DEPARTMENT OF
ECOLOGY
State of Washington

# Quality Assurance Project Plan

# Trends Monitoring for Organic PBTs: Revisions for the 2009 Spring Monitoring Effort

May 2009

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Ecology's Project Tracker Code for this study is 07-501-03

Waterbody Numbers

| | |
|---|---|
| Lake Washington | WA-08-9350 |
| Lower Columbia River | WA-CR-1010 |
| Middle Columbia River | WA-CR-1026 |
| Queets River | WA-21-1030 |
| Spokane River | WA-54-1020 |
| Upper Columbia River | WA-CR-1040 |
| Walla Walla River | WA-32-1010 |
| Yakima River | WA-37-1010 |

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# Quality Assurance Project Plan

## Trends Monitoring for Organic PBTs: Revisions for the 2009 Spring Monitoring Effort

May 2009

**Approved by:**

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Signatures are not available on the Internet version.
SWFAP – Solid Waste and Financial Assistance Program.
HWTR – Hazardous Waste and Toxic Reduction Program.
SCS – Statewide Coordination Section.
EAP - Environmental Assessment Program.
EIM - Environmental Information Management system.

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# Introduction

The organic trends component of the Washington State Toxics Monitoring Program begins its third year of sampling in spring 2009. Levels of organic contaminants in water are estimated with the use of a passive sampling technology called a semi-permeable membrane device (SPMD). SPMDs were successfully deployed at 11 locations in major rivers and one large urban lake for a period of one month twice a year during 2007 and 2008. Evaluation of chlorinated pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) began in 2007. Polycyclic aromatic hydrocarbons (PAHs) were added in 2008.

The goal of the trends monitoring program for persistent, bioaccumulative[1], and toxic chemicals (PBTs) is to determine changes in levels of selected PBTs over time. Results may be helpful in evaluating whether actions designed to reduce inputs of these chemicals are effective.

Monitoring efforts for PBTs in other environmental media included monitoring for mercury trends in fish and in sediment cores which started in 2005 and 2006, respectively. Monitoring for lead in suspended particulate matter began in 2008. PAHs were also added to the sediment core work in 2008.

A Quality Assurance (QA) Project Plan for this project was developed in 2007 (Johnson, 2007). An addendum to the project was written in 2008 to address the addition of PAHs and lead (Meredith and Furl, 2008).

This abbreviated QA Project Plan describes revisions to the 2009 spring sampling effort. Data collected during this spring sampling will guide development of standard operating procedures for processing and reporting SPMD data. A revised QA Project Plan for long-term continuation of this trend monitoring program is planned for the spring of 2010.

## Problem Statement

Contamination of the sampling system has compromised the usefulness of sample results even though corrective actions were taken as contamination became apparent. Contamination of field and lab blanks by PCBs, PBDEs, and PAHs occurred in 2007 and 2008. Usefulness of these data for meeting the project goals of detecting trends over time and among sites depends on certainty associated with each data point. The level of certainty is defined by quality control (QC) procedures such as replicate samples, field trip blanks, and lab blanks.

The QC procedures used during sampling events have helped determine corrective actions needed. In 2007, one replicate sample, one field trip blank, one manufacturing lab blank, and one lab method blank were analyzed. In 2008, the spring sampling was similar to 2007, but two more field trip blanks were added for the fall sampling. Before the 2008 fall sampling, additional testing was done to reduce lab blank contamination. A summary of contamination identified and actions taken is found in Table 1.

[1] Bioaccumulative pollutants are pollutants that build up in the food chain.

Table 1. Contamination Identified and Action Taken Before the 2008 Fall Sampling Event.

| Contamination Identified | Action Taken/Information Needed |
|---|---|
| PCB congeners from analytical laboratory. | Changed analytical laboratory for PCB congeners. |
| PCB congeners in spiking solutions. | Changed manufacturer of certain solutions. |
| Pesticide in manufactured SPMDs. | Eliminated major source. (EPA shut down neighboring business). Need additional information for addressing some inconsistencies. |
| PCB and PBDE congeners and PAHs in manufactured SPMDs. | Need additional information. Increase QC. |
| PCB and PBDE congeners and PAHs in extraction and dialysis of SPMDs. | Need additional information. Increase QC. |

## Current Action Plan

Four actions are being taken to address contamination of the sampling and analytical system used in the organic trend monitoring program:

### 1. Review existing SPMD data from Ecology studies.

A compilation and review of all SPMD data from Washington State Department of Ecology (Ecology) studies has been started to help improve usefulness of the data and guide future efforts. So far, this effort has helped identify characteristics of results and data which are summarized below. Compilation should be completed by June 30, 2009. Reviews of the data will help guide development of a centralized data management system, SOPs for sampling and reporting practices, and QA Project Plans for this and future projects.

Issues identified to date by parameter include:

- Levels of contamination in field trip blanks and certain lab blanks have been high and variable. The lab blanks affected are those used during the manufacture and preparation of SPMD membranes. Contaminant values among two or three blanks for most analytes range within 10%-40% relative standard deviation (RSD).
- PCBs: The 2008 fall results indicated a reduction of contamination in lab method blanks by a factor of 3 compared to 2007. Nearly the same magnitude of reduced contamination was found in the three field trip blanks. A review of the 2008 data found that about 15% of PCB congener analytes accounted for nearly 70% of the contamination in field trip blanks. These 22 individual congeners and co-eluting groups could be excluded from data analyses and possibly help avoid the need for using blank correction procedures. None of these 22 congeners include the 12 dioxin-like PCBs.
- PBDEs: Three of the most important congeners (47, 99, and 100) were found at significant levels in the blanks. Use of blank correction for some congeners may be possible, yet blank

correction for others may not work. In 2007, results showed significant levels of PBDEs in the Spokane River, which matched the same findings in the statewide PBDE study by Johnson et al. (2006). Preliminary results for 2008 also show higher levels of PBDEs in the Spokane River. Levels of PBDEs at other sites were difficult to quantify because of the extent of blank contamination.

- PAHs: Sampling for PAHs began in 2008, and preliminary results indicate SPMDs readily concentrate PAHs. The low molecular weight PAHs were found in blanks at relatively high concentrations compared to the samples. Concentrations of some high molecular weight PAHs found in blanks in the fall samples were also high, accounting for 20%-80% of the value found in samples. More time is needed to evaluate data collected thus far to determine how blank contamination will affect the ability to detect trends.
- Chlorinated Pesticides: Few pesticides were found in the 2007 blanks. In 2008, blanks had no contamination indicating that corrective actions appear to be resolving contamination with some pesticides. Yet a different study (Era-Miller, 2008) had several pesticides in the blanks. The inconsistency in the levels and frequencies of contamination in blanks indicate that more work is needed to identify and reduce sources or contamination.

## 2. Recommend changes for 2009 spring sampling.

Changes recommended for the 2009 spring sampling include the following:

- Focus the monitoring on sites and analytes likely to provide the most useful information.
- Discontinue monitoring at some sites because environmental levels of selected parameters are too low to be distinguished from contamination found in blanks.
- Increase the QC effort to improve the quality of data for this and future SPMD projects. Specifically:
  - Identify the sources and magnitude of contamination by increasing the number of blanks. Data from some of these will also provide the option of blank-correcting sample results. These blanks are:
    - Field-Trip Blanks (from three to seven).
    - Day0-Dialysis Blanks (from one to three).
    - Fresh Day0 Blanks (from one to three, depending on target analyte).
    - Extended Exposure Field Air Blanks. Three new blanks were added to help evaluate the potential level of contamination by ambient air at sites during deployment and retrieval. Field blanks collected to date have not been useful indicators of site-specific contamination because of the high level of variability of contamination found in field blanks.
  - Improve information about sampling variability and reduce chance of losing data at the highest quality sites (Spokane, Lower Columbia) and one rotating site by increasing the number of field replicates from one to three.
  - Help define the limits at which trends could be detected.

- Explore appropriate methods of blank-correcting for field or lab contamination by PCB congeners, PBDEs, PAHs, and chlorinated pesticides. This will also help development of the SOP described below.

## 3. Develop standard operating procedure (SOP) for processing and reporting SPMD data.

The target date for this action is December 2009.

The SOP will address handling of data from receipt of lab results to reporting in various formats. Topics will include:

- Procedures for reviewing sample and QC results from the field and laboratory. In particular, verification lab data (Manchester Environmental Laboratory and contract lab) and calculations used with performance reference compounds (PRCs) and surrogates.
- Procedures for the blank-correction of data and determining adequate numbers of field and lab blanks needed for blank correction.
- Data analyses using individual analytes rather than summed values. This will yield more useful information for PCB congeners, PBDE congeners, and individual PAHs.
- Procedures for translating raw residue data into dissolved and total water concentrations. This will include selection and documentation of model inputs, assumptions made, and reporting of results.
- Standard reporting format for EIM, Ecology publications, and a centralized data management system to capture ancillary SPMD information. This will reduce confusion about comparability among studies.

## 4. Long-term plan: Revise QA Project Plan to include changes.

The target date for this action is March 2010.

Revision of the original QA Project Plan will include changes to the program, some of which were recommendations in the 2007 PBT Trends Report (Sandvik, 2009).

- Incorporate the 2008 addendum to the original QA Project Plan, for adding PAHs as target analytes.
- Revise list of sample sites.
- Select appropriate analytical methods for each parameter in SPMD projects.
- Add QC and QA procedures.
- Revise SOPs for SPMD deployment methods.
- Add new SOPs for data reduction methods.
- Incorporate standardized data management and reporting practices.

**Summary of the 2009 Spring Sample Plan**

- The 2009 spring sampling budget proposal is approximately $60,000. The temporary increase is for additional QC work needed to better understand the nature of blank contamination for this and other projects.
- Four of the original 12 sites are excluded because lower levels of contaminants found at these sites in 2007 and 2008 make trends detection unlikely. Sites dropped are the Snohomish, Duwamish, Wenatchee, and Okanogan Rivers.
- Table 2 summarizes lab costs for the proposed 2009 spring sampling. Labs include Ecology's Manchester Environmental Laboratory (MEL), Environmental Sampling Technologies (EST), and Analytical Perspectives (AP).
- Table 3 list EST's estimated costs. The EST total is also included in Table 2.
- Table 4 shows the analytical plan for field samples and field trip blanks by site.
- Table 5 shows the number and type of EST's QC blanks.

Table 2. Total Cost Estimate for the 2009 Spring Samples.

| Lab | Analyses | Field Samples[a] | Field Replicates[b] | Field Trip Blanks[c] | Day0-Dial & other EST QC Blanks | MEL Matrix Spike | # Analyses | Cost/ Sample | Cost to TSU | SIC |
|---|---|---|---|---|---|---|---|---|---|---|
| MEL | Chlorinated Pesticide | 6 | 2 | 10 | 3 | 1 | 22 | $240 | $5,280 | DST00/DSTPF |
| MEL | PBDE | 5 | 3 | 10 | 9 | 1 | 28 | $155 | $4,340 | DST23 |
| MEL | PAH | 8 | 3 | 10 | 9 | 1 | 31 | $335 | $10,385 | DST23 |
| EST | SPMD Dialysis+GPC | - | - | - | - | - | - | $310 | $11,709 | DST00/DSTPF |
| AP | PCB Congeners[d] | 3 | 3 | 10 | 9 | 1 | 26 | $1,063 | $27,625 | DST00/DSTPF |
| MEL | Total Organic Carbon[e] | 24 | 0 | 0 | - | 3[f] | 24 | $33 | $792 | DST00/DSTPF |
| MEL | Total Suspended Solids[e] | 24 | 0 | 0 | - | NA | 24 | $11 | $264 | DST00/DSTPF |
| Average cost for a SPMD sample | | | | | | | | $2,102 | | |
| **Total** | | | | | | | | | **$60,395** | |
| Subtotal DST00/DSTPF23 | | | | | | | | | $45,670 | |
| Subtotal DST23 | | | | | | | | | $14,725 | |

a. Samples may or may not be analyzed for all parameters.
b. Field Replicates may or may not be analyzed for all parameters.
c. Field trip blanks are analyzed for all parameters.
d. Cost/sample is $850 + 25% MEL surcharge: $850 + 212.5 = $ 1062.50.
e. 3 samples per station, minus replicates.
f. MS no charge.
NA = not analyzed.
TSU = Toxics Studies Unit.
SIC = Super Index Code
GPC = gel permeation chromatography
Costs include 50% discount for analyses done by MEL.

Table 3. SPMD Preparation and Extraction for 3009 Spring Samples.

| Service Provided | Number of Stations | Membranes per Station | Total Membranes | Unit Cost | Cost Subtotals |
|---|---|---|---|---|---|
| Field Samples[a] | 9 | 5 | 45 | $57 | $2,565 |
| Field Replicates | 3 | 5 | 15 | $57 | $855 |
| Field Blanks | 10 | 5 | 50 | $57 | $2,850 |
| Dialysis + GPC[b] | 21 | | | $252 | $5,287 |
| PRC & Surrogate Spikes[c] | 22 | 5 | 110 | $1 | $110 |
| Matrix Spikes | | | | no charge | -- |
| EST Lab Blanks | | | | no charge | -- |
| PRC & Surrogate solutions | | | | flat rate | $42 |
| Cost for a SPMD sample | | | | $310 | |
| **EST total** | | | | | **$11,709** |

a. Includes one spare SPMD sample. The spare SPMD sample will be either not used or used as a replacement.
b. Dialysis + GPC = sum of samples + replicates + field trip blanks -1 replacement.
c. PRC & Surrogate Spikes = sum of samples + replicates + field trip blanks.

Table 4. 2009 Spring Analysis by Site.

| Site | Description | Field Samples[a] | Field Trip Blanks[b] | # of CL PEST | # of PBDE | # of PAH | # of PCB Cong. |
|---|---|---|---|---|---|---|---|
| LCR | Lower Columbia River | 1 | 1 | 2 | 2 | 2 | 2 |
| MCNARY | McNary Dam | 1 | 1 | 2 | 1 | 2 | 1 |
| QUEETS | Queets River | 1 | 1 | 2 | 2 | 2 | 2 |
| ROCK | Rock Island Dam | 1 | 1 | 2 | 1 | 2 | 1 |
| SPOK | Spokane River | 1 | 1 | 1 | 2 | 2 | 2 |
| WALLA | Walla Walla River | 1 | 1 | 2 | 1 | 2 | 1 |
| WASH | Lake Washington | 1 | 0 | 0 | 1 | 1 | 0 |
| YAK | Yakima River | 1 | 1 | 2 | 2 | 2 | 1 |
| REPLCR | Field Replicate | 1 | 0 | 1 | 1 | 1 | 1 |
| REPSPOK | Field Replicate | 1 | 0 | 0 | 1 | 1 | 1 |
| REP(rotating)[c] | Field Replicate | 1 | 0 | 1 | 1 | 1 | 1 |
| EXXFAIR[d] | Air Exposure Blank | 0 | 3 | 3 | 3 | 3 | 3 |
| **Total** | | **11** | **10** | **18** | **18** | **21** | **16** |

a. Samples may or may not be analyzed for all parameters.
b. Field trip blanks are analyzed for all parameters.
c. REP(rotating) = field replicate will be rotated yearly.
d. EXXFAIR = extended exposure field air blanks.

Table 5. 2009 Spring Laboratory Blanks Summary.

| EST QC Blanks | # of CL PEST | # of PBDE | # of PAH | # of PCB Cong. |
|---|---|---|---|---|
| DAY0-DIAL | 3 | 3 | 3 | 3 |
| DIALNOSPK[a] | 0 | 2 | 2 | 2 |
| SOL-GPC[a] | 0 | 1 | 1 | 1 |
| FRDAY0 | 0 | 3 | 3 | 3 |
| SPIKEBLK[b] | held frozen | | | |
| SOLVNTBLK[b] | held frozen | | | |
| PRCSOLN[b] | held frozen | | | |
| SURROSOLN[b] | held frozen | | | |
| **Total** | **3** | **9** | **9** | **9** |

a. Analyzed for PCB congeners in fall 2008.
b. Held frozen at MEL. May be analyzed, if needed, to help locate sources of contamination.

# Schedule

Table 6. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

| | |
|---|---|
| Field and laboratory work | |
| Field work completed | April – September 2009 |
| Laboratory analyses completed | August – December 2009 |
| Environmental Information System (EIM) system | |
| EIM data engineer | Callie Meredith |
| EIM user study ID | SPMDTR09 |
| EIM study name | WSTMP SPMD Trend Monitoring |
| Data due in EIM | July 31, 2010 |
| Final report | |
| Author lead | Patti Sandvik |
| Schedule | |
| Draft due to supervisor | March 31, 2010 |
| Draft due to client/peer reviewer | April 30, 2010 |
| Draft due to external reviewer(s) | NA |
| Final report due on web | July 31, 2010 |

# References

Era-Miller, 2008. Potholes Reservoir Assessment of Dieldrin and Other Chlorinated Contaminants. Washington State Department of Ecology, Olympia, WA. Publication No. 08-03-101. www.ecy.wa.gov/biblio/0803101.html.

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Johnson, A., K. Seiders, C. Deligeannis, K. Kinney, P. Sandvik, B. Era-Miller, and D. Alkire, 2006. PBDEs Flame Retardants in Washington Rivers and Lakes: Concentrations in Fish and Water, 2005-06. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-027. www.ecy.wa.gov/biblio/0603027.html.

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Sandvik, Patti, 2009. Trends Monitoring for Chlorinated Pesticides, PCBs, and PBDEs in Washington Rivers and Lakes, 2007. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-013. www.ecy.wa.gov/biblio/0903013.html.

# Appendix: Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this document.

| | |
|---|---|
| AP | Analytical Perspectives |
| CL PEST | Chlorinated pesticide |
| Ecology | Washington State Department of Ecology |
| EIM | Environmental Information Management database |
| EPA | U.S. Environmental Protection Agency |
| EST | Environmental Sampling Technologies |
| MEL | Manchester Environmental Laboratory |
| PAH | Polycyclic aromatic hydrocarbon |
| PBDE | polybrominated diphenyl ether |
| PBT | Persistent, bioaccumulative, toxic chemical |
| PCB | polychlorinated biphenyl |
| QA | Quality assurance |
| QC | Quality control |
| SOP | Standard operating procedure |
| SPMD | Semi-permeable membrane device |