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Addendum 3 to
Quality Assurance Project Plan

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

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EAP: Environmental Assessment Program
EIM: Environmental Information Management database

Overview

Ecology's Persistent, Bioaccumulative, and Toxics (PBT) Monitoring Program began a long-term study to assess PBT chemical trends through age-dated freshwater sediment cores in 2006. A single deep sediment core is collected from three lakes per year to construct historical deposition profiles of PBTs in the environment. This addendum describes changes in sampling locations and target analytes in 2013.

Sampling Locations

New study locations are selected every year based on criteria outlined in the Quality Assurance Project Plan (QAPP) (Coots, 2006). Consideration for site selections includes achievement of statewide coverage and a range of potential sources, knowledge of in-lake depositional patterns, lake accessibility, and results from existing datasets. In 2013 sediment cores will be collected from Lake Cavanaugh, Kitsap Lake, and Lake Sawyer. Study locations and information behind the selection of these lakes are described in the next section.

Target Analytes

Lead and Mercury have been analyzed in sediment core samples since 2006. In addition to lead and mercury, the following PBTs have been analyzed:

- Polycyclic aromatic hydrocarbons from 2008 - 2011
- Perfluorinated compounds (PFCs) in 2012

A QAPP addendum written in 2012 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. In 2013, hexabromocyclododecane (HBCD) will be added to the analyte list and PFCs will be removed. Lead and mercury will remain on the target analyte list.

HBCD is a brominated flame retardant listed as a PBT of concern in the Washington State PBT Rule (WAC 173-333). It was selected as a target analyte in order to gather environmental data on the occurrence and temporal trends of flame retardants in Washington State. Other flame retardants listed in the PBT Rule were considered, but not chosen for analysis in 2013 for the following reasons: lack of laboratory capabilities (hexabromobiphenyl), evidence against the chemical's stability in sediments (tetrabromobisphenol A), budget constraints (short-chain chlorinated paraffins), and sufficient datasets already in existence (polychlorinated diphenyl ethers). Johnson and Friese (2012) reported measurable levels of HBCD in fish tissue from Washington State lakes and recommended including the contaminant in future monitoring studies.

HBCD is a high production volume chemical used primarily in extruded and expanded polystyrene (EPS and XPS) foam as thermal insulation in building construction. It is also used as a flame retardant for textiles in furniture upholstery and other products, such as latex binders, adhesives, and paints (Environment Canada, 2011). HBCD is an additive flame retardant and is not bound to material. Therefore, it has the potential to enter the environment through the use or disposal of products containing HBCD and thus may be present in wastewater treatment plant effluent and landfill and incinerator emissions (EPA, 2010). At construction sites, HBCD has the potential to be released to the soil, with subsequent transfer to air or runoff (Environment Canada, 2011). HBCD is ubiquitous in the environment and has been reported in air, sediment, water, and aquatic biota samples (Covaci et al., 2006).

Location Descriptions

Lakes selected for 2013 analysis are described in Table 1 and displayed in Figure 1. Lake Cavanaugh is located in a remote, rural setting, with moderate-density residences along the shoreline. Cavanaugh is included in the 2013 study for its minimal watershed development, which will reflect baseline levels primarily from atmospheric deposition.

Kitsap Lake lies within a suburban watershed which contains a portion of Naval Base Kitsap and represents a mixed-use watershed. Lake Sawyer was selected for its source potential coming from recent residential development in the watershed. Lake Sawyer has also historically received wastewater treatment plant effluent through discharges to a nearby wetland.

Table 1. 2013 Sediment Core Study Lakes.

Waterbody	County	Max Depth (feet)	Mean Depth (feet)	Lake Area (acres)	Watershed Area (acres)
Lake Cavanaugh	Skagit	80	44	800	4,710
Lake Sawyer	King	58	26	300	8,320
Kitsap Lake	Kitsap	29	18	250	1,750

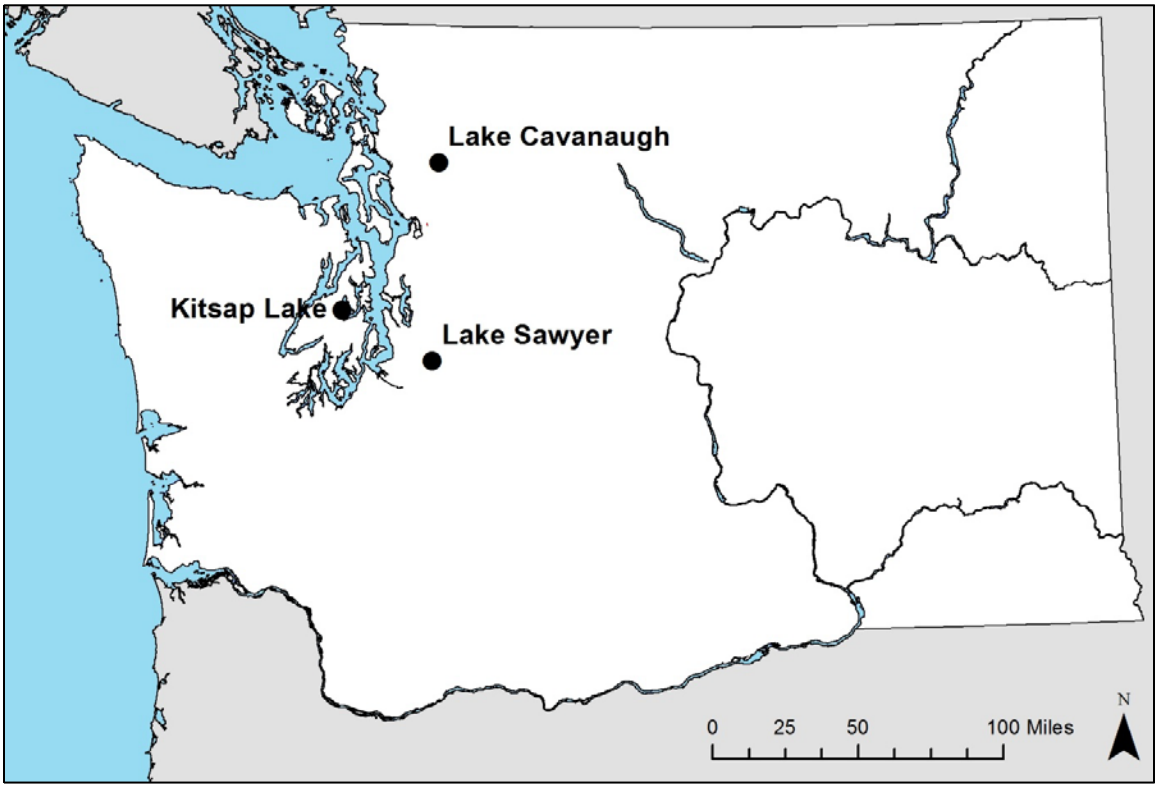

Figure 1. 2013 Sediment Core Study Locations.

Budget

Table 2 outlines the estimated laboratory costs for the 2013 sampling year. The budget includes a 50% discount on all analyses performed by Ecology's Manchester Environmental Laboratory (MEL). For analyses that will be conducted by external laboratories, MEL will manage the contract and perform data quality reviews at a 25% surcharge. The budget reflects this surcharge.

Table 2. Laboratory Budget.

Analyte	Field Samples	QA Samples^	Cost per Sample	Total Cost
Lead*	45	6	$ 50	$ 2,550
Mercury*	45	6	$ 52	$ 2,652
TOC*	30	3	$ 46	$ 1,518
^{210}Pb†	45	3	$ 190	$ 9,120
Grain Size†	3	2	$ 100	$ 500
HBCD†	27	2	$ 640	$ 18,560
				$ 34,900

^ Number includes only QA samples that are charged separately.
* Price includes MEL 50% discount.
† Price includes MEL 25% surcharge for contracting services.

Sampling and Measurement Procedures

Sampling Procedures

Sampling will be conducted using the same protocol described in the original QAPP. Changes made to the sampling plan are described below.

Nine sediment layers will be selected per core for analysis of HBCD, using the 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 will be spaced farther apart moving down the core. Sediments dated prior to 1960 are not expected to contain HBCD, as production did not begin until this time. Therefore, more samples will be analyzed in the most recent sediments. However, a few older sediment samples will be analyzed to support the data quality assessment.

All utensils and equipment for sediment sampling will be cleaned with the following procedure: (1) hand washed with Liquinox soap and hot water, (2) hot tap water rinsed, (3) 10% nitric acid rinsed (to remove metals), (4) deionized water rinsed, and (5) pesticide-grade acetone rinsed (to remove organics).

Containers, holding times, and preservation methods for HBCD are presented in Table 3. One hundred to one hundred fifty grams of wet sediments will be subsectioned for HBCD analysis.

Table 3. Container, Preservation, and Holding Time for HBCD Analysis.

Analyte	Container	Preservation	Holding Time
HBCD	Amber glass	cool to ≤ 4° C	28 days from extraction[1]

[1] Holding times from time of sample collection have not been established for this method.

Laboratory Procedures

An external laboratory will conduct the HBCD analysis. The analysis will be performed under a contract managed by MEL. The contract laboratory will analyze HBCD using liquid chromatography – tandem mass spectrometry (LC-MS/MS). The extraction and analysis method is laboratory-specific and will be described in the 2013 sampling results report.

HBCD refers to a commercial mixture of three main diastereomers: alpha (α-HBCD), beta (β-HBCD), and gamma (γ-HBCD), with traces of other isomers. The contract laboratory will report all three diastereomers separately and use labeled surrogates for each measured isomer. The final report summarizing sediment core results will include data analyses using the separated diastereomers and a summed HBCD value. Summed HBCD values will include only detected diastereomers (i.e., non-detects will be treated as "0").

Table 4 describes the number of samples, expected range of results, and the laboratory methods. Washington State does not currently provide accreditation for HBCD analysis in sediments. Therefore, a waiver will be obtained for this analysis. The contract laboratory will be required to demonstrate that they have successfully performed this analysis in the past and provide client references for the requested analysis.

Table 4. Laboratory Measurement Methods for HBCD Analysis.

Analyte	Number of Samples	Expected Range of Results	Reporting Limit	Method Description	Analytical Method
HBCD	27	< 0.25 - 20 ng/g	0.25 ng/g	LC-MS/MS	Lab-specific

Quality Control Procedures

Laboratory

The contract laboratory will perform the quality control (QC) tests described in Table 5. MEL will review the data package from the contract laboratory and provide case narratives to the project manager documenting holding times, instrument calibrations, results of QC tests, and any other information regarding the quality of the data analysis.

Table 5. Laboratory Quality Control Procedures.

Analyte	LCS	Lab Duplicate	Method Blank	Surrogates
HBCD	1/batch	1/batch	1/batch	every sample

LCS: laboratory control sample
Batch: 20 or fewer samples

Measurement Quality Objectives

Anticipated Measurement Quality Objectives (MQOs) for the HBCD analysis are outlined in Table 6. The contract laboratory will be expected to meet MQOs. In the event that QC tests are below MQOs during the analysis, the laboratory will contact the project manager to discuss possible corrective action.

Table 6. Measurement Quality Objectives.

Analyte	LCS (% recov.)	Lab Duplicates (RPD)	Method Blanks	Surrogate (% recov.)
HBCD	70 - 130%	<40%	< LOQ	40 - 150%

LCS: laboratory control sample RPD: relative percent difference

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