Not applicable
NPDES	(See Glossary above)
QA	Quality assurance
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
TMDL	(See Glossary above)
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area

#### Units of Measurement

m	meter
mg/L	milligrams per liter (parts per million)
mL	milliliters
SU	standard unit
umhos/cm	micromhos per centimeter
µs/cm	microsiemens per centimeter, a unit of conductivity