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Addendum 4 to Quality Assurance Project Plan

Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores

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

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID: SEDCORE14.

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September 2014

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
EIM: Environmental Information Management database

3.0 Background

Ecology's Persistent, Bioaccumulative, and Toxics (PBT) Monitoring Program began a long-term study to assess PBT chemical trends through age-dated lake sediment cores in 2006. A single sediment core is collected from three lakes per year to construct historical deposition profiles of PBTs in the environment. New lakes are chosen each year to achieve a broad spatial coverage of the state, as well as to target waterbodies based on the parameters to be analyzed. Ecology selects lakes in an attempt to capture data about a range of potential contaminant sources.

A previous Quality Assurance Project Plan (QAPP) Addendum for this study outlined a schedule to rotate target PBT chemicals into the analyte list to provide depositional and temporal data on a wider range of PBTs (Mathieu, 2012). This information helps policy makers prioritize PBTs addressed by chemical action plans (CAPs) and provides data for existing CAP reduction strategies.

This addendum describes the 2014 sampling locations and the following changes in target analytes:

- Chlorinated paraffins will be added to the target analyte list in 2014.
- Hexabromocyclododecane will be taken off the target analyte list in 2014.

Sections not included in this addendum remain unchanged from the original QAPP (Coots, 2006).

3.1 Study area and surroundings

Lakes selected for 2014 sampling are described in Table 1 and displayed in Figure 1. Bead Lake is located in the northeastern area of Washington State, in rural Pend Oreille County. The lake shoreline contains some residences, but the watershed is predominantly undeveloped forest land. Several streams flow into Bead Lake which has no outlet and the watershed receives an average of 38" of precipitation annually. The basin is made up of gravelly sand soils (Schroeder, 1952).

Lake Goodwin is located 10 miles northwest of the city of Everett, in Snohomish County. The watershed consists of residential and forested land, with a densely populated lake shoreline. Lake Goodwin is part of a series of lakes receiving inflow from Crabapple Lake and draining into Lake Shoecraft. The drainage area receives 32" of mean annual precipitation and basin geology consists of glacial drift with gravelly loam soils (Bortleson et al., 1976).

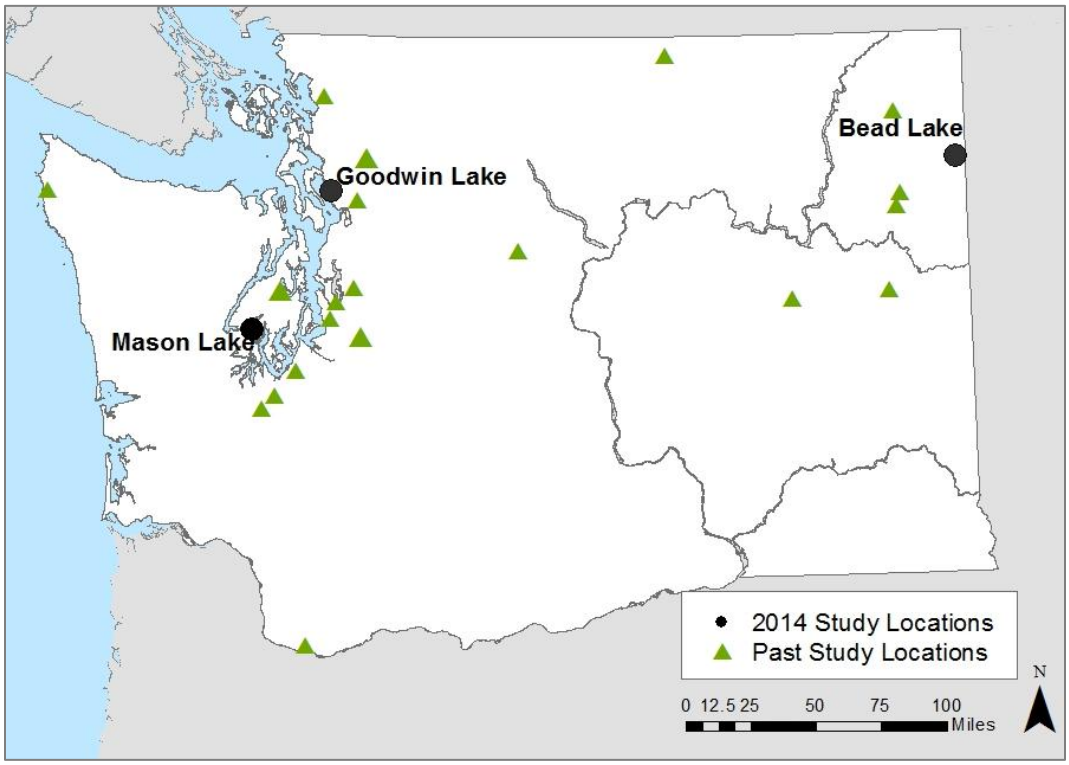
Mason Lake is located in Mason County, ten miles northeast of Shelton. Mason Lake has a densely developed shoreline with a largely rural watershed, consisting mostly of commercial timberland. The lake has year-round inflow from Shumocher Creek as well as numerous small intermittent streams. It then flows out through Sherwood Creek. The watershed receives 68" mean annual precipitation and has mostly gravelly, sandy loam soils with some silt clay loam (Bortleson et al., 1976).

Table 1. 2014 Sediment Core Study Lakes.

Waterbody	County	Max Depth (feet)	Mean Depth (feet)	Lake Area (acres)	Watershed Area (acres)
Bead Lake	Pend Oreille	170	n/a	720	6,000
Lake Goodwin	Snohomish	50	23	560	3,315
Mason Lake	Mason	90	48	100	13,440

n/a = not available

Figure 1. 2014 Sediment Core Study Locations.



3.1.1 Logistical problems

No logistical problems were found when conducting reconnaissance of the study lakes.

3.1.2 History of study area

The lakes selected for 2014 sampling were chosen based on criteria outlined in the QAPP, such as achieving broad spatial coverage of the state and covering a range of land use and contamination potential. Bead Lake was selected to help characterize sediments in Eastern Washington and for its undeveloped watershed to reflect baseline levels from atmospheric deposition. Goodwin Lake was chosen for its relative proximity to industrial areas near Everett, with potential for regional deposition of chlorinated paraffins. Mason Lake was chosen to represent a mixed rural-residential area lake in the southwest Puget Sound area. The three lakes also cover a range of physical characteristics likely to affect contaminant deposition profiles

from the surrounding watersheds. Bead and Goodwin Lakes have relatively small watershed area to lake surface area ratios, whereas Mason Lake has a much larger ratio and therefore may represent a lake with shorter particle residence times and higher sediment accumulation rates.

3.1.3 Contaminants of concern

Chlorinated paraffins are a group of chemicals used as industrial flame retardants, lubricants, and plasticizers, as well as additives in adhesives, paints, rubber, and sealants (Muir et al., 2000). The term chlorinated paraffins refers to complex mixtures of polychlorinated alkanes with varying carbon chain lengths and chlorine contents. The target chlorinated paraffin compounds are listed in Table 2, along with their carbon chain length.

Table 2. Chlorinated Paraffins on the Target Analyte List."

Chlorinated Paraffin Group	Carbon Chain
Short-chain (SCCP)	C10 - C13
Medium-chain (MCCP)	C14 - C17
Long-chain (LCCP)	C18 - C20

Short-chain chlorinated paraffins (SCCPs) are listed on Ecology's PBT List because they are persistent, bioaccumulative, and toxic to aquatic organisms at low concentrations. SCCPs have also been classified as "reasonably anticipated to be human carcinogens" based on animal studies (NTP, 2011). Medium-chain (MCCPs) and long-chain (LCCPs) chlorinated paraffins are also persistent and bioaccumulative but appear to have lower toxicity because of their lower solubility. However, the toxicity of MCCPs and LCCPs is not as well researched as SCCPs (EPA, 2009).

SCCPs have been found in water, sediment, air, aquatic organisms, terrestrial wildlife, and humans (reviewed by Tomy et al., 1998 and Bayen et al., 2006), as well as in remote sediments where long-range atmospheric transport was the attributed source (Tomy et al., 1999). SCCPs persist in sediments and have been reported in sediment core samples dating back to the 1940s (Government of Canada, 2008; Iozza et al., 2008; Marvin et al., 2003). The greatest mode of release to the environment is thought to be from manufacturing and lubricant applications, primarily via metal-working activities (EPA, 2009).

3.1.4 Results of previous studies

No previous studies have assessed chlorinated paraffins in sediments collected in Washington State, to the authors' knowledge. A 2011 Ecology study analyzed chlorinated paraffins in fish tissue collected from four freshwater sites (Johnson and Friese, 2012). Chlorinated paraffins were found in all of the fish tissue samples analyzed and the authors recommended including the

analytes in future monitoring studies. Short- and medium-chain chlorinated paraffin concentrations were particularly elevated out of the eight PBTs assessed in the study. Table 3 displays the results from the Johnson and Friese (2012) study.

Table 3. Chlorinated Paraffin Results in Washington State Freshwater Fish Tissue (*ng/g, wet weight*), from Johnson and Friese (2012).

Sample Type and Collection Site	SCCPs (ng/g)	MCCPs (ng/g)	LCCPs (ng/g)	ΣCPs (ng/g)
Common carp / muscle				
Lake Washington	194	107	18	320
Lower Columbia River	242	132	31	404
Lower Yakima River	459	190	39	687
Lake Spokane	340	208	29	577
Largescale sucker / whole				
Lake Washington	895	663	108	1,670
Lower Columbia River	391	259	53	703
Lower Yakima River	541	480	90	1,110
Lake Spokane	353	245	66	665

SCCPs = short-chain chlorinated paraffins
MCCPs = medium-chain chlorinated paraffins
LCCPs = long-chain chlorinated paraffins
ΣCPs = sum of short-, medium-, and long-chain chlorinated paraffins

3.1.5 Regulatory criteria or standards

No regulatory criteria or standards exist in Washington State for chlorinated paraffins in freshwater sediment.

The Environmental Protection Agency (EPA) is currently reviewing SCCPs and intends to initiate action under the Toxic Substances Control Act (TSCA) section 6(a) to ban or restrict the manufacture, import, processing, or distribution in commerce, export, and use of SCCPs based on their PBT properties and their presence in the environment. The EPA also intends to evaluate whether MCCPs and LCCPs should be addressed under TSCA section 6(a).

4.5 Study boundaries

At each study lake, a sediment core will be collected from a discrete sampling point in the deepest part of the lake. Figure 2 displays target sampling locations.

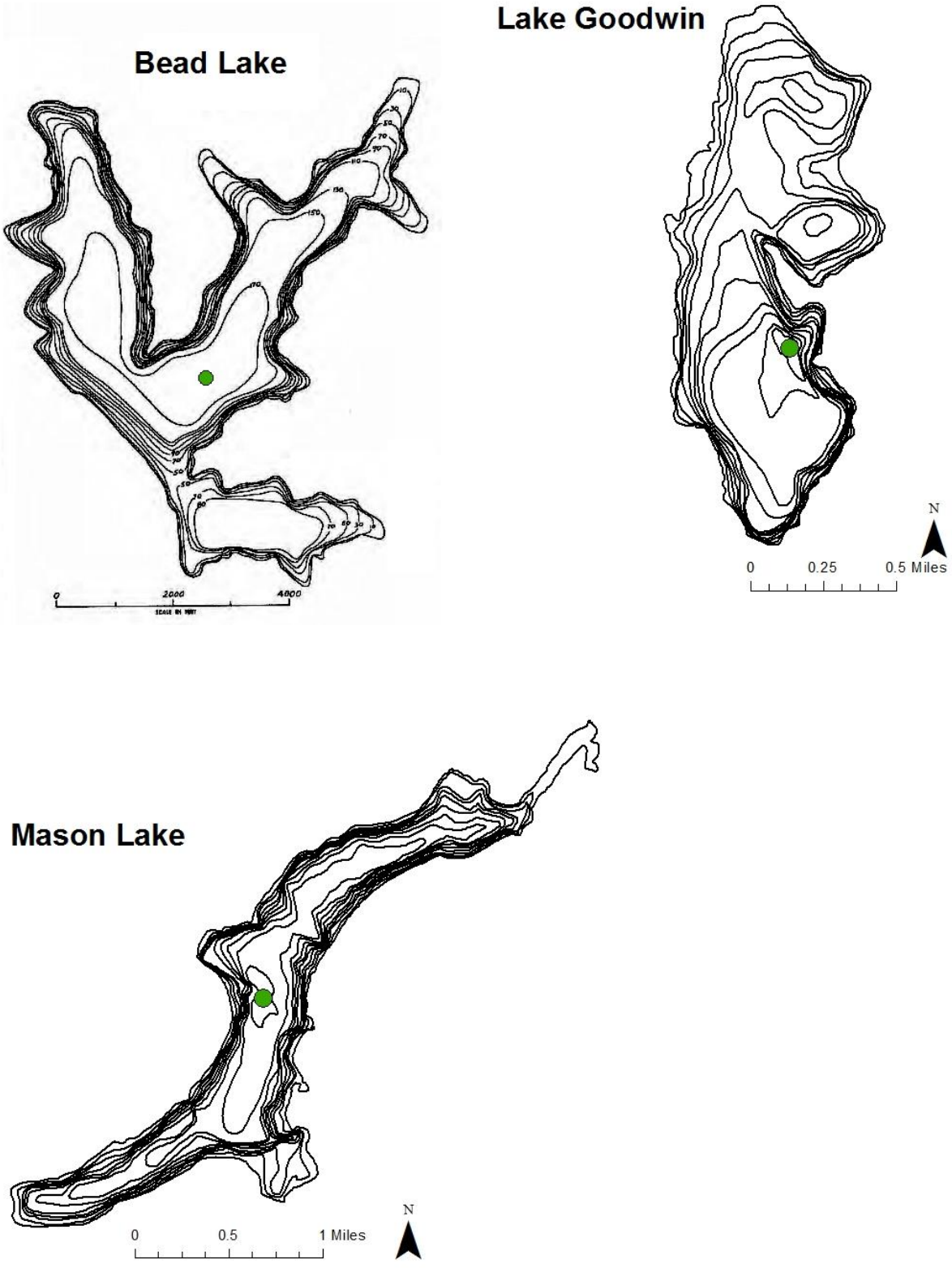


Figure 2. Target Sampling Locations for Sediment Core Collection (green circles).

WRIAs

- Bead Lake: 62
- Lake Goodwin: 7
- Mason Lake: 14

HUC numbers

- Bead Lake: 17010216
- Lake Goodwin: 17110019
- Mason Lake: 17110019

5.1 Key individuals and their responsibilities

Staff changes have been made since the original QAPP (section "Organization" on page 11). Table 4 outlines staff involved with this project.

Table 4. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies W2R Program Phone: 360-407-7398	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Callie Mathieu Toxics Studies Unit SC Section Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the QAPP. Oversees field sampling and laboratory contracts. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Christopher Clinton Toxics Studies Unit SC Section Phone: 360-407-6060	Field Lead	Collects samples, records field information, oversees transportation of samples to the laboratory. Enters data into EIM.
Dale Norton Toxics Studies Unit SC Section Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SC Section Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan

5.6 Budget and funding

Table 5 presents the laboratory budget for 2014 sampling. This reflects a change from the original QAPP outlined in the "Budget" section on page 12.

Table 5. 2014 Laboratory Budget.

Parameter	Field Samples (# of samples)	QA Samples* (# of samples)	Total Number of Samples	Cost per Sample	MEL Subtotal	Contract Lab Subtotal	MEL Contract Fee
Lead	45	6	51	$50	$2,550	---	---
Mercury	45	6	51	$52	$2,652	---	---
TOC	45	3	48	$46	$2,208	---	---
^{210}Pb	45	3	48	$190	---	$9,120	$2,280
Grain Size	3	2	5	$100	---	$500	$125
Chlorinated Paraffins	27	0	27	$670	---	$18,090	$4,523
				MEL subtotal	**$7,410**	**---**	**---**
				Contracting Subtotal	**---**	**$34,638**	
				Lab Grand Total	**$42,048**		

*only includes QA samples that are not free of charge with the analysis.

6.2 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) for the analysis of chlorinated paraffins are described in Table 6.

Table 6. Measurement Quality Objectives.

Analyte	LCS (% recov.)	Lab Duplicates (RPD)	Method Blanks	Surrogate Standards (% recov.)	Lowest Concentration of Interest
Chlorinated Paraffins	70 - 130%	<40%	< LOQ	40 - 150%	2 ng/g

8.2 Containers, preservation methods, holding times

Table 7 provides information on sample containers, preservation techniques, and holding times for chlorinated paraffins. This is an addition to the information provided in the original QAPP, Table 3, page 17, under section "Sampling Procedures".

Table 7. Sample Containers, Preservation, and Holding Times.

Parameter	Matrix	Container	Sediment Needed	Preservation	Sample Holding Time[1]	Holding Time from Extraction
Chlorinated paraffins	sediment	glass	10-15 g wet	cool to < 4° C	1 year	not defined

[1]Recommended holding time.

8.3 Invasive Species

All study locations are in areas of moderate concern for invasive species. Boat and sampling gear will be inspected and cleaned, following Ecology's SOP EAP070, *Procedures to Minimize the Spread of Invasive Species Version 2.0* (Parsons et al., 2012).

8.4 Equipment Decontamination

Field staff will follow Ecology's SOP EAP090, *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Friese, 2014), to clean the sampling equipment prior to field collection. Acrylic liners and subsectioning equipment will be scrubbed with Liquinox and hot tap water, followed by sequential rinses with 10% nitric acid, deionized water, acetone, and hexane.

9.2 Lab procedures table

The lab procedures for chlorinated paraffins are outlined in Table 8. The solicitation for laboratories to bid on this work included a stipulation for the lab to describe their analysis method. The laboratory must already have an established method, which will be reviewed by MEL's QA officer and the project manager.

Table 8. Lab Procedures.

Analyte	Matrix	Number of Samples	Expected Range of Results	Reporting Limit	Method Description	Analytical Method
Chlorinated paraffins	sediment	27 (to be sent on 8/26/14)	< 2 - 200 ng/g	2 ng/g*	Lab-specific	Lab-specific

*This reporting limit is anticipated; actual reporting limits will be specified by labs bidding on the contract.

9.3 Sample preparation method(s)

The preparation and extraction methods for chlorinated paraffins will depend on the lab awarded the contract for this project. Extraction steps may include: (1) mixing the wet sediment material with sodium sulphate and allowing to dry, (2) adding a surrogate standard, (3) grinding the material to a powder, and (4) extraction with a solvent mixture.

9.4 Special method requirements

The analysis of chlorinated paraffins is not a routine method. Chlorinated paraffins are a contaminant of emerging concern and little research has been conducted on this suite of chemicals. Consequently, very few labs offer this service. MEL has posted a solicitation for bids on this analysis, which specifies that the lab must describe their in-house method for analysis. This method will be reviewed by the MEL QA officer and the project manager to ensure that it meets the requirements of the study. The contract laboratory will need to have an established method prior to awarding the contract.

9.5 Lab(s) accredited for method(s)

No laboratories are currently accredited to analyze chlorinated paraffins in sediment. A waiver will be obtained from Ecology's Quality Assurance Officer.

10.1 Table of field and lab QC required

Table 9 presents laboratory QC sample types and the frequency at which they will be tested during the chlorinated paraffins analysis. This is an addition to QC procedures presented in the original QAPP on page 20, in the "Quality Control Procedures" section. No change was made to the field QC procedures from the original QAPP.

Table 9. QC Samples, Types, and Frequency.

Parameter	LCS	Method Blank	Analytical Duplicate	Surrogates	Matrix Spikes
Chlorinated Paraffins	1/batch	1/batch	1/batch	every sample	none

Batch = 20 samples or fewer

10.2 Corrective action processes

In the event that QC tests are below MQOs during the analysis, the laboratory will contact the project manager to discuss possible corrective action.

11.2 Laboratory data package requirements

The laboratory will be required to deliver an EPA Tier IV data package with the analytical results. This will include all field sample data, as well as relevant QC data.

11.3 Electronic transfer requirements

The laboratory will send an electronic data deliverable in the form of an Excel spreadsheet with the analytical results.

12.1 Number, frequency, type, and schedule of audits

No field or laboratory audits will be made for this study.

13.2 Lab data verification

MEL's QA officer will review the Tier 4 data package from the contract laboratory to verify that the analytical method was followed correctly and data were reported without omissions or errors. MEL will provide a case narrative to the project manager, documenting holding times, instrument calibrations, QC test results, and any other information regarding the quality of the data analysis.

14.1 Process for determining whether project objectives have been met

The project manager will follow the original QAPP for data usability assessment (page 22, "Data Quality (Usability) Assessment" section).

15.0 References

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