

# **Quality Assurance Project Plan**

# Myron Lake (Yakima County) Verification Monitoring

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#### **Publication Information**

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 completing the study, Ecology will post the final report of the study to the Internet.

The plan for this study is available on Ecology's website at <u>https://fortress.wa.gov/ecy/publications/SummaryPages/1203117.html</u>.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at <u>www.ecy.wa.gov/eim/index.htm</u>. Search User Study ID, MIKA4002.

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### **Quality Assurance Project Plan**

### Myron Lake (Yakima County) Verification Monitoring

#### October 2012

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Signatures are not available on the Internet version. EAP: Environmental Assessment Program

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## Abstract

In 1988 and 1989, the Department of Ecology conducted a joint investigation with the Washington Department of Fish and Wildlife into fish kills at Myron Lake in Yakima County. The study found strong evidence of hypolimnetic anoxia in the lake. The fish kills were attributed to rapid consumption of available oxygen during autumnal lake turnover. A hypolimnetic withdrawal was installed in Myron Lake to reduce oxygen demand by both removing anoxic water and encouraging migration of oxygenated water from the epilimnion into the hypolimnion. No fish kills have been observed since 1988.

Myron Lake is included on the 303(d) list for ammonia based on samples collected during the 1988 sampling effort. This study primarily focuses on collecting the data needed by Ecology staff to determine if the installation of the hypolimnetic withdrawal has reduced ammonia concentrations in the waterbody sufficiently to remove it from the 303(d) list. Additional nutrients, chemical characteristics, and physical parameters of the lake will be sampled to give staff a more complete picture of lake quality and to support future studies and modeling efforts.

# Background

### **Location and Characteristics**

Myron Lake (also referred to as Lake Myron) is located on the north side of the city of Yakima, Washington along U.S. Route 12 and the Yakima Greenway Trail (Figure 1). The lake formed in an abandoned gravel pit in 1970, and has since been used primarily as a recreation resource. Myron Lake is stocked with rainbow trout by the Washington Department of Fish and Wildlife (WDFW). In March and April of 2012, 1,205 rainbow trout ranging from approximately half a pound to one and a half pounds were released in the lake.

Water input to Myron Lake is primarily from springs and seeps with minor contributions from direct precipitation and surface runoff. The lake drains to Union Canal, which in turn drains to the Naches River near its confluence with the Yakima River. Myron Lake has a maximum depth of 13.1 meters and an average depth of 9.1 meters (Figure 2). The surface area of the lake is 49,000 square-meters, and it holds a volume of 447,000 cubic-meters of water. Because of its depth, the lake is thermally stratified during the summer months.



Figure 1. Myron Lake and surrounding area

### Lake Stratification

Thermally stratified lakes can be divided into three vertical layers:

- The epilimnion is the top layer of the lake. It is the warmest layer, and can directly exchange gases with the atmosphere. Most plant and phytoplankton growth occurs in the epilimnion.
- The metalimnion is a zone of relatively rapid temperature change that acts as a boundary between the epilimnion and the hypolimnion. The depth of the metalimnion can vary diurnally. Little or no exchange of the water above and below the metalimnion normally occurs.
- The hypolimnion is the bottom layer of the lake. Because it is cut off from direct contact with the atmosphere, the hypolimnion tends to become less oxygenated over time. Decomposition of organic matter that sinks down into the hypolimnion can add to oxygen consumption, resulting in the hypolimnion becoming essentially anoxic.

The relative thickness of the three layers can vary both diurnally and throughout the seasons.

Thermal stratification typically breaks down when changing air temperature cools the epilimnion to the point at which it has a higher density than the hypolimnion. This causes the metalimnion to break down and the waters of the epilimnion and the hypolimnion to freely mix. This phenomenon is known as lake turnover and most frequently occurs in the fall. In lakes cold enough for winter stratification to occur, turnover can also happen in the spring. In some cases, mechanical mixing from wind or other events can also cause the breakdown of thermal layering.

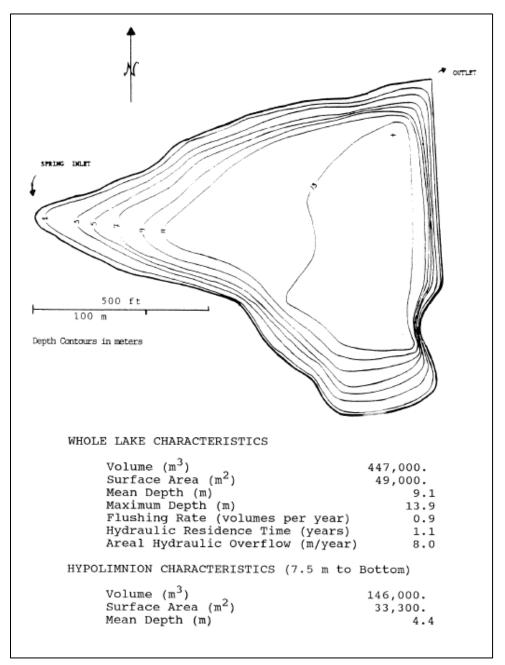


Figure 2. Myron Lake bathymetric map and statistics (from Pelletier et al., 1990).

### **Historical Studies**

A fish kill at Myron Lake in November of 1987 was investigated by the Departments of Ecology and Wildlife (Pelletier et al., 1990). Another similar event occurred in the fall of 1988. The fish kills resulted from low dissolved oxygen concentrations in the lake caused by the mixing of anoxic hypolimnetic waters into the epilimnion during the autumnal lake turnover. To address the problem, a drain was installed which pulled water from the bottom of the lake. Drawing water from the lake bottom reduces the amount of anoxic water and high biochemical oxygen demand (BOD) material stored in the lake as well as disrupting stratification and encouraging the migration of oxygenated water into the lower depths of the lake. However, it can result in the discharge of poor quality water from the lake. Yakima CBS television affiliate KIMA in October 2011 reported on odor complaints at Myron Lake. This suggests that there may be quality issues with the drain water (Spears, 2011).

The study conducted by Pelletier et al. in 1990 also resulted in Myron Lake being placed on the 303(d) list for ammonia. The 303(d) list is a list of impaired waters maintained by the states under the requirements of the Clean Water Act. Six samples collected during the 1988 sampling had ammonia concentrations that exceed state water quality standards. These samples were collected beginning in July and ending in November. Only the November sampling event had no samples in which ammonia concentrations were higher than allowable limits. All of the samples which exceeded water quality standards for ammonia were collected from near the lake bottom. Subsequent sampling in the winter of 1988-89 and spring/summer of 1999 did not test for ammonia concentration.

### Ammonia

Ammonia is classified as a toxic pollutant by the United States Environmental Protection Agency (EPA). It can originate from various wastes, from fertilizers, as well as naturally occurring in the environment. Elevated levels of ammonia are known to cause fish kills as well as cause chronic problems in fish such as reductions in growth and gill condition (EPA, 2010). Ammonia can be found in both unionized (NH<sub>3</sub>) and ionized (NH<sub>4</sub>+) forms, but is typically measured as total ammonia, which includes both NH<sub>3</sub> and NH<sub>4</sub>+. Total ammonia is used to determine whether a waterbody is meeting water quality standard. Temperature and pH both affect the toxicity of ammonia and must be measured concurrently with ammonia sample collection.

In anoxic environments like that found at the bottom of Myron Lake, ammonia levels may be elevated because the oxidation of ammonia into nitrite and nitrate is limited by the lack of oxygen. Ammonia may even be reduced from organic nitrate and nitrite under some conditions. Strongly negative oxidation-reduction potential measurements taken during the 1988 sampling suggest that this is likely in the case of Myron Lake. The BOD exerted by the ammonia found at the bottom of the lake likely contributed to the consumption of dissolved oxygen that resulted in the 1988 and 1989 fish kills.

# **Project Description**

### Overview

This project is a verification study on ammonia concentrations in Myron Lake, Yakima County, Washington. The lack of recurrence of fish kill events at Myron Lake suggests that the remediation efforts that have already been put in place may have improved the water quality in the lake.

The primary goal of this sampling effort is to provide the client with sufficient data to determine whether or not Myron Lake should remain on the 303(d) list for ammonia as a Category 5 waterbody. To ensure that the data is of sufficient quality and scope to make such a decision, the requirements to change a Category 5 determination must be considered.

At the current time, guidelines for verification studies on toxics in thermally stratified lakes are not clearly defined. Myron Lake provides an excellent example of the difficulty in applying standards designed for rivers to lakes. Water samples from rivers are taken from well-mixed zones, and are assumed to be representative of the water column as a whole. That is clearly not the case in Myron Lake where all of the samples that exceeded state water quality standards for ammonia were collected near the bottom of the lake.

There are two potential paths to a finding that Myron Lake can be reclassified on the 303(d) list. If it can be shown that ammonia concentrations no longer exceed surface water standards, then the lake can be reclassified as unimpaired. Alternatively, if it can be shown that the waterbody cannot meet the assigned criteria due to natural conditions and is supporting its assigned beneficial uses, a reclassification could also be considered. In either case, the best approach going forward is to sample in a manner comparable to the sampling that led to the initial Category 5 determination. It is not necessary to replicate the prior sampling effort entirely however.

The secondary objective of this sampling effort will be to collect data to support future lake assessments and modeling efforts. This data will include expanded nutrient data, chlorophyll-a, total and dissolved organic carbon, volatile and non-volatile suspended solids, and alkalinity. To reduce lab costs, some of these parameters will be collected as composites from the hypolimnion and metalimnion. In addition, at least once during the course of the summer, a Hydrolab® MiniSonde will be deployed overnight to capture diel variations in temperature, pH, and dissolved oxygen.

## Sampling Design

The 1990 study showed little change in water chemistry within each thermal layer, with the exception of the very bottom of the hypolimnion. Rather than sampling throughout each layer, targeted samples will be collected from the top and bottom of each layer. This approach will substantially reduce field time and cost while still giving a clear picture of water quality both throughout the water column and in the known problem areas.

A field crew will collect samples once a month at Myron Lake for the sample period, ideally from June to November. Samples will be collected at approximately the deepest point in the lake and will be collected in the same location at each sample event (Figure 3.). A Secchi depth measurement and a profile of depth, pH, conductivity, dissolved oxygen, and temperature will be taken at the start of each sampling event. Using field measurements of temperature and depth, field crew will make a determination of the location of the metalimnion in the water column. A Kemmerer lake sampler will then be used to collect samples at 0.5 meters below the surface, 1 meter above the metalimnion, 1 meter below the metalimnion and 0.5 meters above the lake bottom. Should the hypolimnion become so thin that the two samples collected there are less than a meter apart, only the bottom sample will be collected. In the case that the metalimnion cannot be identified, samples will be collected at 1/3 and 2/3 of the lake's depth as well as at the surface and bottom. Field personnel will take grab samples, a Hydrolab measurement, and a flow measurement at the outfall from the lake.

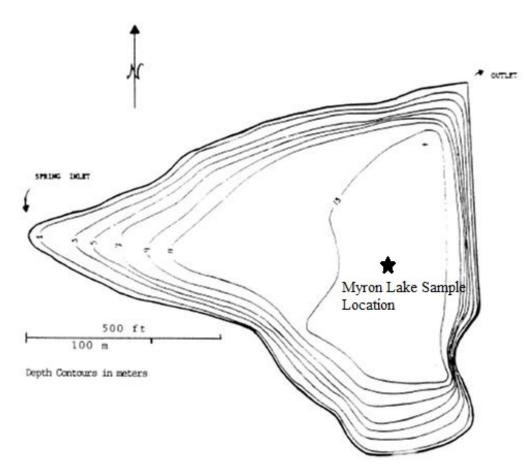


Figure 3. Approximate location of sample collection on Myron Lake.

To maximize the value of the sampling effort, the crew will collect nitrite-nitrate, total persulfate nitrogen, orthophosphate, and total phosphorus samples as well as ammonia at each depth sampled. Additionally, water from each layer will be composited and analyzed for total organic carbon (TOC), dissolved organic carbon (DOC), alkalinity, silica, and total non-volatile suspended solids. Chlorophyll samples will be collected 0.5 meters below the surface to aid in determining the trophic state of the lake.

To capture diel variations in dissolved oxygen, temperature, and pH a Hydrolab multiprobe will be deployed at the sample site for a 24-hour or greater period at least once during the warmer months (August and September).

The sampling locations, number of sites, or length of the sampling period may be altered if required by conditions in the field.

## **Goals and Objectives**

The goals of this sampling effort are to (1) provide a sufficient quantity and quality of data to allow the client to assess the 303(d) status of Myron Lake, and (2) simultaneously collect data useful to current and future lake assessments and modeling efforts. To achieve these goals, the following objectives need to be accomplished:

- Collect samples within the critical period between June and November.
- Collect samples from the outfall to determine if the hypolimnetic drain is operating.
- Sample in a manner that is comparable with the original effort that resulted in the listing of Myron Lake, is consistent with current Ecology practices, and is cost effective.
- Provide field crews with instruction and hands-on training to ensure that data is collected in a manner consistent with the methods described in this document.
- Produce a technical memo after the project has been completed which includes:
  - A summary table of chemical and physical data collected.
  - Discussion of data quality and the significance of problems encountered.
  - Narrative evaluation of the data collection effort and results.
  - Assessment of the trophic state of Myron Lake.
  - Comparison of data collected to numeric water quality standards.
  - Recommendation for further data collection if needed.

# **Organization and Schedule**

Table 1 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 2 presents the proposed schedule for this project.

| Staff<br>(all are EAP except client)  | Title  | Responsibilities  |
|---|--|---|
| Gregory Bohn<br>Water Quality<br>Central Regional Office<br>Phone: (509) 454-4174         | Client   | Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.  |
| Michael Anderson<br>Freshwater Monitoring<br>Unit<br>EOS Section<br>Phone: (509) 662-0480 | Project Manager                                      | Writes the QAPP. 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 report and final report. |
| Eiko Urmos-Berry<br>EOS Section<br>Phone: (509) 575-2397                                  | Field Lead   | Helps collect samples and records field information.<br>Assists with data review and entering data into EIM.  |
| Amy Cook<br>EOS Section<br>Phone: (509) 454-4244  | Field Assistant                                      | Helps collect samples and records field information.  |
| Jenifer Parsons<br>EOS Section<br>Phone: (509) 457-7136                                   | Acting Section<br>Manager for the<br>Project Manager | Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.   |
| Joel Bird<br>Manchester<br>Environmental<br>Laboratory<br>Phone: (360)871-8801            | Director   | Approves the final QAPP.  |
| William R. Kammin<br>Phone: (360) 407-6964  | Ecology Quality<br>Assurance<br>Officer              | Reviews the draft QAPP and approves the final QAPP.   |

| Table 1. | Organization | of project staff | and responsibilities |
|----------|--------------|------------------|----------------------|
|          | 0            |                  |                      |

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

EOS: Eastern Operations Section

QAPP: Quality Assurance Project Plan

| Table 2. 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                   | November 2012                                 | Michael Anderson             |  |  |  |
| Laboratory analyses completed          | December 2012                                 |                              |  |  |  |
| Environmental Information System (EIM) | ) database                                    |                              |  |  |  |
| EIM user study ID                      | ID number                                     |                              |  |  |  |
| Product                                | Due date                                      | Lead staff                   |  |  |  |
| EIM data loaded                        | January 2013                                  | Michael Anderson/Field Staff |  |  |  |
| EIM QA                                 | February 2013                                 | TBD                          |  |  |  |
| EIM complete                           | March 2013 Michael Anderson                   |                              |  |  |  |
| Final Memo to Client                   | Final Memo to Client                          |                              |  |  |  |
| Author lead / Support staff            | Michael Anderson / Eiko Urmos-Berry/ Amy Cook |                              |  |  |  |
| Due Date                               | April 2013                                    |                              |  |  |  |

Table 3. Laboratory cost estimate.

| Sample<br>Type   | Sample<br>Type         | Sites                              | QA (replicate)                             | Visits  | Field<br>Blanks | Analytical<br>cost per<br>sample <sup>1</sup> | Subtotal  |
|------------------|------------------------|------------------------------------|--|---------|-----------------|---|-----------|
| Surface<br>Water | Nutrients <sup>2</sup> | 4 depths<br>plus one at<br>outfall | 4 during<br>project (1 from<br>each layer) | 6       | 2               | \$78.90                                       | \$2840.53 |
| water            | Chlorophyll            | 1                                  | 1  | 6       | 0               | \$44.64                                       | \$267.84  |
|                  | Composite <sup>3</sup> | 2                                  | 2  | 6       | 1               | \$128.17                                      | \$2327.51 |
|                  |                        |                                    |  | Total l | aboratory c     | ost estimate:                                 | \$5435.88 |

<sup>1</sup>Costs include 50% discount for Manchester Laboratory.

<sup>2</sup>Includes ammonia, nitrate-nitrite, total persulfate nitrogen, orthophosphate, and total phosphorus.

<sup>3</sup>Includes Alkalinity, TOC, DOC, Silica, and TNVSS

# **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 in this Quality Assurance Project Plan (QAPP). Procedures provided in this QAPP 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., 2006).

#### **Measurement Quality Objectives**

EPA defines measurement quality objectives 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                        |                            | Bias<br>(deviation<br>from true<br>value) | Precision<br>(replicate<br>median RSD) | Method Lower<br>Reporting Limit<br>and/or<br>Resolution | Expected<br>Range    |
|--|----------------------------|---|--|---|----------------------|
| Field Measurements                     |                            |   |  |   |                      |
| Water Temperature <sup>1</sup>         | Hydrolab <sup>®</sup>      | n/a                                       | +/- 0.2 °C                             | 0.01 °C   | 0 – 30 °C            |
| Specific Conductance <sup>2</sup>      | Hydrolab <sup>®</sup>      | n/a                                       | 5% RSD                                 | 0.1 µS/cm   | 20 – 200 µS/cm       |
| $pH^1$                                 | Hydrolab <sup>®</sup>      | n/a                                       | 0.20 s.u.                              | 0.01 s.u.   | 1 to 14 s.u.         |
| Dissolved Oxygen                       | Hydrolab <sup>®</sup>      | n/a                                       | 5% RSD                                 | 0.1 mg/L  | 0.1 - 15  mg/L       |
| Dissolved Oxygen <sup>1</sup>          | Winkler Titration          | n/a                                       | +/- 0.2 mg/L                           | 0.1 mg/L  | 0.1 - 15  mg/L       |
| Laboratory Analyses                    | Laboratory Analyses        |   |  |   |                      |
| Total Alkalinity                       | SM <sup>4</sup> 2320       | 10%                                       | 10% RSD <sup>3</sup>                   | 5 mg/L  | 5-100  mg/L          |
| Chlorophyll a -water                   | SM <sup>4</sup> 10200H(3)  | 5%  | 20% RSD <sup>3</sup>                   | 0.05 μg/L   | $0.1 - 100  \mu g/L$ |
| Dissolved Organic Carbon               | SM <sup>4</sup> 5310-B     | 10%                                       | 10% RSD <sup>3</sup>                   | 1 mg/L  | 1-20  mg/L           |
| Total Organic Carbon                   | SM <sup>4</sup> 5310-B     | 5%  | 10% RSD <sup>3</sup>                   | 1 mg/L  | 1-20  mg/L           |
| Total Persulfate Nitrogen              | SM <sup>4</sup> 4500-NO3-B | 15%                                       | 10% RSD <sup>3</sup>                   | 0.025 mg/L  | 0.025-20 mg/L        |
| Ammonia                                | SM <sup>4</sup> 4500-NH3-H | 10%                                       | 10% RSD <sup>3</sup>                   | 0.01 mg/L   | 0.01-20  mg/L        |
| Nitrate/Nitrite                        | 4500-NO3- I                | 15%                                       | 10% RSD <sup>3</sup>                   | 0.01 mg/L   | 0.01 - 10  mg/L      |
| Orthophosphate                         | SM <sup>4</sup> 4500-P G   | 20%                                       | $10\% \text{ RSD}^3$                   | 0.003 mg/L  | 0.003 – 1 mg/L       |
| Total Phosphorus                       | SM <sup>4</sup> 4500-P F   | 10%                                       | $10\% \text{ RSD}^3$                   | 0.001 mg/L  | 0.005 - 10  mg/L     |
| Total Non-Volatile<br>Suspended Solids | EPA 160.4                  | 10%                                       | 10% RSD <sup>3</sup>                   | 0.01 mg/L   | 0.1 – 100 mg/L       |
| Silica (derived from Silicon)          | EPA 200.7                  | 15%                                       | 20% RSD <sup>3</sup>                   | 0.10 mg/L   | 0.1 – 100 mg/L       |

Table 4. Measurement quality objectives.

<sup>1</sup> as units of measurement, not percentages.

 $^{2}$  replicate results with a mean of less than or equal to 5X the reporting limit will be evaluated separately.

<sup>3</sup> replicate results with a mean of less than or equal to 5X the reporting limit will be evaluated separately.

SM: Standard Methods for the Examination of Water and Wastewater, 20th Edition (APHA, 1998).

#### Representativeness

The study is designed to have enough sampling sites and sufficient sampling frequency to meet study objectives. Some parameter values are known to be highly variable over time and space. Sampling variability can be somewhat controlled by strictly following standard procedures and collecting quality control samples, but natural spatial and temporal variability can contribute greatly to the overall variability in the parameter value. Resources limit the number of samples that can be taken at one site spatially or over various intervals of time.

# **Sampling and Measurement Procedures**

Field sampling and measurement protocols will follow those listed in an Environmental Assessment Program protocols manual (Ecology, 1993). Safety procedures detailed in the Environmental Assessment Program's Safety Manual (Ecology, 2006) will be followed for all sampling.

Field measurements will follow approved Environmental Assessment Program SOPs (Ecology, 2012):

- EAP011 Instantaneous Measurement of Temperature in Water
- EAP013 Determining Global Positioning System Coordinates
- EAP015 Manually Obtaining Surface Water Samples
- EAP023 Winkler Determination of Dissolved Oxygen
- EAP031 Measurement of pH in Freshwater
- EAP032 Measurement of Conductivity in Freshwater
- EAP033 Hydrolab® DataSonde and MiniSonde Multiprobes
- EAP034 Collection, Processing, and Analysis of Stream Samples
- EAP070 Minimizing the Spread of Aquatic Invasive Species from areas of Moderate Concern
- EPA 360.1 Dissolved Oxygen: Use section 3.2 for collection of dissolved oxygen samples for Winkler titration at depths of over 5 feet

The sampling site will be located using a handheld Global Positioning System and landmarks on the lake shore.

Secchi depth measurements and surface temperature will be collected at the beginning and end of each sample event to document variability in conditions over the course of the sample collection.

Conductivity, temperature, pH, and dissolved oxygen will be profiled using a Hydrolab® multiprobe. The profile will consist of discrete measurements taken at depths of 0.5m, 1m, and then at 1-meter intervals to the bottom of the lake. The water at lake outfall will also be measured.

Nutrient 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 will also

provide a local-water rinse prior to sample collection. Sample bottles will be filled directly from the sampler.

Composite samples will be collected using a Kemmerer sampler in a manner identical to the collection of nutrient samples. Individual samples will be emptied into the composite container, to form the composite sample. Sample bottles will be filled from the composite container. The composite container will be triple-rinsed with deionized water between each composite sample.

Table 5 lists the sample size, containers, preservation, and holding time for each parameter in this study. Sample containers will be provided by Manchester Laboratory. Sample containers will be filled, tagged, and put on ice.

| Parameter                              | Sample<br>Matrix | Container  | Preservative   | Holding<br>Time                               |
|--|------------------|--|--|---|
| Ammonia                                | Surface<br>water | 125 mL clear poly  | H <sub>2</sub> SO <sub>4</sub> to pH<2;<br>Cool to 4 °C                                | 28 days                                       |
| Nitrate/Nitrite                        | Surface<br>water | 125 mL clear poly  | H <sub>2</sub> SO <sub>4</sub> to pH<2;<br>Cool to 4 °C                                | 28 days                                       |
| Total Persulfate<br>Nitrogen           | Surface<br>water | 125 mL clear poly  | H <sub>2</sub> SO <sub>4</sub> to pH<2;<br>Cool to 4 °C                                | 28 days                                       |
| Orthophosphate                         | Surface<br>water | 125 mL amber poly with<br>Whatman Puradisc <sup>™</sup> 25PP<br>0.45um filters | Filter in field with<br>0.45um pore size<br>filter; Cool to 4°C                        | 48 hours                                      |
| Total Phosphorous                      | Surface<br>water | 125 mL clear poly  | 1:1 HCl to pH<2;<br>Cool to 4 °C   | 28 days                                       |
| Chlorophyll <i>a</i>                   | Surface<br>water | 1 L amber poly   | None if unfiltered,<br>90% acetone filtered  | 24 hours<br>unfiltered<br>28 days<br>filtered |
| Total Organic<br>Carbon                | Surface<br>water | 60 mL clear poly   | 1:1 HCl to pH<2;<br>Cool to 70-6 °C  | 28 days                                       |
| Dissolved Organic<br>Carbon            | Surface<br>water | 60 mL poly with:<br>0.45um pore size filters <sup>1</sup>                      | Filter in field with<br>0.45um pore size<br>filter; 1:1 HCl to<br>pH<2; Cool to 0-6 °C | 28 days                                       |
| Alkalinity                             | Surface<br>water | 500 mL poly – NO<br>Headspace  | Cool to 0-6 °C; Fill<br>bottle <u>completely;</u><br>Don't agitate sample              | 14 days                                       |
| Total Non-Volatile<br>Suspended Solids | Surface<br>Water | 1000 mL Poly   | Cool to 0-6 °C   | 28 days                                       |
| Silica                                 | Surface<br>Water | 250 mL Poly  | HNO3 to pH<2. Cool to 4 °C   | 28 days                                       |

Table 5. Sample containers, preservation, and holding times.

For overnight deployments, a Hydrolab multiprobe will be secured to an anchored buoy at the lake sample site. Data will be logged at 15-minute intervals throughout the deployment period. A calibration check will be conducted at the beginning and end of each deployment.

# **Quality Control Procedures**

### Field

Hydrolab meter measurements will conform to the quality control parameters in Table 4 and the calibration drift parameters in Table 6. Meter dissolved oxygen measurements will be compared to Winkler samples. To bracket the expected range of dissolved oxygen, Winkler samples will be collected at the lake surface (0.5 meters depth) and at the outfall. 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, or by using a standard dissolved oxygen funnel.

Conductivity, pH, temperature, and dissolved oxygen data from the Hydrolab will be verified using pre- and post-deployment calibration checks, which will be recorded and kept with field data.

To assess field variability, a duplicate Hydrolab profile will be taken at least twice during the course of the project. Secchi measurements will be taken at both the beginning and end of each sampling event to measure both natural variability and to aid in field detection of measurement errors.

Table 6. Hydrolab® equipment individual probe calibration end drift requirements.

| Parameter        | Calibration Drift<br>End Check |
|------------------|--------------------------------|
| Dissolved Oxygen | $\pm 4\%$                      |
| Temperature      | N/A                            |
| Conductivity     | ± 10%                          |
| pH               | $\pm 0.2$ s.u.                 |

### Laboratory

Total variability for laboratory analysis will be assessed by collecting replicate samples. Quality control samples will be taken at intervals summarized in Table 7. This represents a 13% duplication for nutrient samples and 17% duplication for composite and chlorophyll samples. 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 for nutrient parameters will be submitted twice during the study using the same sampling equipment and procedures used to take regular samples with the exception that the Kemmerer sampler will not be lowered into the water. The sampler will be triple-rinsed with de-ionized (DI) water and then filled with DI water which will be poured into the sample bottles. Orthophosphate blanks will be run through a clean filter prior to bottling. One blank will be submitted for the composite samples using a similar procedure, with the addition that DI water will be poured into the compositing container from the Kemmerer sampler prior to processing.

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

| Analysis                               | Field<br>Replicates  | Check<br>Standard | Method<br>Blank | Duplicate       | Matrix<br>Spikes |
|--|--|-------------------|-----------------|-----------------|------------------|
| Total Nitrogen                         | 4 samples over<br>the course of the<br>study, one at each<br>sampled depth | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Ammonia Nitrogen                       |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Nitrate + Nitrite Nitrogen             |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Orthophosphate                         |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Total Phosphorus                       |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Chlorophyll                            | 1 sample taken<br>w/ surface<br>replicate                                  | N/A               | 1/batch         | 1/20<br>samples | N/A              |
| Alkalinity                             | 2 samples over<br>the course of the<br>study, one from<br>each composite   | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Total Organic Carbon                   |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Dissolved Organic Carbon               |  | 1/batch           | 1/batch         | 1/20<br>samples | 1/20<br>samples  |
| Total Non-volatile<br>Suspended Solids |  | N/A               | 1/batch         | 1/20<br>samples | N/A              |

Table 7. Sample quality control samples and intervals.

## **Data Management Procedures**

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

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

All monitoring data will be available in EIM, via the Internet, once the project data have been validated. The URL address for this geospatial database is <u>www.ecy.wa.gov/eim/index.htm</u>. All data will be uploaded to EIM by the EIM data engineer after the data have been reviewed for quality assurance and finalized.

All spreadsheet files, paper field notes, and GIS device products created as part of the data analysis will be kept with the project data files.

# **Audits and Reports**

At the conclusion of this study the project lead will write a technical memo to the client, summarizing the study findings. This memo will include a brief analysis of whether Myron Lake is meeting water quality standards for ammonia based on the current listing policy (WQP Policy 1-11). It will also assess the lake's trophic state, and compare the concentrations of other nutrients to water quality standards.

# **Data Verification**

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® (Microsoft, 2007) 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 project manager will check data received from LIMS for omissions against the Request for Analysis forms. Field replicate sample results will be compared to quality objectives in Table 7. The project manager will review data requiring additional qualifiers.

After data verification and data entry tasks are completed, all field and laboratory 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

After the project data have been reviewed and verified, the project lead will determine if the data are of sufficient quality to meet the study objectives. The project memo from the project lead to the client will discuss data quality and whether project objectives were met.

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# Appendix. Glossary, Acronyms, and Abbreviations

### Glossary

**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.

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

**Epilimnion:** The top layer of water in a thermally-stratified lake. It is the warmest layer, can directly exchange gases with the atmosphere, and is usually mechanically mixed by wind-surface processes.

**Hypolimnion:** The bottom layer of water in a thermally-stratified lake. Physical and chemical processes within the hypolimnion can result in anoxic and/or toxic conditions in the hypolimnion.

**Metalimnion:** A thin layer in a thermally stratified lake in which temperature decreases more rapidly with depth than in adjacent layers. The metalimnion acts as a barrier between the hypolimnion and the epilimnion. It is also commonly referred to as the thermocline.

**Nonpoint source:** Pollution that enters any waters of the state from any dispersed land-based or water-based activities. This includes, but is not limited to, atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

**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:** 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.

**Point source:** Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

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

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

**Trophic state:** The weight of the biomass in a waterbody. Determined using an index which uses the more easily measured parameters phosphorus, Secchi depth, and/or chlorophyll-a. Trophic state is commonly used as a general indicator of lake health.

**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 standard, and are not expected to improve within the next two years.

### **Acronyms and Abbreviations**

Following are acronyms and abbreviations used frequently in this report.

| Washington State Department of Ecology        |
|---|
| Environmental Information Management database |
| U.S. Environmental Protection Agency          |
| Environmental Assessment Program              |
| And others                                    |
| Geographic Information System software        |
| Manchester Environmental Laboratory           |
| Quality assurance                             |
| Relative standard deviation                   |
| Standard operating procedures                 |
|   |

| TMDL | (See Glossary above)                       |
|------|--|
| WAC  | Washington Administrative Code             |
| WDFW | Washington Department of Fish and Wildlife |

#### Units of Measurement

| degrees centigrade                                  |
|---|
| feet  |
| meter   |
| milligrams per liter (parts per million)            |
| standard units                                      |
| micrograms per liter (parts per billion)            |
| micrometer  |
| microsiemens per centimeter, a unit of conductivity |
|   |