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Addendum 3 to Quality Assurance Project Plan

A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program

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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 PbTrends15.

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May 2015

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
W2R: Waste 2 Resources Program

3.0 Background

Ecology began collecting suspended particulate matter (SPM) from 15 long-term monitoring sites throughout Washington in 2008 to evaluate temporal trends in environmental lead levels. Lead was added to the list of parameters for monitoring at established monitoring sites for organic PBT trends (Johnson, 2007). This is described in a 2008 QAPP addendum (Meredith and Furl, 2008).

The present addendum outlines the following changes to take place in 2015:

- Monitoring will be discontinued at eight sites.
- A sediment trap will be deployed at two of the active monitoring sites during regular sampling.
- Cadmium, copper, and zinc will be added to the analysis of the Upper Columbia River site.

3.1 Study area and surroundings

Sampling at the following sites will be discontinued in 2015: Duwamish River, Columbia River at McNary Dam, Columbia River at Rock Island Dam, Hylebos Creek, Lower Columbia River, Queets River, Wenatchee River and Yakima River. The reason these sites are being discontinued is that no statistically significant trends have been detected after six years of monitoring and lead concentrations are consistently low (Clinton and Mathieu, 2015).

Sampling will continue at the sites where higher levels have been observed: Spokane River, Upper Columbia River, and the small urban streams (Leach Creek, Longfellow Creek, and Thornton Creek). Huge Creek, a stream similar in size to the urban streams, will also remain a monitoring site to reflect reference conditions for small streams.

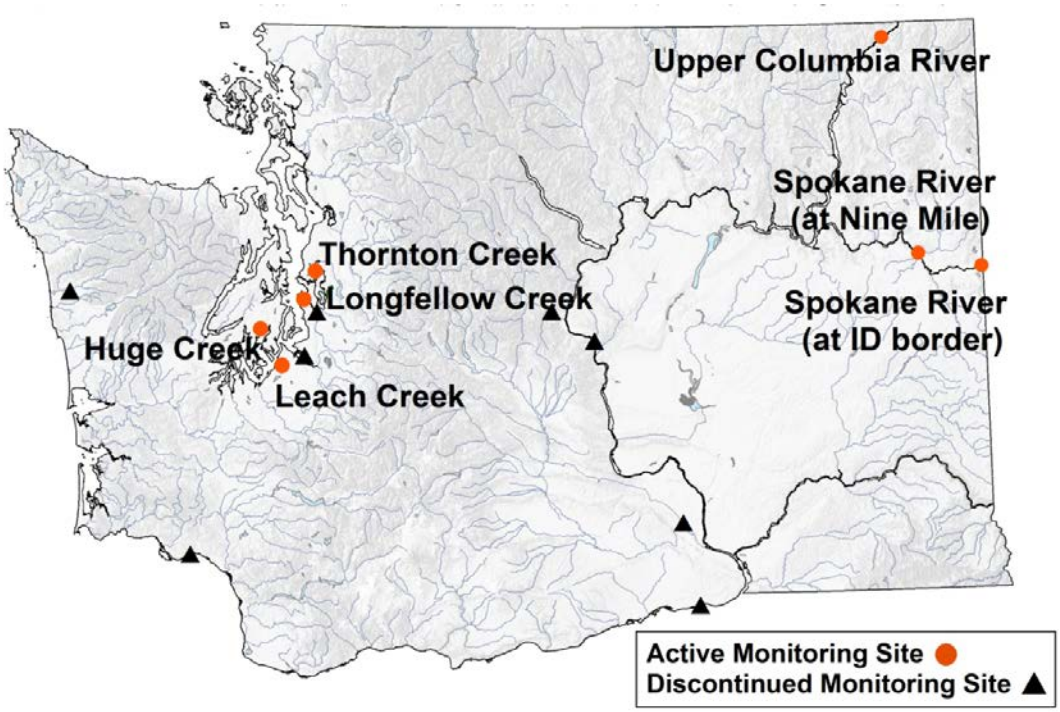

Figure 1. Study Locations for 2015 Lead in SPM Monitoring.

3.1.4 Results of previous studies

Since 2009, Ecology has published annual reports summarizing results of lead in SPM collected from the monitoring sites. These reports are listed and available for download at http://www.ecy.wa.gov/programs/eap/toxics/lead.html. Elevated lead concentrations have been consistently measured in samples collected from the Spokane River (range = 135-3,121 mg/kg, median = 593 mg/kg), followed by the small urban streams (range = 63-287 mg/kg, median = 165 mg/kg) and Upper Columbia River (range = 21-386 mg/kg, median = 112 mg/kg). Concentrations of lead measured in SPM collected at all other sites were low, ranging from 4.8 – 101 mg/kg, with a median of 19.8 mg/kg and mean of 25.8 mg/kg.

The most recent report evaluated the first six years of monitoring and found no statistically significant temporal trends for any of the monitoring sites (Clinton and Mathieu, 2015). This report recommended the following changes to the long-term monitoring program:

- Add more urban streams to the monitoring site list. The lead concentrations in small, urban streams are likely to be the most dynamic as CAP reduction strategies are implemented. Increasing the frequency of small-stream sampling should also be considered.
- Discontinue sampling from most river monitoring sites, as no significant trends have been detected after six years of monitoring. Lead concentrations measured from the mid-size river sites are low, and trends are not likely to be seen.
- Continue monitoring the Upper Columbia River and Spokane River sites, since they remain

elevated in lead, although they lack apparent trend.

- Research other methods of collecting SPM that would integrate time and allow for larger sample material size, such as sediment traps.

4.2 Project objectives

The original goal of evaluating temporal trends in environmental lead levels of Washington remains the primary purpose of this long-term project. Additional objectives for the 2015 sampling year include:

- Deploy sediment traps at a subset of the monitoring sites to determine whether this type of sample collection would be feasible for future monitoring of lead.
- Analyze cadmium, copper, and zinc in Upper Columbia River samples to characterize and track contamination of these metals in the river.

4.7 Practical constraints

Practical constraints may apply to the deployment of the sediment traps. Issues that may arise include: vandalism, loss of equipment due to high velocity, and/or not obtaining enough fine material for analysis of lead and grain size. Ecology staff will attempt to minimize the possible loss of equipment by tethering the sediment traps to the shore with a stainless steel cable.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies W2R 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	Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Michael Friese* Toxics Studies Unit SC Section Phone: 360-407-6737	Field Assistant	Helps collect samples and records field information.
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
W2R: Waste 2 Resources Program
SC: Statewide Coordination Section
QAPP: Quality Assurance Project Plan
*2015 sampling year only

5.6 Budget and funding

The laboratory budget for 2015 sample analyses is presented in Table 2.

Table 2. Project budget.

Parameter	Collection Method	Number of samples	Number of QC samples	Total number of samples	Cost per sample	MEL Subtotal
Pb	In-line filtration	24	6	30	$48.78	$1,463.40
Pb	Sediment trap	4	2	6	$48.78	$292.68
Grain Size	Sediment trap	4	4	8	$100	$800.00
Cd, Cu, Pb, Zn*	In-line filtration	4	6	10	$100.00	$1,000.00
					Lab Total	$3,556.08

*Upper Columbia River site only.

6.0 Quality Objectives

6.2 Measurement Quality Objectives

Table 3. Measurement Quality Objectives.

Parameter	Matrix	Field replicates (RPD)	Lab control samples (% recov.)	Matrix spike (% recov.)	Matrix spike duplicate (RPD)	Lab duplicates (RPD)
Pb	SS[1]	---	85-115%	70-130%	≤ 20%	---
Grain size	SS[1]	n/a	n/a	n/a	n/a	≤ 25%[2]
Cd, Cu, Zn[3]	SPM	< 50%	85-115%	70-130%	n/a	n/a

[1] Suspended sediment collected from sediment traps.
[2] Lab triplicate analyses (relative standard deviation).
[3] Upper Columbia River site only.

6.2.1 Targets for Precision, Bias, and Sensitivity

6.2.1.1 Precision

Precision of lead analysis in suspended sediments collected from sediment traps will be assessed through matrix spike duplicates. Precision for cadmium, copper, and zinc data will be assessed

through field duplicates. Laboratory duplicates are not possible with in-line filtration, due to the limited sample material available. Field duplicates will be collected and analyzed in the same manner as outlined for lead in QAPP Addendum 1 (Meredith and Furl, 2008). Targets for these tests are outlined in Table 3.

6.2.1.2 Bias

Bias for lead analysis in suspended sediment collected from sediment traps will be assessed through laboratory control samples, matrix spikes, and method blanks. Bias for cadmium, copper, and zinc data will be assessed through analysis of laboratory control samples, matrix spikes, method blanks, and field blanks. Field blanks will be collected and analyzed in the same manner as outlined for lead in QAPP Addendum 1 (Meredith and Furl, 2008). Targets for these tests are included in Table 3.

6.2.1.3 Sensitivity

The lowest concentration of interest for all metals is equal to the method reporting limit. The laboratory will report lead in suspended sediments collected from sediment traps down to 0.1 mg/kg dw. The laboratory will report results for cadmium, copper, and zinc down to 0.05, 0.25, and 2.5 ug/filter, respectively. Assuming a 0.005 g sample, which is the average sample weight for the Upper Columbia River site, this reporting limit translates to 10, 50, and 500 mg/kg dw, for cadmium, copper, and zinc, respectively. Reporting limits are included in Table 6.

6.2.2 Targets for Comparability, Representativeness, and Completeness

6.2.2.1 Comparability

Sampling crew will continue to follow Ecology's *Standard Operating Procedure for Collecting Freshwater Suspended Particulate Matter Samples using In-Line Filtration* (Mathieu, 2014) to ensure temporal comparability.

6.2.2.2 Representativeness

Currently, this monitoring program collects two samples (spaced four weeks apart) in the spring and fall to represent high and low flow periods, respectively. While flow data on sampling dates for the first six years of sampling has generally shown that desired conditions have been sampled, sediment traps are being deployed at a subset of sites in 2015 to assess whether this type of sampling may yield a more representative sample. Sediment traps can be deployed for any length of time and thus integrate temporal variability. Samples collected from sediment traps may be more representative of the season or flow regime of interest.

6.2.2.3 Completeness

Completeness targets remain unchanged from those described in QAPP Addendum 1 (Meredith and Furl, 2008).

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

The primary change to the study design in 2015 is the discontinuation of monitoring at the river sites where low lead concentrations were consistently recorded over the first six years of sampling. The Spokane River and Upper Columbia River sites were kept as part of the study design because of the elevated concentrations recorded at these sites and continued interest in the data, due to upstream cleanup activities. Monitoring of the urban streams will continue, due to the elevated lead concentrations of these sites. Monitoring urban streams will also help to characterize changes resulting from Chemical Action Plan (CAP) strategies, such as the lead wheel-weight ban (RCW 70.270).

Sediment traps will be deployed at two of the small stream sites (Thornton and Longfellow Creeks) in order to evaluate whether this sampling procedure is a feasible replacement for the current in-line filtration protocol in the future. Thornton and Longfellow Creeks were selected for sediment trap deployment because both streams have had consistently high levels (with no samples less than reporting limits). In contrast, Huge Creek had >80% of the SPM samples below reporting limits. Leach Creek, the third urban stream, was also considered for sediment trap deployment; however, unlike the other two urban streams, stormwater is diverted away from the stream during high flow events. Deployment at Thornton and Longfellow Creeks will be a better representation of how the sediment trap will perform under natural flow conditions.

The project manager will assess the amount of fine material obtained by the traps and compare lead concentrations in the trap samples to the in-line filtration samples collected at the same sites. This information will help the project manager choose possible alternative sampling methods to use in the future in order to obtain a more representative (time-integrated) sample.

Sediment traps will be deployed at the time of the first in-line filtration sampling event and retrieved at the time of the last sampling event, for both seasons. Sampling events are spaced approximately four weeks apart. Field staff will check on the traps half-way through the deployment to ensure that the equipment is still there and in proper working order. Field staff doing the mid-check will take notes on features such as amount of material present and biofouling.

Cadmium, copper, and zinc are being added to the laboratory analysis of the samples collected from the Upper Columbia River site to characterize concentrations of these metals in the river due to contamination from upstream smelting activities. No other on-going monitoring of metals is currently being conducted at this site.

7.1.2 Sampling location and frequency

Table 4. 2015 Sampling locations, sample types, and approximate collection dates.

Sampling location	Type of sampler	Analyte	Number of samples/collection date*			
			5/4/2015	6/1/2015	9/1/2015	9/29/2015
Huge Creek	In-line filt.	Pb	1	1	1	1
Leach Creek	In-line filt.	Pb	1	1	1	1
Longfellow Creek	In-line filt.	Pb	1	1	1	1
	Sed. trap	Pb, grain size	(deploy)	1	(deploy)	1
Thornton Creek	In-line filt.	Pb	1	1	1	1
	Sed. trap	Pb, grain size	(deploy)	1	(deploy)	1
Spokane R. (ID border)	In-line filt.	Pb	1	1	1	1
Spokane R. (Nine Mile)	In-line filt.	Pb	1	1	1	1
Upper Columbia R.	In-line filt.	Pb, Cd, Cu, Zn	1	1	1	1

*Collection date is approximate.

7.1.3 Parameters to be determined

Lead and grain size (clay/gravel/sand/silt fractions) will be analyzed in the sediment trap samples deployed in 2015. Cadmium, copper, and zinc are being added to the analysis of Upper Columbia River in-line filtration samples.

7.3 Assumptions underlying design

Material collected from sediment traps is assumed to be of suitably comparable grain size (i.e., > 62.5 um) to that collected via in-line filtration (> 0.45 um). The project manager will evaluate that assumption through examination of grain-size results from sediment traps samples.

7.5 Characteristics of existing data

Results of the first six years of analyzing lead in SPM at the monitoring sites revealed no significant temporal trends (Clinton and Mathieu, 2015). The current study design outlines annual collections of two samples in the spring and two samples in the fall. This discrete sampling frequency may not be adequate to characterize trends. Sediment traps integrate temporal variability over their deployment period and thus may be a more suitable sampling protocol for long-term trend monitoring.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

Sediment Traps

Suspended sediment will be collected through Hamlin sediment traps deployed for four weeks at two of the monitoring sites (Longfellow and Thornton Creeks). Lubliner (2012) carried out a study to assess the usefulness of several types of sediment traps for use in stormwater drains. The study showed that the Hamlin sampler was efficient at collecting fine-grained material over a relatively short amount of time, in stormwater. The Hamlin sediment trap has also been used successfully in a small stream by another Ecology study (Marshall et al., 2014).

The Hamlin sediment trap is constructed of 14-gage stainless steel, with the dimensions of 21.5L x 9.25W x 4H inches. The weight of the sampler (25 pounds) allows for direct deployment (without securing to a fixed substrate) during periods of low flow (Lubliner, 2012). Because flows at the time and site of deployment for this project range from 1-10 cfs, the sediment trap will either be placed directly onto the bed of the stream if appropriate, or secured to a concrete block. Sediment traps will be deployed as close to the thalweg as is logistically possible. A stainless steel cable will be attached to the side of the sediment trap and tethered to the bank to minimize equipment loss.

The sediment traps will be deployed in early May/September and will be retrieved four weeks later. At the time of retrieval, fine material within the trap will be removed with stainless steel spoons into glass 1-L jars and homogenized. Jars will be placed on ice and brought back to Ecology Headquarters. Sample material will be centrifuged to remove excess water prior to shipment to the laboratory for analysis.

In-line Filtration

Cadmium, copper, and zinc will be analyzed in the same in-line filtration sample as is currently collected for lead analysis at the Upper Columbia River site. Sampling procedures for in-line filtration are documented in the QAPP Addendum (Meredith and Furl, 2008) and Ecology's standard operating procedure (Mathieu, 2014).

8.2 Containers, preservation methods, holding times

Table 5 lists the containers, preservation methods, and holding times for sediment trap samples (lead and grain size). Analysis of cadmium, copper, and zinc will be conducted on the same filter sample as is already collected for analysis of lead at the Upper Columbia River site. Container, preservation, and holding time information for filter samples are unchanged from Addendum 1 (Meredith and Furl, 2008).

Table 5. Sample containers, preservation methods, and holding times.

Parameter	Container	Preservation	Holding time
Pb*	4 oz glass	Cool to ≤ 6° C	6 months
Grain size	8 oz plastic	Cool to ≤ 6° C	6 months

*Collected from sediment traps

8.4 Equipment decontamination

The sediment traps and all equipment coming into contact with the sediment trap sample (sampling spoon) will be decontaminated using the following procedure: hot tap water rinse and scrub with Liquinox© detergent, followed by a 10% nitric acid rinse and deionized water rinse. All equipment will be dried and stored in aluminum foil prior to use in field.

9.0 Measurement Methods

9.2 Lab procedures table

Table 6. Lab procedures table.

Analyte	Matrix	Number of samples	Expected range of results	Analytical method	Method reporting limit
Pb	Suspended sediment*	4	< 1 - 500 mg/Kg	EPA 6020	0.1 mg/kg dw
Grain size	Suspended sediment*	4	1 - 100%	PSEP 1986	1%
Cd	SPM	4	< 10 - 500 mg/Kg	EPA 6020	10 mg/kg dw^
Cu	SPM	4	< 50 - 500 mg/Kg	EPA 6020	50 mg/kg dw^
Zn	SPM	4	< 500 - 5,000 mg/Kg	EPA 6020	500 mg/kg dw^

* Collected from sediment traps.
^ Assuming 0.005 g sample, which is the average weight of samples collected from the Upper Columbia River site.

9.3 Sample preparation methods

Lead samples collected from sediment traps will be prepared following EPA Method 3050B. Cadmium, copper, and zinc will be prepared in the same manner as lead in filter samples, following EPA Method 3050B.

9.5 Lab accredited for method

Manchester Environmental Laboratory (MEL) will conduct all metals analyses. MEL is accredited for these methods. A contract lab accredited for method PSEP-1986 will be chosen to conduct grain size analysis.

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

Table 7. Field and lab QC samples, type, and frequency.

Analyte	Matrix	Field		Laboratory				
		Blanks	Replicates	LCS	Matrix spikes	Matrix spike duplicate	Method blanks	Analytical duplicates
Pb	SS*	n/a	none	1/batch	1/batch	1/batch	1/batch	---
Grain size	SS*	n/a	none	---	---	---	---	1/batch^
Cd, Cu, Zn	SPM	1/batch	1/batch	1/batch	1/batch	n/a	1/batch	n/a

* Suspended sediment collected from sediment traps.
^ Lab triplicate analysis.
One batch = 20 or fewer samples.

10.2 Corrective action processes

The project manager will examine the data and case narratives to identify samples that fall outside of QC criteria. If an exceedance occurs, the project manager will determine whether the data should be re-analyzed, rejected, or used with appropriate qualification.

15.0 References

Clinton, C. and C. Mathieu, 2015. PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter, 2013 Results. Washington State Department of Ecology, Olympia, WA. Publication No. Publication No. 15-03-012. https://fortress.wa.gov/ecy/publications/SummaryPages/1503012.html

Johnson, A., 2007. Quality Assurance Project Plan: A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-104. https://fortress.wa.gov/ecy/publications/summarypages/0703104.html

Lubliner, B., 2012. Evaluation of Stormwater Suspended Particulate Matter Samplers. Washington State Department of Ecology, Olympia, WA. Publication No. 12-03-053. https://fortress.wa.gov/ecy/publications/summarypages/1203053.html

Marshall, R., B. Era-Miller, and S. Collyard, 2014. Integrated Ambient Monitoring Follow-up Study of Indian Creek: An Investigation of the Causes of Biological Impairment and a Further Demonstration of the Instream Monitoring Approach. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-050. https://fortress.wa.gov/ecy/publications/SummaryPages/1403050.html

Mathieu, C., 2014. Standard Operating Procedure for Collecting Freshwater Suspended Particulate Matter Samples using In-Line Filtration. Washington State Department of Ecology, Olympia, WA. SOP No. EAP041. http://www.ecy.wa.gov/programs/eap/quality.html

Meredith, C. and C. Furl, 2008. Addendum #1 to Quality Assurance Project Plan: A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-104ADD1. https://fortress.wa.gov/ecy/publications/summarypages/0703104ADD1.html