DEPARTMENT OF
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Addendum 2 to Quality Assurance Project Plan

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

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Publication Information

Addendum

This addendum is on the Department of Ecology's website, below the original Quality Assurance Project Plan, at https://fortress.wa.gov/ecy/publications/SummaryPages/1203119.html

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

Original Publication

Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores.

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SUBJECT: Addendum 2 to Quality Assurance Project Plan for Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores
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In 2000, the Washington State Department of Ecology (Ecology) created a strategy to reduce persistent, bioaccumulative, and toxic (PBT) chemicals in the state (Gallagher et al., 2000). Through this initiative, chemical action plans (CAPs) have been developed to evaluate uses and releases of mercury (Peele et al., 2003), polybrominated diphenyl ethers (Peele et al., 2006), lead (Davies et al., 2009), and PAHs (Davies, 2012). Ecology plans to develop CAPs for perfluorinated compounds (PFCs) and other PBTs in the future.

The Environmental Assessment Program (EAP) receives funding for PBT monitoring to support development of control strategies. In particular EAP has collected age-dated sediment cores from freshwater lakes since 2006. Data from the sediment cores are used to help track the occurrence and temporal trends of PBTs in Washington State. The first two years examined trends in mercury concentrations only (Coots, 2006). Lead and PAHs were added in 2008 (Meredith and Furl, 2008). This addendum outlines changes to the planned analytes list in 2012.

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Experimental Design

Ecology's PBT Monitoring Program collects a single deep sediment core from three lakes per year to construct historical deposition profiles for several PBTs. New study locations are selected every year based on criteria outlined in the Quality Assurance (QA) Project Plan (Coots, 2006). Consideration for site selections include achievement of statewide coverage, knowledge of lake depositional patterns, lake accessibility, and results from other studies such as Ecology's Mercury Trends in Fish Tissue study (Seiders, 2006). In 2012, the selection criteria will be modified to include proximity to potential PFC contamination and to cover a range of possible PFC sources. Sites selected for 2012 are described in the next section.

Sediment core samples have been analyzed for mercury and lead since 2006, with the addition of polycyclic aromatic hydrocarbons (PAHs) in 2008. This addendum outlines the following changes to analytes of interest in 2012:

- Discontinue PAH analysis
- Add PFCs to the analyte list
- Change ^{210}Pb analytical method from gamma to alpha spectroscopy

To provide depositional data on a wider range of PBTs we anticipate rotating PBT chemicals into the analyte list in the future. Separate QA Project Plan addendums will be developed each year to document changes in analytes.

The addition of PFCs to the sediment core analyte list in 2012 is intended to provide information on temporal trends to support development of a CAP, which is scheduled to begin development in 2012. PAH analysis is being discontinued to allow room in the budget for other PBTs lacking in information and that are scheduled for CAPs. PAHs were analyzed from 2008 – 2011 in sediment cores and have been well-characterized.

The change in analytical method for ^{210}Pb analysis will provide a higher sensitivity for better age-dating of sediment cores. The alpha spectroscopy method requires 20 grams less dry sediment material than the gamma method, ensuring better ^{210}Pb data in lakes with low percent solids.

Study Locations

Sites selected for 2012 analysis are described in Table 1 and displayed in Figure 1. Deer Lake was chosen to characterize PFC inputs from atmospheric deposition and because of its inclusion in the Mercury Trends in Fish Tissue study. Lake Stevens lies in an area characterized by rapid development since the 1970s and was selected for its potential urban and suburban sources of PFCs. West Medical Lake surface water samples contained the highest concentrations of total PFCs out of 14 waterbodies surveyed in 2008, likely caused by wastewater treatment plant effluent discharges (Furl and Meredith, 2010). The lake was chosen for the 2012 sediment core study to gain information on temporal trends of PFCs there.

Table 1. 2012 Study Lakes.

Waterbody	County	Maximum Depth	Mean Depth	Lake Area	Watershed Area
Deer Lake	Stevens	75'	52	1,100 ac	11,650
Lake Stevens	Snohomish	155'	63'	1,040 ac	4,370
West Medical Lake	Spokane	35'	22'	220 ac	1,180

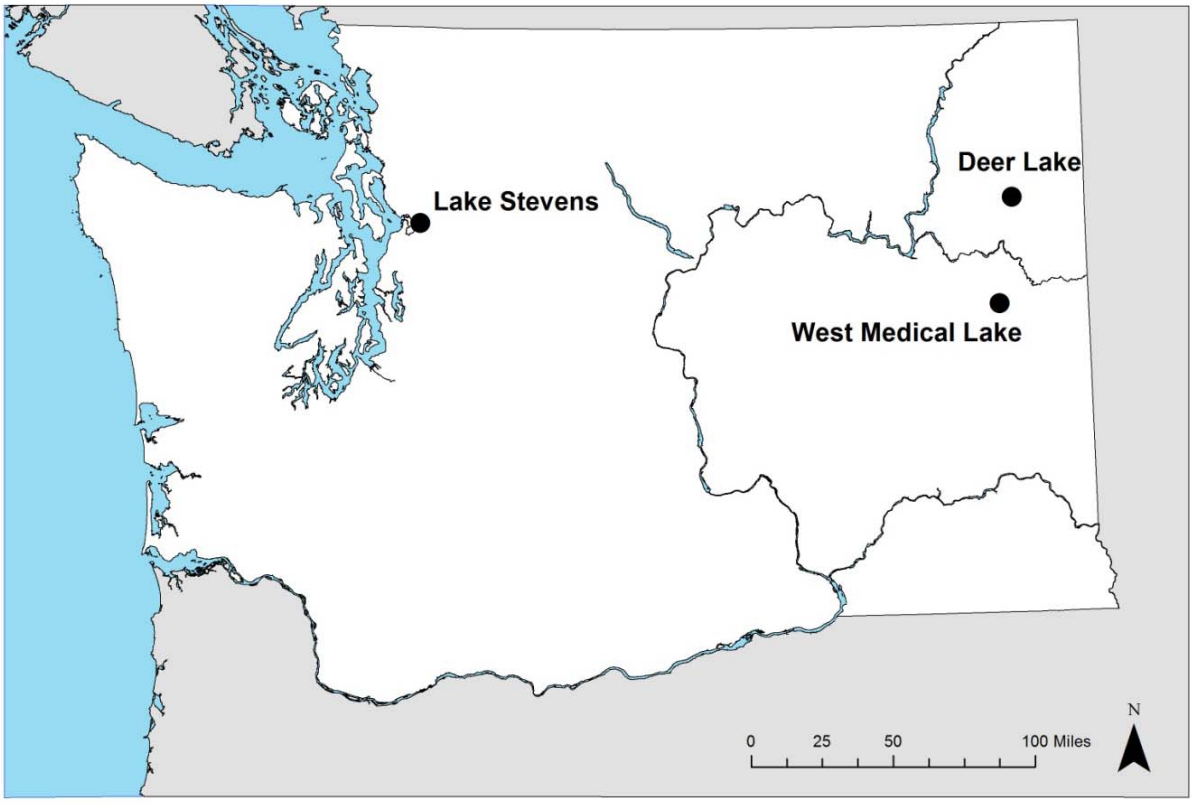

Figure 1. 2012 Study Locations.

Organization and Schedule

Table 2 displays the current staff and roles associated with this project. No changes will be made to the project schedule. A final report detailing sampling results is published annually in August.

Table 2. Organization of Project Staff.

Name	Organization	Phone Number	Role
Callie Mathieu	EAP-WES-TSU	360-407-6965	Project Lead
Andy Bookter		360-407-6060	Project Assistance
Michael Friese		360-407-6737	Project Assistance
Dale Norton		360-407-6765	Unit Supervisor
Holly Davies	W2R	360-407-7398	Client
Carol Kraege		360-407-6906	Client
Joel Bird	MEL EAP	360-871-8801	Lab Director
William Kammin		360-407-6964	Ecology QA Officer

Budget

Table 3 describes estimated laboratory costs for the 2012 sampling year.

Table 3. Project Budget.

Analyte	Field Samples	QA Samples[1]	Cost per sample	Total Cost
Lead[2]	45	3	$ 49	$ 2,352
Mercury[2]	45	3	$ 52	$ 2,506
TOC[2]	30	3	$ 46	$ 1,502
$^{Pb}210$[3]	45	3	$ 260	$ 12,480
Grain size[3]	3	3	$ 100	$ 600
PFCs[3]	24	---	$ 562	$ 13,488
				$ 32,928

[1]Number includes only QA samples that are charged separately.

[2]Price includes MEL 50% discount.

[3]Price includes MEL 25% surcharge for contracting services.

Analytical Laboratory

A contract laboratory selected by Ecology's Manchester Environmental Laboratory (MEL) will analyze up to 24 sediment core samples (8 per core) for the PFCs listed in Table 4. Another contract laboratory will analyze 45 sediment core samples (15 per core) for ^{210}Pb using alpha spectrometry.

Table 4. Perfluorinated Compound List.

Name	Acronym
Perfluorobutane sulfonate	PFBS
Perfluorohexane sulfonate	PFHxS
Perfluorooctane sulfonate	PFOS
Perfluorooctane sulfonamide	PFOSA
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoDA

Sampling and Measurement Procedures

Sampling Procedures

Sediment cores will be collected using the same protocol described in the QA Project Plan (Coots, 2006). Changes made to the sampling plan are described below.

EAP discontinued surface sediment sampling for analysis of mercury, selenium, and TOC in 2008. Surface sediments were originally collected as composite grab samples to help the Mercury Trends in Fish Tissue program make future site selections. As of 2008, all fish collection sites had been selected and are now being re-sampled every year on a rotating basis. Therefore, the extra analyses are no longer needed. Surface sediments are still analyzed for grain size.

All utensils and equipment for sediment sampling will be cleaned with the following procedure: hand washed with Liquinox soap and hot water, hot tap water rinse, nitric acid rinse (to remove metals), and 100% methanol rinse (to remove organic compounds). Utensils and equipment will be dried between chemical rinses.

While sectioning the core in the field, each layer will be homogenized in a stainless steel bowl and a subsection of the sediment will be placed directly into pre-cleaned (methanol-rinsed) high-density polyethylene (HDPE) jars for PFC analysis. All other sediment will be placed into an 8 oz. glass jar for further processing in the laboratory as described in the QA Project Plan (Coots, 2006). This step was added to avoid contamination of the PFC samples from the glass jar lids that are lined with Teflon.

Eight sediment layers will be selected per core for analysis of PFCs, using a weighted sediment layer selection process described in Meredith and Furl (2008). A higher density of intervals will be tested near the top, while the selected layers are spaced farther apart moving down the core. Fifteen sediment layers per core will be analyzed for ^{210}Pb data to assign sedimentation rates and ages to the sediment intervals.

Containers, holding times, and preservation methods for new analytes are displayed in Table 5.

Table 5. Sample Containers, Preservation, and Holding Times.

Analyte	Container	Preservation	Holding Time
PFCs	8 oz HDPE	cool to ≤ 4° C	30 days from extraction[1]
^{210}Pb	4 oz Glass	cool to ≤ 4° C	n/a

[1]Holding times from time of sample collection have not been established for this method.
HDPE: high-density polyethylene

Laboratory Procedures

The laboratory procedures for analysis of PFCs and ^{210}Pb are listed in Table 6.

Table 6. Measurement Procedures and Reporting Limits.

Analyte	Method Description	Analytical Method	Reporting Limit
PFCs	LC-MS/MS	AXYS Method MLA-040	0.2 ng/g
^{210}Pb	Alpha Spectroscopy	Lab-specified	0.45 pCi/g

Quality Control Procedures

Field

As outlined in the QA Project Plan (Coots, 2006), no field quality control samples will be collected for this study.

Laboratory

The contract laboratories will perform the laboratory quality control tests described in Table 7. MEL will conduct a data quality assessment of contract laboratory data and provide the project manager with case narratives describing holding times, instrument calibrations, and results of quality control tests.

Table 7. Laboratory Quality Control Procedures.

Analyte	LCS	Lab Duplicates	Method Blanks	Surrogates
PFCs	1/batch	1/batch	1/batch	every sample
^{210}Pb	1/batch	1/batch	1/batch	n/a

batch: 20 samples

Quality Objectives

Measurement quality objectives (MQOs) for PFC and ^{210}Pb analyses are outlined in Table 8. The contract laboratories will be expected to meet the MQOs.

Table 8. Measurement Quality Objectives.

Analyte	LCS (% recov.)	Lab Duplicates (RPD)	Method Blanks	Surrogates (% recov.)
PFCs	70 - 130%	<40%	< RL	40 - 150%[1]
^{210}Pb	80 - 120%	<30%	< RL	---

[1]13C4-PFBA range: 20 - 150%
RL: reporting limit

Data Management

All data management procedures will follow those stated in the original QA Project Plan (Coots, 2006).

Audits and Reports

Oversight of the project will occur through established practices within Ecology. Ecology will select contract laboratories that participate in audits that include review of laboratory facilities, capabilities, and analytical performance. Ecology does not anticipate conducting separate audits of the contract laboratories for this project.

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

Data Verification

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

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