DEPARTMENT OF ECOLOGY
State of Washington

Addendum to Quality Assurance Project Plan

Measuring Mercury Trends in Freshwater Fish in Washington State

May 2021

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Contact Information

Publications Coordinator
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360-407-6764

Washington State Department of Ecology – ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

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Measuring Mercury Trends in Freshwater Fish in Washington State

by Jakub Bednarek and Callie Mathieu

May 2021

Approved by:

Signature:	Date:
Jessica Archer, Client and Statewide Coordination Section Manager, EAP	
Signature:	Date:
Jim Medlen, Client and Toxic Studies Unit Supervisor, EAP	
Signature:	Date:
Callie Mathieu, Author / Project Manager, EAP	
Signature:	Date:
Jakub Bednarek, Author / Field Lead, EAP	
Signature:	Date:
Alan Rue, Director, Manchester Environmental Laboratory	
Signature:	Date:
Arati Kaza, Ecology Quality Assurance Officer	

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

Table of Contents

The numbered headings in this document correspond to the headings used in the original QAPP. Only relevant sections are included; therefore, some numbered headings are missing.

3.0 Background

3.1 Introduction and problem statement

Washington State Department of Ecology (Ecology) conducts annual monitoring for mercury in freshwater fish tissues. The program informs long-term trends and characterizes mercury levels in largemouth and smallmouth bass across Washington State. The program has shown inconsistent trends throughout the state with some lakes increasing and others decreasing in mercury content of fish tissue over the last 15 years.

Ecology's Mercury in Fish Program monitors total mercury (THg) as a surrogate for methylmercury (MeHg), the organic, neurotoxic, and bioaccumulative form of mercury. This is a common practice for mercury monitoring programs due to the simplicity and significant cost reduction of THg analysis. A major assumption of this analysis is that MeHg makes up to 95% of THg found in fish tissue (Bloom 1995, Driscoll et al. 1994).

Although this assumption is true for upper trophic level species such as Walleye, recent studies have shown many species do not fit the assumption. Bass are often described as tertiary consumers. However, smaller and younger bass may feed at lower levels of the food web. Zanden et al. (1997) used dietary data to calculate the mean trophic position of smallmouth and largemouth bass to be lower than walleye. In this regard, it is possible that %MeHg in bass could be less than the expected 95%. No data exists yet on the %MeHg bioaccumulation in bass.

This study will better characterize the %MeHg found in bass and should provide a better understanding of long-term trends, variability, and comparability of data to Washington State human health and water quality thresholds, as detailed in the original Quality Assurance Project Plan (QAPP). This QAPP is an addendum to Ecology's long-term Mercury in Freshwater Fish monitoring program. This addendum serves to detail the additional analysis of MeHg on a subset of archived largemouth and smallmouth bass samples collected in 2020.

3.2 Study Area

The 2020 monitoring sites will be used for this 2021 study: Loon Lake, Spokane River, Liberty Lake, and Silver Lake. The sites are described in detail in the original QAPP (Mathieu, C and J. Bednarek. 2020). The only deviation from this plan was that we were unable to sample the Yakima River due to COVID restrictions.

3.2.2 Summary of previous studies and existing data

The relationship between %MeHg, size, and age has been widely documented. Also, trophic level has played an increasingly important role in predicting %MeHg.

- A Lake Washington study showed that trophic position was a major indicator of biomagnification (McIntyre and Beauchamp 2007).
- Arcagni et al. (2018) also found a relationship between trophic levels and %MeHg among trout, catfish, perch, as well as non-fish species.

- In 2018, Lescord et al. observed that the 95% estimate commonly used by monitoring programs does not apply to all piscivores. Their study showed MeHg varying between 39% - 100% in five fish species (walleye, northern pike, white sucker, sculpins, and shiners). Lescord found significant relationships between %MeHg and trophic level among these species.

To date, regional studies have not been conducted to determine %MeHg in freshwater bass.

3.2.3 Parameters of Interest

Fish fillet tissue will be analyzed for MeHg in addition to the previously planned THg analysis. MeHg is a neurotoxin produced from inorganic mercury by the metabolic processes of anaerobic bacteria in wetland soils, lake sediment or the water column. MeHg can make up to 100% of the THg in organisms but the mechanisms of bioaccumulations and biomagnification are complex; habitat characteristics, physiology, and fish behavior can all affect rates of bioaccumulation. A regional, species-specific study is important for understanding the relationship between MeHg and THg accumulation in fish.

4.0 Project Description

4.1 Project goals

The primary goal of this project is to confirm (or refute) assumptions made about %MeHg in fish tissue. Like most programs, our monitoring monitors THg and uses established models to assume %MeHg. This study will reinforce the original project goal of characterizing mercury levels in freshwater fish by clarifying what the levels mean in reference to human and aquatic health.

4.2 Project objectives

The project objectives remain the same as described by Mathieu and Bednarek (2020) with the additional objective:

- Determine the proportion of MeHg to THg in bass muscle tissue.

4.4 Tasks required

- Write a scope of work for project lab analysis.
- Contract with accredited lab for MeHg analysis.
- Deliver archived samples to the lab.
- Review and assess data quality of THg and MeHg lab results.
- Analyze data and include discussion of findings in the annual report for mercury trends in fish.

5.0 Organization and Schedule

5.4 Proposed project schedule

MeHg laboratory analysis will be performed by an accredited lab beginning in May 2021. Archived samples will be shipped to the lab upon completion of this QAPP. Results are expected within 90 days of sample submittal. Field work, data management, and reporting component timelines are described in original QAPP (Mathieu and Bednarek 2020).

Table 1. Proposed schedule for completing additional analysis.

Task	Due date	Lead staff
Fish Collection	Completed Oct 2020	Jakub Bednarek
Fish Tissue Processing	Completed Dec 2020	Jakub Bednarek
Laboratory Analyses	May 2021	Lab TBD
Lab Data to Project Manager	June 2021	Lab TBD

5.5 Budget and funding

Table 2 shows the estimated laboratory cost for additional analysis.

Table 2 Laboratory budget details.

Parameter	Number of Samples	Number of QA Samples*	Total Number of Samples	Cost Per Sample	Lab Total	MEL Contract Fee	Total Cost
Methylmercury	40	6	46	$225	$10,350	$3,105	$12,420

*Number of QA samples includes only those for which additional fees are charged (matrix spikes, matrix spike duplicates, and laboratory control sample duplicates). QA sample that are typically included in the fee of analysis are not included here.

6.0 Quality Objectives

6.2 Measurement quality objectives

The MQOs for method blanks, laboratory control samples, laboratory duplicates, matrix spikes, and matrix spike duplicates will be used by the lab as acceptance limits and by the project manager to inform the reliability of data.

Table 3 Measurement Quality Objectives

Parameter	Method Blank	Laboratory Control Samples (% recovery)	Duplicates (RPD)	Matrix Spikes (% recovery)
Methylmercury	≤ 0.5 ng/L	75 – 125	≤ 20	75 - 125

9.0 Laboratory Procedures

9.1 Lab Procedure table

Table 4 Measurement methods

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Methylmercury	Tissue	40 / May 2021	0.020 – 1.50 mg/kg ww	0.017 mg/kg ww	EPA 1630	EPA 1630

Ten largemouth or smallmouth bass were collected from five sampling locations in 2020. Both were collected at Liberty Lake and Potholes Reservoir. All 72 samples were submitted for THg in 2020. Remaining tissue is archived by Ecology's Toxic Studies Unit staff at Ecology Headquarters in a -20 degree C freezer. Holding times for tissue samples analyzed for mercury are 1-year, according to EPA method. Due to budget constraints, only 40 samples will be analyzed for MeHg. Ten samples from Loon Lake (largemouth), Silver Lake (largemouth), Liberty Lake (largemouth), and Lake Spokane (smallmouth) will be submitted for MeHg analysis.

9.3 Special method requirements

EPA method 1630 describes analysis for an aqueous solution. Mercury methods are often adapted for solid and tissue matrix. The lab will adapt methods for fish tissue and provide documentation of adaptation upon request.

9.4 Laboratories accredited for methods

THg was analyzed by Ecology's Manchester Environmental Lab (MEL) in January 2021, but MEL is not currently accredited for MeHg analysis. The project team will choose an accredited lab for analysis of MeHg. The lab will be chosen based on its ability to meet the MQOs, budget, and a level 2b data package. Using a third party lab is not expected to affect comparability of results because standardized methods are being used for analysis.

10.0 Quality Control Procedures

10.1Table of laboratory quality control

Quality control (QC) procedures will follow those outlined in the original QAPP (Mathieu and Bednarek 2020).

Table 5. Quality control samples, types, and frequency

Parameter	Laboratory Control Samples	Laboratory Control Sample Duplicate	Laboratory Method Blanks	Matrix Spikes	Matrix Spike Duplicates
Methylmercury	1/batch	1/batch	1/batch	1/batch	1/batch

11.0 Data Management Procedures

11.2 Laboratory data package requirements

The selected lab will provide an electronic data deliverable that includes results of samples and QC tests. The lab will also provide case narratives explaining the condition of samples upon receipt, sample preparation methods, methods of analysis, instrument calibrations, and results of QC test. Narratives will address (1) any problems that occurred during analysis and corrective actions taken, (2) deviations from the reference method, and (3) an explanation of the data qualifiers. All documentation required for level 4 validation will be provided. However, level 4 validation will be considered as an option. For this project, level 2b validation should be sufficient.

11.3 Electronic transfer requirements

The laboratory data package will be provided in electronic format. Acceptable data formats include Excel spreadsheet or comma separated value (CSV) file. Data tables and case narratives will be provided by email.

13.0 Data Verification

13.2 Lab data verification

MeHg data will be verified for errors, omissions, and compliance with method acceptance criteria according to the analytical scope of work and this QAPP addendum. MEL staff will follow data verification steps outlined as part of an EPA Stage 2b data validation described below in section 13.3.

13.3 Validation requirements, if necessary

MEL will be responsible for carrying out validation of the MeHg data. A data validation equivalent to an EPA Stage 2b validation, as defined in EPA (2009), will be required for this project.

14.0 Data Quality (Usability) Assessment

14.3 Data analysis and presentation methods

Mean %MeHg will be presented. The data will be presented in comparison with THg analysis completed by MEL. Data will be grouped by species and location. Additional analysis will be considered if relevant to the context of the study.

15.0 References

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