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Addendum 1 to Quality Assurance Project Plan

Long-Term Monitoring of Persistent, Bioaccumulative, and Toxic Chemicals using Age-Dated Lake Sediment Cores

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Addendum

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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 SEDCORE17.

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Addendum to Quality Assurance Project Plan

Long-Term Monitoring of Persistent, Bioaccumulative, and Toxic Chemicals using Age-Dated Lake Sediment Cores

September 2017

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program.
QAPP: Quality Assurance Project Plan

3.0 Background

The Department of Ecology's (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. Sediment core samples are analyzed for a rotating PBT contaminant selected annually to fill data gaps in Washington State. New study locations are selected every year as well. Ecology selects lakes in an attempt to cover a range of potential contaminant sources.

As outlined in the updated Quality Assurance Project Plan (QAPP) for this study (Mathieu, 2016), annual addenda are written to document the target PBT analyte and study locations of that sampling year. This addendum describes the 2017 sampling locations and the following changes in target analytes:

- Polycyclic aromatic hydrocarbons (PAHs) will be the focus of the target analyte list in 2017.
- Polychlorinated biphenyls (PCBs) will be taken off the target analyte list in 2017.

PAHs were selected for analysis in 2017 to assess recent changes in deposition following actions taken in the last ten years to reduce PAHs in Washington State. In 2012, Ecology and the state Department of Health (DOH) published a Chemical Action Plan (CAP) for PAHs and identified several actions that were either currently being carried out or could be implemented (Ecology and Health, 2012). Priority recommendations to limit PAH exposure to the environment included reducing residential wood-smoke emissions, outreach programs to reduce exposure from vehicles (e.g., eliminating drips and leaks and anti-idling campaigns), and investigate and/or remove creosote-containing products such as pilings and roofing materials.

Studies by the United States Geological Survey (USGS) in the 2000s identified coal tar sealcoats as a major source of PAHs to lake sediments (Mahler et al., 2005). PAH concentrations found in Washington State waterbodies are more in alignment with asphalt-based sealcoats, which are much lower in PAHs. However, modeling of lake sediment PAH concentrations by Van Metre and Mahler (2010) showed a coal tar sealcoat signature in one small, urban Washington Lake – Lake Ballinger. Estimates from the Washington State Department of Transportation (WDOT) suggested that coal tar based sealcoats have been used in Washington, but public and private use moved towards a blended product (20% coal tar pitch and 80% asphalt emulsion) in the 2000s. In 2011, Washington State passed a coal tar sealant ban (RCW 70.295), which prohibited all use or application of the products by 2013.

Figure 1 displays target analytes for each year of this program from 2006 through the planned analytes in 2017.

Sections not included in this addendum remain unchanged from the original QAPP (Mathieu, 2016).

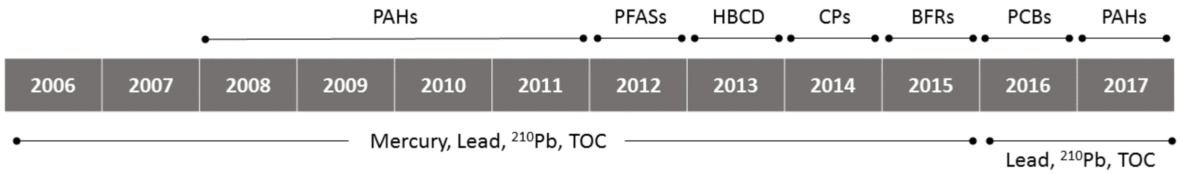


Figure 1. Target Analytes in Sediment Cores from 2006 to 2017.

PAHs: polycyclic aromatic hydrocarbons; PFASs: per- and poly-fluoroalkyl substances; HBCD: hexabromocyclododecane; CPs: chlorinated paraffins; BFRs: brominated flame retardants; PCBs: polychlorinated biphenyls.

3.1 Study area and surroundings

Three waterbodies are selected each year for sediment core collection. Selection of target waterbodies is based primarily on proximity to known and potential sources. Each year, approximately two lakes are chosen close to or within known/potential sources of the target organic PBT. The third lake is located far from sources or in an area where atmospheric deposition is the predominant source. Other considerations for waterbody selection include:

- Spatial distribution to achieve statewide coverage.
- Suitable access to the waterbody for the coring boat.
- Waterbodies where data from other studies are available.
- Watersheds within a range of land-use types.
- Physical features of the lake and watershed, including lake depositional patterns, maximum and mean depths, and elevation.
- Collaboration with other programs and agencies.

Figure 2 displays the waterbodies where sediment cores were collected between 2006 and 2016, as well as 2017 coring locations. In 2017, sediment cores will be collected from Bosworth Lake (Snohomish County), Martha Lake “Alderwood Manor” (Snohomish County), and Lake Wilderness (King County).

Martha Lake and Lake Wilderness were selected to capture PAH concentrations in a lake with new urban and/or residential development in the watershed. During study location selection, dates of recently constructed residential and commercial properties were assessed for several urban lake watersheds. Martha and Wilderness Lakes had comparatively new development, with 14 and 78 newly constructed parcels, respectively, since Washington’s coal tar sealant ban in 2011.

Bosworth Lake is located in a forested area with little development. This lake was selected as a reference site, as it is similar in size to Martha and Wilderness Lakes, as well as having comparable elevation and watershed area to lake surface area ratios.

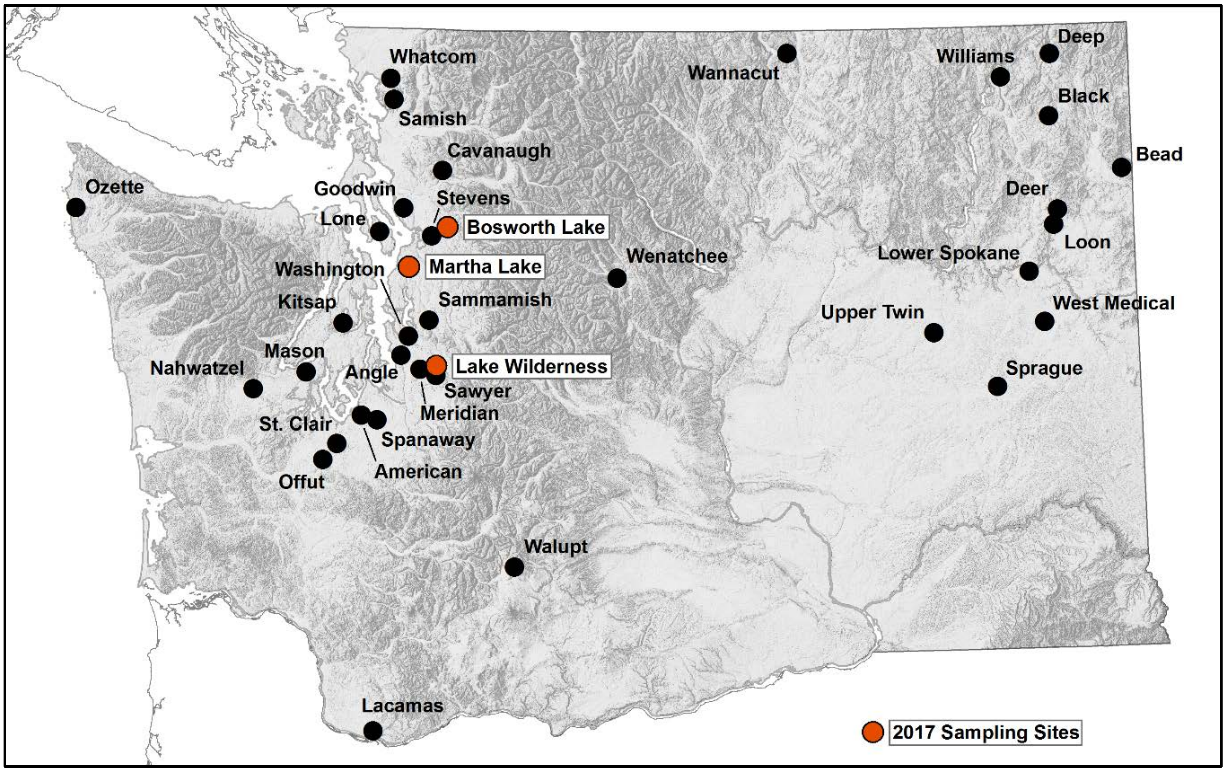


Figure 2. Sediment Core Sample Locations from 2006 to 2016 (black circles), along with 2017 Sampling Sites (red circles).

Table 1. 2017 Sediment Core Study Lakes.

Waterbody	County	Elevation (ft)	Max Depth (ft)	Mean Depth (ft)	Lake Area (ac)	Watershed Area (ac)	WA:LA
Martha Lake	Snohomish	455'	48'	24'	57	512	9
Bosworth Lake	Snohomish	563'	79'	35'	110	902	8
Lake Wilderness	King	470'	38'	21'	69	422	6

WA:LA = watershed area to lake area ratio

3.1.1 Logistical problems

Suitable access has been a limiting factor for waterbody selection in the past. Previous sediment core collections have been aboard a 26' research vessel that requires highly developed boat launch access. While Ecology has researched modifications to a smaller boat to gain access to a broader range of waterbodies, it has been determined not to be a feasible option. Crew safety and equipment weight prohibit modification to the boats in Ecology's current fleet. Sampling will continue to be conducted from the current research vessel.

3.1.2 History of study area

The 2017 sampling locations were chosen based on previously determined criteria in the original QAPP and described in Section 3.1. The lakes have not been cored previously as part of this project. There are no known PAH data available for the 2017 study locations and therefore no known history of PAH contamination in the lakes. Sources of PAHs to the lakes are likely to be from wood smoke, vehicle emissions, and PAH-containing products, such as asphalt shingles and roofing.

3.1.3 Parameters of interest

In 2017, PAHs will be the target PBT analytes (Table 2). PAHs are highly persistent in the environment, bioaccumulative, and have toxicity concerns for human health including cancer, heart defects, reduced growth, immune-suppression, and effects on reproduction (Davies et al., 2012). Ecology and DOH published a CAP for PAHs in 2012, which describes major sources and pathways of PAHs, exposure to PAHs, toxic effects, and recommendations for actions to protect human health and the environment (Davies et al., 2012).

Table 2. PAH Compounds to be Analyzed in 2017.

Analyte	PBT List	CWA PP
1,6,7-trimethylnaphthalene		
1'1 biphenyl		
1-Methylnaphthalene		
1-Methylphenanthrene		
2,6-dimethylnaphthalene		
2-Chloronaphthalene		
2-Methylfluoranthene		
2-Methylnaphthalene		
2-Methylphenanthrene		
4-Methyldibenzothiophene		
5-Methylchrysene		
9H-Fluorene, 1-methyl-		
Acenaphthene		x
Acenaphthylene		x
Anthracene		x
Benzo(a)anthracene		x
Benzo(a)pyrene		x
Benzo(b)fluoranthene	x	x

Analyte	PBT List	CWA PP
Benzo(ghi)perylene	x	x
Benzo(k)fluoranthene	x	x
Benzo[e]pyrene		
Carbazole		
Chrysene		x
Dibenzo(a,h)anthracene	x	x
Dibenzofuran		
Dibenzothiophene		
Fluoranthene	x	x
Fluorene		x
Indeno(1,2,3-cd)pyrene	x	x
Naphthalene		x
Perylene		
Phenanthrene		x
Phenanthrene, 3,6-dimethyl-		
Pyrene		x
Retene		

PBT List = Ecology's PBT List (http://www.ecy.wa.gov/programs/hwtr/RTT/pbt/list.html)
CWA PP = Clean Water Act Priority Pollutant List

Annual target PBT analytes continue to be total lead (Pb), ^{210}Pb, and total organic carbon (TOC) for age-dating and interpretation of the sediment core. Grain size will continue to be analyzed in surface sediment grab samples (0-2 cm).

Copper, titanium, and zinc that were sampled for at Deep Lake in 2016 will not be targeted in 2017. The additional metals were added at the request of Ecology's Eastern Regional Office (ERO) in 2016 and were of specific interest to that lake.

3.1.4 Results of previous studies

Ecology's PBT Monitoring Program publishes annual reports summarizing sediment core data on the website: http://www.ecy.wa.gov/programs/eap/toxics/cores.html. PAHs were a target analyte for this monitoring program between 2008 and 2011. Table 3 summarizes PAH results from these studies.

Table 3. PAHs Reported in Previous Sediment Core Studies in Washington State by the PBT Monitoring Program.

Lake	Year sampled	Date of surface layer (year)	T-PAH surface conc. (ng/g dw)	Peak T-PAH conc. (year)	Peak T-PAH conc. (ng/g dw)	T-PAHs min. conc. (ng/g dw)	Ref.
Lacamas	2008	2006	33J	<1850	577	33J	(1)
Offut	2008	2006	82	2004	219J	60NJ	(1)
Washington	2008	2007	638J	1990	1117	167J	(1)
American	2009	2008	290U	1931	1825	161J	(2)
Black	2009	2005	210U	1974	236	41U	(2)
Upper Twin	2009	2008	150U	2008	150U	36U	(2)
Sprague	2010	Not dated	137	Not dated	174	127	(3)
Wenatchee	2010	2007	140	1963	347	50	(3)
Lone	2010	Not dated	1,973	Not dated	2,317	1151	(3)
Samish	2011	2010	1,203	1923	2,536	200J	(4)
Nahwatzel	2011	Not dated	5,494	Not dated	7,214	304J	(4)
Angle	2011	2008	7,110	1999	7,606	946J	(4)

(1) Furl et al., 2009; (2) Furl and Roberts, 2010; (3) Furl and Roberts, 2011; (4) Mathieu and Friese, 2012.

In general, PAH trends in sediment cores collected in Washington State have varied at each sample site (Furl et al., 2009; Furl and Roberts, 2010; Furl and Roberts, 2011; Mathieu and Friese, 2012).

- PAH concentrations in Lake Washington sediments rose over the 20th century, peaked in 1990, and then declined through recent sediments.
- Lacamas Lake sediments displayed decreasing trends for PAH concentrations and increasing trends in sedimentation rates over most of the 20th century.
- Offut Lake PAH concentrations were generally low but had higher concentrations in more recent sediments.
- American Lake had a peak PAH concentration in the 1930s. After peaking, American Lake showed declines in PAH concentrations over the latter half of the 1900s through recent times to near background levels.

- PAHs were infrequently detected in Black Lake sediments, and concentrations showed no trend throughout the core.
- Upper Twin Lake had no PAH detections above the quantification limit.
- Lake Wenatchee sediment PAH concentrations peaked in 1960 and steadily decreased through modern sediments.
- Angle Lake had the highest PAH concentrations of all sediment cores analyzed for this monitoring program, with slight decreases in the modern layer.
- Samish Lake PAH concentrations peaked in the 1920s and decreased steadily to the time of sampling.
- Lake Nahwatzel displayed peak PAH concentrations near the top of the core, at levels similar to Angle Lake. Due to issues with ^{210}Pb data, the Nahwatzel core was not dated.

Van Metre and Mahler (2010) investigated coal tar sealant as a contributor to PAH levels in post-1990 lake sediments. The nationwide survey included sediment cores taken from Lake Washington and Lake Ballinger. The study showed a PAH signature at Lake Ballinger in Mountlake Terrace consistent with recent contribution from coal tar based sealant, though at concentrations much lower than in eastern U.S. waterbodies.

3.1.5 Regulatory criteria or standards

This study does not collect data to determine compliance with regulatory standards or criteria. However, freshwater sediment standards may exist for target analytes.

The sediment cleanup objective and sediment cleanup screening level for total PAHs[1], based on protection of the benthic community in freshwater sediment, are 17,000 and 30,000 ug/kg dw, respectively (WAC 173-204-563). The 17,000 ug/kg dw sediment cleanup objective corresponds to a sediment quality that results in no adverse effects to the benthic community.

4.0 Project Description

4.2 Project objectives

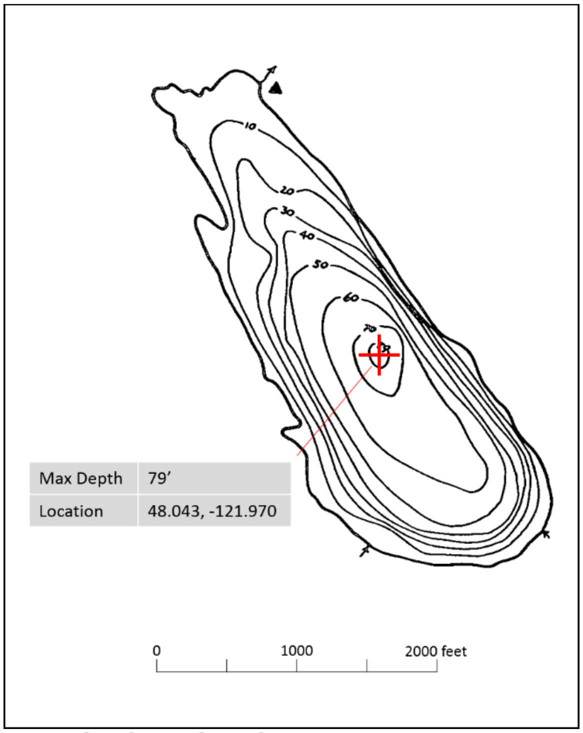
Specific objective changes for this project are to:

- In 2017, the target PBT analyte will be PAHs. PCBs, copper, titanium, and zinc will not be analyzed as was done in 2016.

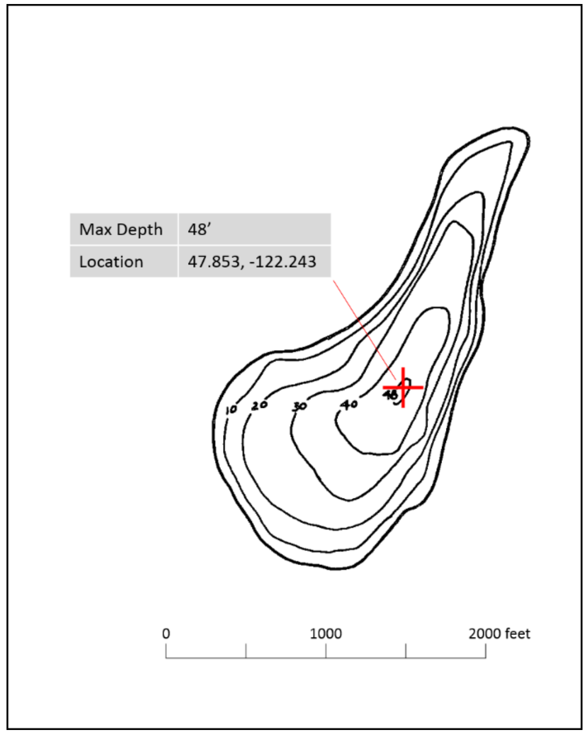
4.5 Study boundaries

At each study lake, a sediment core will be collected from a discrete sampling point in the deepest flat part of the lake. Figure 3 displays the target sampling locations for 2017.

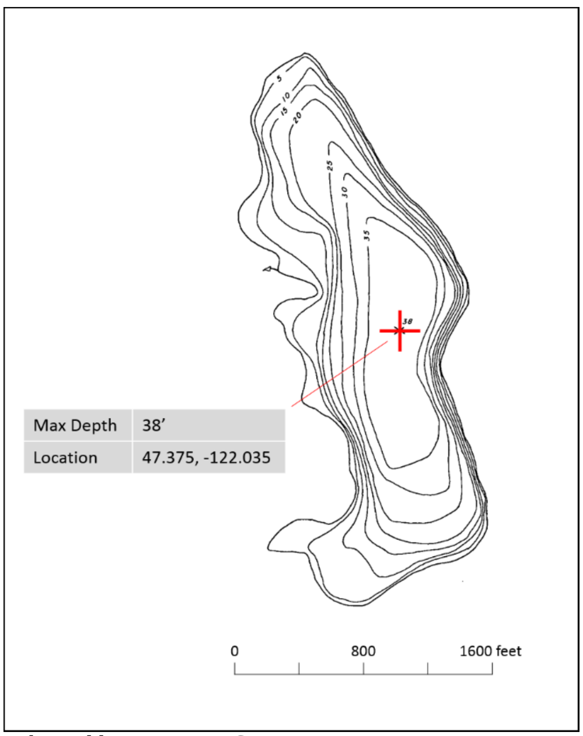
[1] Sum of the following PAHs: 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(ghi)perylene, chrysene, dibenz(ah)anthracene, fluoranthene, fluorene, indeno(123-cd)pyrene, naphthalene, phenanthrene, pyrene, and total benzofluoranthenes (b+k+j).



Bosworth Lake, Snohomish County



Martha Lake (Alderwood Manor), Snohomish County



Lake Wilderness, King County

Figure 3. Target Sampling Locations for 2017 Sediment Core Collection (red cross).

WRIAs
- Bosworth Lake: 7
- Martha Lake: 8
- Lake Wilderness: 9

HUC numbers
- Bosworth Lake: 17020011
- Martha Lake: 17110012
- Lake Wilderness: 17110013

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 4. Organization of project staff and responsibilities.

EAP Staff	Title	Responsibilities
Debby Sargeant Toxics Studies Unit SCS Phone: 360-407-6775	Client and Supervisor for the Project Manager	Clarifies scope of the project. Provides internal review of the QAPP addendum, and final report. Approves the final QAPP and addendums. Manages budget and staffing needs.
Jessica Archer SCS Phone: 360-407-6698	Client and SCS Manager	Clarifies scope of the project. Provides internal review of the QAPP addendum and final report. Approves the final QAPP addendum.
Callie Mathieu Toxics Studies Unit SCS Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the original QAPP and final report. Coordinates with MEL and contract laboratory. Oversees field collections. Conducts QA review of data, analyzes and interprets data.
Christopher Clinton Toxics Studies Unit SCS Phone: 360-407-6060	Field Lead	Writes the QAPP addendum, leads field collections, records field information, and sends samples to the laboratory. Enters data into EIM.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP addendum.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP addendum and the final QAPP addendum.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section

5.3 Organization chart

Tables 4 and 5 outline the organization for this study.

5.4 Project schedule

Table 5 provides the project schedule for 2017 sampling.

Table 5. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	09/2017	Christopher Clinton
Laboratory analyses completed	12/2017	
Environmental Information System (EIM) database		
EIM Study ID	SEDCORE17	
Product	Due date	Lead staff
EIM data loaded	06/2018	Christopher Clinton
EIM data entry review	07/2018	Melissa McCall
EIM complete	08/2018	Christopher Clinton
Final report		
Author lead / Support staff	Callie Mathieu	
Schedule		
Draft due to supervisor	05/2018	
Draft due to client/peer reviewer	06/2018	
Final (all reviews done) due to publications coordinator	07/2018	
Final report due on web	08/2018	

5.5 Limitations on schedule

No limitations to the schedule are expected for this project.

5.6 Budget and funding

Table 6 presents the laboratory budget for the 2017 sediment core samples.

Table 6. Project Budget and Funding.

Parameter	Field Samples (# of samples)	QA Samples* (# of samples)	Total Number of Samples	Cost per Sample	MEL Subtotal	Contract Lab Subtotal	MEL Contract Fee
T-PAHs	30	6	36	$396	$14,256	---	---
T-Pb	30	4	34	$50	$1,700	---	---
TOC	30	2	32	$46	$1,472	---	---
^{210}Pb	45	3	48	$120	---	$5,760	$1,440
Grain Size	3	2	5	$100	---	$500	$125
				MEL subtotal	**$17,428**	---	---
				Contracting Subtotal	---	**$7,825**	
				Lab Grand Total	**$25,253**		

* Includes only QA samples that are not free of charge with the analysis (laboratory duplicates, matrix spikes, and matrix spike duplicates).

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

This study does not require decision quality objectives.

6.2 Measurement Quality Objectives

MQOs are shown in Table 7. MQOs for total lead, TOC, ^{210}Pb, and grain size remain unchanged and can be found in the original QAPP for this study (Mathieu, 2016).

Table 7. Measurement Quality Objectives.

Analyte	LCS (recovery)	Lab Duplicates (RPD)	Matrix Spike (recovery)	Matrix Spike Duplicates (RPD)	Surrogate Standards (recovery)
PAHs	50 - 150%	<40%	50 - 150%	<40%	20-200%[1]

LCS = laboratory control sample; RPD = relative percent difference
[1] With the exception of: Dimethylphthalate-D6 = 50-150%

6.2.1 Targets for Precision, Bias, and Sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Laboratory analysis precision will be assessed through laboratory duplicate samples. Table 7 shows the MQOs for laboratory duplicate samples.

No field replicates will be collected for this project.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Laboratory analysis bias will be assessed through laboratory control samples, matrix spikes, and surrogate standards. MQOs for these tests are included in Table 7.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above background noise. Laboratory analysis sensitivity is defined for the study as the quantitation limit. See Table 9 for quantitation (reporting) limits.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

7.1.3 Parameters to be determined

In 2017, sediment core samples will be analyzed for PAHs, as well as parameters outlined in the original QAPP: total lead, TOC, ^{210}Pb, and grain size.

7.2 Maps or diagram

The study area and sampling locations are displayed in Figure 3.

8.0 Sampling Procedures

8.2 Containers, preservation methods, holding times

Sample containers, minimum sample sizes, preservation methods, and sample holding time requirements are shown in Table 8.

Table 8. Containers, Sample Size, Preservation Methods, and Holding Times.

Parameter	Minimum Quantity Required	Container	Field Preservation	Preservation after Processing	Holding Time
PAHs	20 g dw	8 oz. glass jar	cool to 4° C	freeze, -10° C	14 days cooled; 1 year frozen

dw = dry weight

9.0 Measurement Methods

9.2 Lab procedures table

Table 9. Lab Procedures.

Parameter	Samples		Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical Method
	Number of Samples	Arrival Date				
PAHs	30	9/20/2017	< 1.0 – 10,000 ng/g dw	4-20 ng/g dw	EPA 3541	EPA 8270D SIM

EPA = Environmental Protection Agency
SIM = selective ion monitoring
dw = dry weight

9.3 Sample preparation method

Sediment samples for PAH analyses will be prepared at Ecology's Manchester Environmental Laboratory (MEL) by air drying, then extracted by Soxtherm following sample prep by EPA Method 3541.

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

Table 10. QC Samples, Types, and Frequency.

Parameter	Laboratory					
	LCS	Method blanks	Matrix spikes	Matrix spike duplicates	Laboratory duplicates	Surrogates
PAHs	1/batch	1/batch	1/batch	1/batch	1/batch	Each sample

LCS = laboratory control sample

One batch equals 20 samples or fewer.

14.2 Data analysis and presentation methods

A summary of the data will be presented in the final report. Contaminant results will be presented as both concentrations and fluxes. Fluxes will be calculated as the contaminant concentration multiplied by the sedimentation rate for the sediment core interval.

In 2017, PAHs will be calculated and presented as total (T-) PAHs (sum of 16 priority pollutant PAHs), TOC-normalized T-PAHs, L-PAHs (sum of all low molecular weight PAHs, including compounds with two or three aromatic rings), and H-PAHs (sum of all high molecular weight PAHs, including compounds with four or more aromatic rings).

14.3 Treatment of non-detects

Detected PAHs will be reported down to the method detection limit, and non-detected PAHs will be reported to the method reporting limit, based on the practical quantitation limit. When calculating total values, non-detects will be assigned a value of zero. Summed values in the final report will include only detected compound results that are unqualified and/or that have been qualified "J" (indicating that the analyte was positively identified and the associated numerical value is approximate). Compound values that have been qualified "NJ" (indicating that the analyte has been "tentatively identified" and the associated value represents its approximate concentration) will not be included in sums. If a sample is comprised of all non-detected results, then the final T-PAH value will be assigned "U" for not detected, at the highest reporting limit value. Summed values will be qualified "J" if more than 10% of the total result is composed of congener values containing "J" qualifiers.

11.0 References

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