DEPARTMENT OF
ECOLOGY
State of Washington

# Addendum to
# Quality Assurance Project Plan

# Measuring Mercury Trends in Freshwater Fish in Washington State

October 2010

Publication No. 06-03-103-Addendum1

# Publication Information

### Addendum

This addendum is an addition to an original Quality Assurance Project Plan. The addendum is not a correction (errata) to the original plan.

This addendum is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/0603103Addendum1.html

Ecology's Activity Tracker Code for this study is 06-501.

### Original Publication

Quality Assurance Project Plan: Measuring Mercury Trends in Freshwater Fish in Washington State

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# DEPARTMENT OF ECOLOGY

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**SUBJECT**: Addendum to Quality Assurance Project Plan for Measuring Mercury Trends in Freshwater Fish in Washington State
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In 2003, the first chemical action plan was developed by the Washington State Department of Ecology (Ecology) and the Washington State Department of Health, addressing the threat of mercury in Washington State (Peele, 2003). As a result of the *Mercury Chemical Action Plan*, Ecology initiated a long-term mercury monitoring study in 2005 to assess mercury trends in freshwater fish throughout the state (Seiders, 2006).

The purpose of the mercury trends program was to monitor fish in six waterbodies annually on a five-year frequency to characterize mercury trends in freshwater fish tissue. Currently, five years of monitoring (30 sites) have been completed. These sites will be re-sampled over the next five-year period to quantify temporal trends in fish tissue mercury levels. This addendum outlines changes to the monitoring program to be initiated in 2010.

CM:jl

cc: Keith Seiders, Environmental Assessment Program
Stuart Magoon, Director, Manchester Environmental Laboratory
Bill Kammin, Ecology Quality Assurance Officer

# Experimental Design

The goal of this project is to monitor mercury levels in edible tissue from freshwater fish over time to characterize temporal trends in Washington State. To accomplish this goal the Mercury Trends Fish Monitoring program currently collects and analyzes four types of data: water chemistry, sediment chemistry, physical characteristics of the waterbody, and fish tissue mercury concentrations. Proposed changes to the monitoring framework are outlined below.

## Water

During the first five years (2005 – 2009), water samples from the epilimnion and hypolimnion of lakes were analyzed for dissolved organic carbon, alkalinity, and chlorophyll-*a*. Vertical profiles of dissolved oxygen, pH, temperature, and conductivity were measured in-situ. Visible secchi disk depths were also determined.

Starting in 2010, chlorophyll-*a* analyses will be discontinued and major anions and cations (bromide, chloride, fluoride, sulfate, and nitrate+nitrite) will be added. All other aspects of the water sampling routine will remain the same. While chlorophyll-*a* has been shown to have a minor effect on mercury methylation potential (e.g., Lange et al., 1993), data from the baseline period of the project do not show a significant relationship with fish tissue mercury levels.

Numerous studies have shown that sulfate and chloride have a large control on methylation rates in temperate freshwater lakes (e.g., Hrabik and Watras, 2002). Less is known about the other proposed ions; however, recent research has reported that nitrogen ions can serve a large role in mercury cycling (Todorova et al., 2009).

## Sediment

Previously, surface sediments were collected from the three deepest areas within each waterbody and analyzed for total mercury, total organic carbon, and grain size. Starting in 2010, sediment sampling will be discontinued due to high in-lake mercury concentration variability and no expected changes in sediment mercury levels over a five-year period.

Data from the first five years of sampling showed large variability in sediment mercury levels between samples within each waterbody. High variability between samples makes it difficult to accurately assess the relationship between sediment mercury levels and fish tissue mercury concentrations among waterbodies.

Mercury concentrations in sediments are not expected to significantly change within such a short period of time because sedimentation rates are not great enough to deliver substantial new sediment material within five years. Sediment data collected during the baseline period (2005-2009) should be adequate to estimate current concentrations.

## Waterbody Characteristics

No changes will occur with collection of waterbody physical characteristics. These characteristics are determined from literature reviews and GIS analysis and include: lake morphometry such as depth, area, and volume; watershed size, soils, land use, and wetland area; hydrologic characterization such as flow and retention times; and site classification such as drainage, reservoir, seep, or riverine.

## Fish

Fish collection and analysis will not change. Ten bass or walleye will be collected from each waterbody and analyzed individually for total mercury. Two to three ancillary species will also be collected and composited for mercury analyses, when available.

# Analytical Laboratory

Manchester Environmental Laboratory (MEL) will analyze samples for determination of major ions (bromide, chloride, fluoride, sulfate, and nitrate+nitrite) in water.

# Intended Use

The data will be used to gather information on waterbody characteristics that control mercury concentrations in resident fish.

# Organization and Schedule

Table 1 displays the current staff and roles associated with this project. No changes will be made to the project schedule.

Table 1. Organization of Project Staff.

| Name | Ecology Program | Phone Number | Title/Role |
|---|---|---|---|
| Callie Meredith | EAP-SCS-TSU | 360-407-6965 | Project Lead |
| Chad Furl | | 360-407-6060 | Project Assistance |
| Michael Friese | | 360-407-6737 | Project Assistance |
| Tanya Roberts | | 360-407-7392 | Project Assistance |
| Dale Norton | | 360-407-6765 | Unit Supervisor to Project Lead |
| Holly Davies | W2R | 360-407-7398 | Client |
| Carol Kraege | | 360-407-6906 | Client |
| Maria Peeler | HWTR | 360-407-6704 | Client |
| Ken Zarker | | 360-407-6724 | Client |
| Dean Momohara | MEL | 360-871-8808 | Laboratory Unit Supervisor |
| Stuart Magoon | | 360-871-8801 | Laboratory Director |
| William Kammin | EAP | 360-407-6964 | Ecology QA Officer |

EAP: Environmental Assessment Program.
SCS: Statewide Coordination Section.
TSU: Toxics Studies Unit.
W2R: Waste 2 Resources Program.
HWTR: Hazardous Waste and Toxic Reduction Program.
MEL: Manchester Environmental Laboratory.

# Budget

An estimated annual laboratory budget for the Mercury Trends Fish Monitoring program is shown in Table 2.

Table 2. Project Budget.

| Matrix | Analyte | Count[1] | Cost per sample | Total Cost |
|---|---|---|---|---|
| Water | Alkalinity | 16 | $18 | $288 |
| | Dissolved organic carbon | 16 | $37 | $592 |
| | Ions[2] | 16 | $54 | $864 |
| | Nitrate+Nitrite | 16 | $14 | $224 |
| Tissue | Mercury (individual bass) | 66 | $48 | $3,168 |
| | Mercury (composite) | 40 | $48 | $1,920 |
| Total Laboratory Costs = $7,056 | | | | |

[1] Count includes QA samples.
[2] Includes bromide, chloride, fluoride, and sulfate.

# Quality Objectives

The measurement quality objectives for the major ions analyses are shown in Table 3. MEL will be expected to meet the quality objectives outlined below.

Table 3. Measurement Quality Objectives.

| Analyte | LCS (% recov.) | Lab Duplicates (RPD) | Method Blanks | Matrix Spikes (% recov.) | Field Replicates (RPD) |
|---|---|---|---|---|---|
| Bromide | 90-110 | ≤ 20 | < LOQ | 75-125 | ≤ 20 |
| Chloride | 90-110 | ≤ 20 | < LOQ | 75-125 | ≤ 20 |
| Fluoride | 90-110 | ≤ 20 | < LOQ | 75-125 | ≤ 20 |
| Sulfate | 90-110 | ≤ 20 | < LOQ | 75-125 | ≤ 20 |
| Nitrate+Nitrite | 90-110 | ≤ 20 | < LOQ | 75-125 | ≤ 20 |

LCS: Laboratory Control Sample.
RPD: Relative Percent Difference.
LOQ: Limit of Quantitation.

# Sampling and Measurement Procedures

## Sampling Procedures

Water samples will be collected using the protocol previously described in the original Quality Assurance (QA) Project Plan (Seiders, 2006). Containers and preservation protocol for samples are shown in Table 4.

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

| Analyte | Container | Preservation | Holding Time |
|---|---|---|---|
| Bromide | 500 mL poly | 4 ±2°C | 28 days |
| Chloride | 500 mL poly | 4 ±2 °C | 28 days |
| Fluoride | 500 mL poly | 4 ±2 °C | 28 days |
| Sulfate | 500 mL poly | 4 ±2 °C | 28 days |
| Nitrate+Nitrite | 125 mL poly | 4 ±2 °C; acidified* to pH < 2 | 28 days |

* $H_2SO_4$ added at time of sample collection.

## Laboratory Procedures

The laboratory procedures for the analyses are listed in Table 5.

Table 5. Measurement procedures and reporting limits.

| Analyte | Number of Samples | Method | Reporting Limit |
|---|---|---|---|
| Bromide | 16 | EPA 300.0 | 0.2 mg/L |
| Chloride | 16 | EPA 300.0 | 0.1 mg/L |
| Fluoride | 16 | EPA 300.0 | 0.1 mg/L |
| Sulfate | 16 | EPA 300.0 | 0.5 mg/L |
| Nitrate+Nitrite | 16 | SM 4500-$NO_3^-$I | 0.01 mg/L |

EPA: U.S. Environmental Protection Agency.
SM: Standard Methods.

# Quality Control

## Field

Field quality control procedures for the added analyses will include field blank and field replicate samples. These will be analyzed at the same frequency as outlined for other water samples in the original QA Project Plan (Seiders, 2006). Field blank and replicate samples will be collected for approximately 10% of the sites sampled. Collection procedures for water samples will be conducted in the same manner as current water parameters described in the project plan (Seiders, 2006)

## Laboratory

MEL will conduct the following analyses as part of laboratory quality control procedures: laboratory control samples, laboratory duplicates, method blanks, and matrix spikes (see Table 6 for frequency). MEL will provide the project manager with case narratives describing sample holding times, instrument calibrations, and results of quality control tests.

Table 6. Laboratory Quality Control Procedures.

| Analyte | LCS | Lab Duplicates | Method Blanks | Matrix Spikes |
|---|---|---|---|---|
| Bromide | 1/batch | 1/20 samples | 1/batch | 1/10 samples |
| Chloride | 1/batch | 1/20 samples | 1/batch | 1/10 samples |
| Fluoride | 1/batch | 1/20 samples | 1/batch | 1/10 samples |
| Sulfate | 1/batch | 1/20 samples | 1/batch | 1/10 samples |
| Nitrate+Nitrite | 1/batch | 1/20 samples | 1/batch | 1/20 samples |

# Data Management

All data management procedures will follow those stated in the original QA Project Plan.

# Audits and Reports

In accordance with the original QA Project Plan, MEL will be responsible for performance and system audits of laboratory procedures. Results of those audits are available upon request.

The project lead will continue to complete an annual draft report of the study findings by July, and the annual final report will be published in October.

# Data Verification

Data verification will be consistent with the original QA Project Plan.

# References

Hrabik, T. and C. Watras, 2002. Recent Declines in Mercury Concentration in a Freshwater Fishery: Isolating the Effects of de-Acidification and Decreased Atmospheric Mercury Deposition in Little Rock Lake. The Science of the Total Environment, Vol 297: 229-237.

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