Addendum #1 to

Quality Assurance Project Plan: A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program

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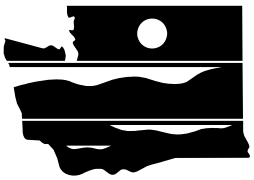

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Quality Assurance Project Plan: A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program

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SUBJECT: **ADDENDUM #1 TO QUALITY ASSURANCE PROJECT PLAN: A TREND MONITORING COMPONENT FOR ORGANIC PBTs IN THE WASHINGTON STATE TOXICS MONITORING PROGRAM**

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In 2007, the Washington State Department of Ecology (Ecology) initiated a trend monitoring component for selected organic chemicals in major rivers and lakes as part of the Washington State Toxics Monitoring Program (WSTMP). This component focused on organic compounds that Ecology has identified as persistent, bioaccumulative, toxic chemicals (PBTs). The Ecology target PBT list is included in Appendix A.

The initial compounds of interest in the *Trend Monitoring Component for Organic PBTs in the WSTMP Quality Assurance Project Plan* (Organic Trends QA Project Plan) included chlorinated pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), with the intention of adding other PBTs over the next few years (Johnson, 2007).

Ecology and the State Department of Health (DOH) are developing chemical action plans to address specific PBTs. The objective of the chemical action plans is to reduce and phase-out PBT uses, releases, and exposures to humans and the environment in Washington (Gallagher, 2007). Chemical action plans for mercury (Peele, 2003) and PBDEs (Geller, 2006) have been completed. As a result, trend monitoring of these chemicals has been initiated as part of the WSTMP (Seiders, 2006; Coots, 2006; Johnson and Seiders, 2005; Johnson, 2007a).

Chemical action plans for lead and polycyclic aromatic hydrocarbons (PAHs) are scheduled to be published in 2008 and 2009, respectively (Gallagher, 2007). As part of the effort to track the success of these chemical action plans, analyses of lead and PAHs will be added to the organic trends monitoring program. This addendum summarizes the addition of PAHs and lead to the *Organic Trends QA Project Plan*.

Experimental Design

Beginning with the spring 2008 semipermeable membrane device (SPMD) deployments, PAHs will be included in the sample analysis of SPMD extracts at all 12 statewide sampling locations. The sampling locations represent a wide range of contamination potential for PAHs. Results will be used to calculate average water column concentrations for the 28-day spring and fall deployments. SPMD design details, deployment and retrieval issues, and location information are detailed in the *Organic Trends QA Project Plan* and will remain consistent (Johnson, 2007a).

To evaluate trends in lead concentrations, suspended particulate matter (SPM) will be collected and analyzed for total lead at all 12 statewide Organic Trends sites, and three additional sites, beginning in spring 2008. The three additional sites were selected based on lead contamination potential. A second SPM sample will be collected at eight of the 15 sampling locations, spaced at least three weeks apart from the first sample collection, to include seasonal variability in the analysis.

An in-line filtration sampling protocol will be used to collect SPM samples. This technique has been reviewed by Odman et al. (1999) and Horowitz (1986). River or lake water will be pumped through 0.45 µm pore-size filters, and the SPM collected on the filters will be analyzed for lead.

In addition to total suspended solids (TSS), conductivity, and temperature, pH measurements will be taken and recorded at each site. Calibration checks of the pH meter will be done at the first, middle, and last station of the day to assess instrument accuracy. These checks will be in accordance with Ecology's standard operating procedure (SOP) for collection and analysis of pH samples (Ward, 2007).

Analytical Laboratory

The SPMDs will be sent to Environmental Sampling Technologies (EST) Laboratory for preparation and extraction. The extracts provided by EST, along with the SPM samples, will be analyzed by Manchester Environmental Laboratory. A list of PAHs included in the analysis is located in Appendix B.

Intended Use

The data will be used to provide a baseline for the contaminant in the environment and measure contaminant trends over time as chemical action plan reduction strategies are implemented.

Quality Objectives

Measurement Quality Objectives

All quality control requirements are to be met by Manchester Laboratory. Project managers worked with the laboratory staff to establish the measurement quality objectives described in Table 1.

Table 1. Measurement Quality Objectives for PAHs and Lead Analyses.

Analysis	Check Stds./Lab Control Samples (% recov.)	Laboratory Duplicates (RPD)	Surrogates (% recov.)	Matrix Spike (% recov.)	Field Replicates (RPD)	Lowest Concentration of Interest
PAHs	40-150%	± 40%	30-150%*	31-150%	n/a	10 ng/SPMD
Lead	± 15% LCS	n/a	n/a	70-130%	50%	1 mg/Kg dw

RPD = relative percent difference.
LCS = laboratory control sample.
* Surrogates: Acenaphthylene-d8 = 50-150%, Pyrene-d = 30-150%.

Representativeness

The sampling will occur at monitoring stations described in the *Organic Trends QA Project Plan.* The selected sites are located in major waterbodies distributed across the state, with a focus on areas having previous contaminant data. Locations with potential for improvements in contamination status were given extra weight during the selection process (Johnson, 2007a).

Completeness

The goal of the organic trends monitoring component is to have 100% completeness. However, there is a potential for data gaps with SPMD and SPM sampling. Loss of SPMD canisters during the deployment period would affect completeness of field data. For SPM sampling, periods of low suspended sediments may result in insufficient sample amounts for laboratory analyses. This may be a greater possibility during sampling in the fall, when suspended sediment concentrations are generally lower.

Comparability

All Ecology crews carrying out SPMD and lead SPM sampling will be trained by the project manager to ensure uniformity of field sampling activities. Sampling will be conducted in accordance with SPMD and SPM collection SOPs (Johnson, 2007b; Meredith, 2008 in preparation).

Sampling and Measurement Procedures

Sampling Procedures

A detailed description of the SPMD sampling procedures can be found in the *Organic Trends QA Project Plan* (Johnson, 2007a). SPMD sampling procedures outlined in the project plan follow Ecology's SOP for sampling with SPMDs (Johnson, 2007b). The only change to the SPMD field sampling procedures will be the addition of a shade mechanism during SPMD deployment to protect the membranes and limit PAH photo degradation. The shade device will consist of a perforated aluminum cylinder, open at both ends, holding the SPMD canister.

Sampling procedures for lead samples will follow Ecology's SOP for SPM collection using in-line filtration (Meredith, 2008 in preparation). Using a peristaltic pump, surface water will be pumped and filtered through a 0.45 µm pore-size (47 mm membrane) nitrocellulose filter with an inline 47 mm membrane Teflon-filter holder. The total volume of water passing through the filter and total time of filtration will be recorded. Water will be pumped 6 – 12 feet from the shoreline. The intake of the tubing will remain 2 – 6 feet below the water surface, suspended above the river or lake bottom while sampling.

Once filters have accumulated enough SPM to restrict water flow, they will be carefully removed with forceps and stored in pre-acid-washed aluminum sample containers. Samples will be stored upright and put in ice coolers for transport back to Ecology headquarters. Samples will be held at 4° C until shipment. The holding time of 6 months will not be exceeded.

The use of in-line filtration provides a simple and inexpensive approach to the collection of SPM samples. Previous studies have used this sampling protocol to assess metal contamination in stream SPM (Bibby and Webster-Brown, 2005; Bibby and Webster-Brown, 2006; Butler et al., 2008).

All sampling materials in contact with the SPM samples will be of Teflon, polyethylene, or aluminum material and decontaminated with nitric acid and distilled/deionized water between each site. Nitrile gloves will be worn by field staff during sampling. The pre-weighed nitrocellulose filters will be provided by Manchester Laboratory. The blank filters have been tested by Manchester Laboratory and lead contamination was below detection limits. The aluminum containers and nitrocellulose filters will be handled with forceps to limit the addition of weight to the containers or filters, and to avoid sample contamination.

Measurement Procedures

The measurement procedures for PAHs and lead are described in Table 2. The number of field samples includes quality control samples. The expected range of results are based on previous PAH and lead data collected statewide. The reporting limit for lead analysis assumes a 0.5 gram field sample.

Table 2. Measurement Procedures for PAHs and Lead Analyses.

Analysis	Number of Field Samples	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical Method
PAHs	14	1 - 1200 ng	10 ng/SPMD	dialysis/GPC*	EPA 3630B/8270**
Lead	29	1 - 600 mg/Kg	0.1 mg/Kg†	EPA 3050B	200.8 ICP-MS

* EST SOPs E14, E15, E19, E21, E33, E44, E48.
** SIM modification.
† Assuming 0.5 g of field sample.

Manchester Laboratory will analyze PAHs in extracts provided by Environmental Sampling Technologies using a modification of EPA method 3630B/8270. The Manchester Laboratory standard list of PAH compounds to be included in the analyses can be found in Appendix B.

Sampling rates for PAHs will be determined using PCB performance/permeability reference compounds (PRCs), as described in the *Organic Trends QA Project Plan.* Due to the ability of these PRCs to predict the uptake rates of compounds with a wide range of K_{ow}'s (Octanol-water partition coefficients) (Huckins et al., 2002; Huckins et al., 2006), the PCB PRC loss rates can be used to determine the uptake rates of PAH compounds.

Manchester Laboratory will prepare the SPM samples using EPA method 3050B. Lead will be analyzed by the laboratory using EPA Method 200.8 (ICP-MS). The laboratory will report total suspended lead concentrations in mg/Kg dry weight and µg/unit. Final results will be reported as mg/Kg dry weight and as µg/L, calculated by dividing the laboratory-reported µg value by the volume of water passed through the filter.

The estimated laboratory costs for the PAHs and lead analyses are shown in Table 3. The addition of PAHs to SPMD analyses has an estimated laboratory cost of $9,750 annually. Costs associated with SPMD preparation and extraction are stated in the *Organic Trends QA Project Plan* and are not changed by the addition of PAH analyses. The laboratory analysis of lead has an estimated yearly cost of $2,610.

Table 3. Estimated Laboratory Costs for PAHs and Lead Analyses.

Parameter	Cost per Sample	Number of Field Samples	Matrix Spikes	Number of QC Samples	Cost per Monitoring Period	Number of Monitoring Periods per Year	Estimated Annual Total Cost
PAHs	$325	12	1	2	$4,875	2	$9,750
Lead	$45	23	2	4	$1,305	2	$2,610

QC = quality control.

Quality Control

Field

Table 4 describes field quality control samples associated with the analyses.

Table 4. Field Quality Control Samples for PAHs and Lead Sampling.

Sample Type	Analysis	Field Replicates	Trip Blanks
SPMDs	PAHs	1	1
Suspended Particulate Matter	Lead	2	2

One SPMD field replicate will be deployed during each sampling season to assess field and laboratory variability. The replicate SPMD will be deployed at rotating sampling sites. An SPMD field trip blank will be taken at the sampling location with the highest contamination potential. The SPMD blank will be exposed to ambient air for the same amount of time as the field sample SPMDs are exposed during deployment and retrieval. The field blank will be analyzed for potential contamination to evaluate field variability. A detailed description of the field blank process can be found in the *Organic Trends QA Project Plan.*

Two SPM field replicates will be collected during each sampling season. Replicates will be taken in the same location immediately after the field sample collection. Two trip blanks will also be collected to determine potential field contamination. The trip blank collection will be conducted in the same manner as field samples, except laboratory-purified water will be used in place of river water. Manchester Laboratory will provide two sets of laboratory-purified water for filtration. Replicates and trip blanks will be collected at rotating sampling sites.

Laboratory

The laboratory quality control plan is shown in Table 5.

Table 5. Laboratory Quality Control Samples for PAHs and Lead Analyses.

Analysis	Method Blanks*	Check Std./ LCS	Surrogate Spikes	Matrix Spike	Duplicates
PAHs	1/batch	1/batch	all samples†	2/batch†	1/batch
Lead	1/batch	1/batch	n/a	1/batch	n/a

* See *Organic Trends QA Project Plan* for additional method blanks prepared by EST.
† to be spiked at EST.
LCS = laboratory control sample.

For both PAHs and lead analyses, Manchester Laboratory will analyze one method blank per sampling season to assess potential laboratory contamination. The laboratory will also analyze check standards to evaluate analytical bias.

Environmental Sampling Technologies will add surrogate spikes to the SPMD composites prior to dialysis. Acenaphthylene-d8 and Pyrene-d10 will be used as the surrogate compounds for PAH analyses. The composites will be spiked with 50 µL of the 40 ng/L surrogate compound solution.

A matrix spike for PAH analyses will be added to all SPMD membranes by Environmental Sampling Technologies. The membranes will be spiked with 50 µL of a 40 ng/µL solution of Manchester Laboratory's standard matrix spike mix at to a single membrane. The membranes to be spiked with the PAH standard matrix spike will also contain the pesticide/PBDE matrix spike described in the *Organic Trends QA Project Plan.* The standard matrix spike will be provided by Manchester Laboratory.

Matrix spikes for lead analysis will be conducted by Manchester Laboratory using field replicate samples. Standard reference material (SRM) and laboratory duplicate analyses are not applicable for this SPM collection method. An SRM would require a filter containing a known value of lead associated with the adhered SPM, and this is not currently available. Laboratory duplicate analyses are not possible because the filter samples do not contain enough sample material to be cut in half for the analysis.

Data Management Procedures

All data management procedures for SPMDs will remain consistent with the *Organic Trends QA Project Plan.*

Audits and Reports

Manchester Laboratory will be responsible for performance and system audits of their laboratory procedures (Johnson, 2007a). The audit results are available upon request.

Results will be reported in the organic trends monitoring component annual progress report. Detailed information on annual progress reports can be found in the *Organic Trends QA Project Plan*. A separate section for lead in SPM will be written and provided to the project manager for inclusion in the annual progress reports.

Data Verification

PAH and lead laboratory data will be reviewed and verified by Manchester Laboratory, in accordance with the *Organic Trends QA Project Plan.*

Data Analysis

Data analysis of PAHs will be conducted as described in the *Organic Trends QA Project Plan.* The data analysis of lead associated with SPM will include comparison of concentrations between sites, relative ranking of sites, and graphical display of the data.

Organization and Schedule

Following is the staff organization and time schedule for this project.

Organization

Name	Organization	Phone No.	Role
Art Johnson	EAP-SCS-TSU	360-407-6766	QA Project Plan Development
Patti Sandvik	EAP-SCS-TSU	360-407-7198	WSTMP Organic Trends Project Manager
Callie Meredith	EAP-SCS-TSU	360-407-6965	Lead SPM Project Manager
Casey Deligeannis	EAP-SCS-TSU	360-407-7395	Field Assistance
Chad Furl	EAP-SCS-TSU	360-407-6060	Field Assistance
Dale Norton	EAP-SCS-TSU	360-407-6765	Toxics Studies Unit Supervisor
Terri Spencer	Environmental Sampling Technologies	816-232-8860	SPMD Preparation and Extraction
John Weakland	Manchester Laboratory	360-871-8820	Organics Supervisor
Dean Momohara	Manchester Laboratory	360-871-8808	Chemistry Units' Supervisor
Stuart Magoon	Manchester Laboratory	360-871-8801	Lab Director
Karin Feddersen	Manchester Laboratory	360-871-8829	Contract Lab Services
Bill Kammin	EAP	360-407-6964	Quality Assurance Officer
Patti Sandvik	EAP-SCS-TSU	360-407-7198	SPMD EIM Data Management
Callie Meredith	EAP-SCS-TSU	360-407-6965	Lead SPM EIM Data Management

EAP = Environmental Assessment Program.
SCS = Statewide Coordination Section.
TSU = Toxics Study Unit.

Schedule

Environmental Information System (EIM) system	
EIM data engineer	Patti Sandvik
EIM user study ID	SPMDTR08
EIM study name	WSTMP SPMD Trend Monitoring
Data due in EIM	July 09; annually thereafter
Progress Report	
Report author lead	Patti Sandvik
Schedule	
Draft report due to supervisor	March 09; annually thereafter
Draft report due to client/peer draft due	April 09; annually thereafter
Draft report due to external reviewers	n/a
Final report due	July 09; annually thereafter

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Appendix A. Chemicals and Chemical Groups on the PBT List (Gallagher, 2007)

Table A-1. Chemicals and Chemical Groups on the PBT List (Gallagher, 2007).

Metals	Flame Retardants	Banned Pesticides	Organic Chemicals
Methyl-mercury	PBDEs Tetrabromobisphenol A Hexabromocyclododecane Pentachlorobenzene	Aldrin/Dieldrin Chlordane DDT/DDD/DDE Heptachlor Epoxide Toxaphene Chlordecone Endrin Mirex	1,2,4,5-TCB Perfluorooctane sulfonates Hexachlorobenzene Hexachlorobutadiene Short-chain chloro paraffin Polychlorinated naphthalenes

Combustion By-Products	Banned Flame Retardants	Banned Organic Chemicals	Metals of Concern
PAHs PCDD PCDF PBDD/PBDF	Hexabromobiphenyl	PCBs	Cadmium Lead

Appendix B. Manchester Environmental Laboratory's Standard List of PAHs and PAH-associated compounds to be included in the SPMD analyses

Table B-1. Manchester Laboratory's Standard List of PAHs and PAH-associated compounds to be included in the SPMD analyses.

Low-molecular weight PAHs	High-molecular weight PAHs	Substituted	Associated Compounds
Anthracene Acenaphthene Acenaphthylene Fluorene Naphthalene Phenanthrene	Benzo(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(ghi)perylene Benzo(k)fluoranthene Chrysene Dibenzo(a,h)anthracene Fluoranthene Indeno(1,2,3-cd)pyrene Pyrene	Retene 1-Methylnaphthalene 2-Chloronaphthalene 2-Methylnaphthalene	Carbazole Dibenzofuran