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State of Washington

Quality Assurance Project Plan

Trend Monitoring for Organic PBTs in Washington Rivers and Lakes

October 2010

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Waterbody Numbers:	Columbia River near Clatskanie	WA-CR-1010
	Lake Washington	WA-08-9340
	Queets River	WA-21-1030
	Spokane River	WA-54-1020
	Walla Walla River	WA-32-1010
	Yakima River	WA-37-1010

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Quality Assurance Project Plan

Trends Monitoring for Organic PBTs in Washington Rivers and Lakes

October 2010

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TSU: Toxics Studies Unit
EAP: Environmental Assessment Program.
EIM: Environmental Information Management database.

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Abstract

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance (QA) Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

Ecology began monitoring 11 rivers and one lake in 2007 as part of a statewide trends program for persistent, bioaccumulative, toxic (PBT) chemicals. Monitoring has continued statewide twice a year, once in the spring and again in the fall, targeting high-flow and low-flow periods. Ecology selected waterbodies for monitoring to represent present and historical contamination from a range of land use types.

Ecology estimated levels of organic contaminants in water by passive sampling technology using semi-permeable membrane devices (SPMDs). Chemicals monitored include chlorinated pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs).

Ecology begins its fourth year of sampling for the organics trends component of the PBT Trends effort in the spring of 2010. Waterbodies being monitored include the Spokane, Yakima, Walla Walla, Columbia (two sites), and Queets Rivers and Lake Washington. Except for the Queets River reference site, these waterbodies have elevated levels of toxic chemicals. Ecology plans continued monitoring to assess trends in contamination levels for these and possibly other waterbodies.

This QA Project Plan describes revisions for the long-term continuation of this trend monitoring program. A revised QA Project Plan was needed to address issues discovered during the first three years of sampling, 2007-09. Revisions include comparability with other work, improved data quality, changes in methodology, and the addition of PAH analysis.

Background

The Washington State Department of Ecology (Ecology) initiated a persistent bioaccumulative toxic (PBT) reduction strategy for toxic chemicals in 2000. The initiative targets slow degrading chemicals that can travel long distances, tend to build up in tissues, and have adverse health effects on humans, fish, and wildlife. At this time, there are 27 substances on the PBT list (Appendix A). More information about Ecology's PBT Initiative can be found at www.ecy.wa.gov/programs/swfa/pbt.

Ecology started the Washington State Toxics Monitoring Program (WSTMP) in 2000 to investigate the occurrences and concentrations of toxic chemicals in the state's waterbodies. One objective of WSTMP was to conduct trend monitoring for PBT chemicals. Johnson (2007a) developed a PBT Trends Study plan for monitoring temporal trends. Sampling began in 2007. Target analytes included chlorinated pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Polycyclic aromatic hydrocarbons were added to the program in 2008 (Meredith and Furl, 2008). Information about WSTMP can be found at www.ecy.wa.gov/programs/eap/toxics/wstmp.htm.

Monitoring for the organic trends component involves sampling two times a year at waterbodies throughout Washington State. In 2007 and 2008, 12 sites were sampled: 11 major rivers and one large urban lake. In 2009, eight river sites and one lake were sampled.

Standardized passive samplers called semi-permeable membrane devices (SPMDs) were successfully deployed for approximately one month in the spring and one month in the fall. SPMDs were used to concentrate and quantify target chemicals over time. Results for the first two years were published (Sandvik, 2009; 2010) as part of the WSTMP Trends Monitoring component.

The ability of SPMDs to detected low levels of chemical concentrations is apparent from the results of the first two years of sampling. Dissolved water concentrations were estimated and compared among sites and between sampling periods, showing close similarities. Table 1 shows where and when maximum concentrations were found during 2007 and 2008.

Table 1. Location of Maximum Concentrations Observed in 2007 and 2008.

Parameter	pg/L[1]	Location
2007 - Spring		
Chlorpyrifos	3800	Walla Walla R.
Toxaphene	1200	Walla Walla R.
Hexachlorobenzene (HCB)	34	Walla Walla R.
Total Chlordane[2]	23	Walla Walla R.
Heptachlor Epoxide	19	Walla Walla R.
Lindane	760	Walla Walla R.
Dacthal	30	Middle Columbia R.
Endosulfan I	2700	Yakima R.
Endosulfan-II	1200	Walla Walla R.

Parameter	pg/L[1]	Location
∑LPAH[5]	na	na
∑PAH[7]	na	na
2007 - Fall		
Endosulfan Sulfate	2700	Walla Walla R.
Pentachloroanisole (PCA)	29	Spokane R.
Dieldrin	71	Yakima R.
DDMU[3]	33	Upper Columbia R.
Total DDT[4]	340	Upper Columbia R.
Total PCBs	80	Spokane R.
Total PBDEs	180	Spokane R.
∑HPAH[6]	na	na
2008 - Spring		
Chlorpyrifos	2,500	Walla Walla R.
Toxaphene	1,100	Walla Walla R.
Hexachlorobenzene (HCB)	47	Walla Walla R.
Total Chlordane[2]	39	Walla Walla R.
Heptachlor Epoxide	19	Walla Walla R.
Lindane	460	Walla Walla R.
Dacthal	40	Spokane R.
Endosulfan I	10,000	Walla Walla R.
Endosulfan-II	3,000	Walla Walla R.
Endosulfan Sulfate	980	Walla Walla R.
DDMU[3]	14	Upper Columbia R.
Total PCBs	110	Spokane R.
∑LPAH[5]	5,100	Snohomish R.
∑PAH[7]	6,500	Lake Washington
2008 - Fall		
Pentachloroanisole (PCA)	37	Duwamish R.
Dieldrin	63	Yakima R.
Total DDT[4]	230	Upper Columbia R.
Total PBDEs	220	Spokane R.
∑HPAH[6]	2,700	Lower Columbia R.

1. Estimated dissolved concentrations.
2. Total Chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.
3. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
4. Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT.
   DDD: p,p'-dichlorodiphenyldichloroethane.
   DDE: p,p'-dichlorodiphenyldichloroethylene.
   DDT: p,p'-dichlorodiphenyltrichloroethane.
5. ∑Total LPAH is low molecular weight PAHs: naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene.
6. ∑Total HPAH (high molecular weight): fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.
7. ∑PAH is the sum of LPAH and HPAH.

na: not analyzed.

In general, results from 2007 and 2008 showed higher concentrations during spring high-flow than during the fall low-flow period. Disagreement between 2007 and 2008 endosulfan results is likely due to the window of time in which it is used. This would apply to chlorpyrifos also, but those results agreed fairly well for 2007 and 2008. Most sites had one or more chemicals of concern above Washington State water quality criteria or U.S. Environmental Protection Agency (EPA) national recommended water quality criteria.

Although passive samplers reduce the variability associated with conventional water and biological samples, contamination in the sampling system threatened to compromise the usefulness of sample results. In 2009, corrective actions were taken, and additional quality-control measures were implemented to define and reduce sampling and laboratory variability.

An abbreviated plan was developed for the spring sampling in 2009 (Seiders and Sandvik, 2009) to guide development of standard operating procedures (SOP) for processing, reporting, and defining variability of SPMD data using additional quality control. Results from the 2009 samples are currently being assessed, and the SOP is under development.

This Quality Assurance (QA) Project Plan includes revisions to the original QA Project Plan (Johnson, 2007a) for the long-term continuation of this trend monitoring program. Revisions include:

- Adding PAHs as target analytes per the 2008 addendum (Meredith and Furl, 2008) to the original QA Project Plan.
- Revising the number of sample sites and analytes.
- Updating analytical methods for some analytes.
- Including additional quality-control and QA procedures.
- Documenting reference to SOPs for SPMD deployment and data reduction methods.
- Incorporating standardized data management and reporting practices.

Project Description

The goal of this project is to determine changes in levels of chlorinated pesticides, PCBs, PAHs, and PBDEs over time in Washington rivers and lakes. Results may be helpful in evaluating whether actions designed to reduce inputs of these chemicals are effective. Beginning in the spring of 2007, this project has monitored up to 11 major Washington rivers and one lake twice a year.

Ecology selected sampling sites where contaminant levels were elevated, sometimes resulting in fish consumption advisories. Background information about contamination of these sites can be found in Appendix B. Starting in the spring of 2010, some sites were discontinued because the level of contamination was low and the ability to detect trends unlikely. Sites dropped are the Snohomish, Duwamish, Wenatchee, and Okanogan Rivers, as well as Rock Island and McNary Dams on the Columbia River.

This study focused on sites and analytes likely to provide the most useful information. The Lower Columbia mainstem will be monitored along with three tributaries: the Spokane, Yakima, and Walla Walla Rivers. Additionally, one large urban lake in Puget Sound, Lake Washington, and one undeveloped river in the Olympic National Park, Queets River, will be sampled. Sites may be added or dropped as new information and resources become available.

A passive sampling technique using an SPMD is employed to reduce variability in the data and improve the ability to detect trends. The SPMDs are deployed for one month in the spring and one month in the fall to provide time-weighted average concentrations for the chemicals of interest. Studies in Washington State have shown that peak levels of these chemicals tend to occur during these two periods.

The success of this trend monitoring project hinges on consistent application of field and laboratory procedures. This project requires coordinating quality-control/QA among several different laboratories working on the same samples. The project manager will provide instructions to each laboratory regarding blanks, spikes, and the handling of each sample based on Ecology's operating standards. The laboratories must adhere closely to the methods and procedures described in this QA Project Plan. They will notify the project manager in advance of any proposed changes in procedures.

This QA Project Plan was prepared following the Ecology guidelines in Lombard and Kirchmer (2004).

Organization and Schedule

The following people are involved in this project (Table 2 and 3). Most are employees of the Washington State Department of Ecology.

Table 2. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies Waste 2 Resources Program Phone: 360-407-7398	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Patti Sandvik Toxic Studies Unit, SCS Phone: 360-407-7198	Author, Project Manager, Principal Investigator	Writes the QAPP. Trains field staff. Oversees field sampling and transportation of samples to the laboratory. Helps develop contacts with non-Ecology laboratories. Coordinates efforts of multiple analytical laboratories. Reviews laboratory data and quality-control efforts. Interprets and manages data. Writes the draft and final report.
Tighe Stuart EOS Phone: 509-329-3476	Field Assistant	Helps collect samples and records field information in the Eastern Washington region.
Kristin Carmack EOS Phone: 509-454-4243	Field Assistant	Helps collect samples and records field information in the Central Washington region.
Jenna Durkee EOS Phone: 509-454-7865	Field Assistant	Helps collect samples and records field information in the Central Washington region.
Callie Meredith Toxic Studies Unit, SCS Phone: 360-407-6965	Data Engineer	Enters results into EIM.
Keith Seiders Toxic Studies Unit, SCS Phone: 360-407-6689	Technical Assistance	Assists with field work, laboratory coordination, SPMD data reduction, QA reviews, reviewing draft reports.
Dale Norton Toxic Studies Unit, SCS 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 SCS Phone: 360-407-6698	Section Manager for the Project Manager and Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: 360-871-8801	Director	Approves the final QAPP. Ensures quality and timely services from Manchester Laboratory, i.e. laboratory coordination, analyses, results, and data packages.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

Staff (all are EAP except client)	Title	Responsibilities
Terri Spencer Environmental Sampling Technologies, Inc. Phone: 816-232-8860	Manager	Prepares and extracts SPMDs.
Yves Tondeur Analytical Perspectives Phone: 910-794-1613	President and CEO	Reviews and approves contracts and laboratory results.
Todd Vilen Analytical Perspectives Phone: 919-260-1119	Project Manager	Conducts laboratory analysis for SPMD extracts.

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

Table 3. 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	June & October 2010, annually	Patti Sandvik
Laboratory analyses completed	April 2011, annually	
Environmental Information System (EIM) database		
EIM user study ID	SPMDTR10 (SPMDTRXX, where XX = sample year)	
EIM study name	Washington State Toxics Monitoring Program (WSTMP), Semipermeable Membrane Devices (SPMDs) Trends Monitoring.	
Product	Due date	Lead staff
EIM data loaded	October 2011, annually	Callie Meredith
EIM quality assurance	November 2011, annually	Jenna Durkee
EIM complete	December 2011, annually	Callie Meredith
Final report		
Author lead / Support staff	Patti Sandvik	
Schedule		
Draft due to supervisor	September 2011, annually	
Draft due to client/peer reviewer	October 2011, annually	
Draft due to external reviewer(s)	(not applicable)	
Final (all reviews done) due to publications coordinator	November 2011, annually	
Final report due on web	December 2011, annually	

Quality Objectives

Manchester Laboratory and their contractors are expected to meet quality-control requirements of methods selected for the project. Quality control procedures used during field sampling and laboratory analyses will provide data for determining the accuracy of the monitoring results. Tables 4 shows the measurement quality objectives (MQOs) for the methods selected for sample analysis.

Table 4. Measurement Quality Objectives.

Analysis	Check Standards/ Lab Control Samples (% recovery)	Laboratory Duplicates (RPD[1])	Surrogates[2] (% recovery)	Matrix Spike[3] (% recovery)	Lowest Concentration of Interest (RL)[4]
Chlorinated pesticides	50-150%	±40%	30-130%	50-150%	10 ng/sample
PAHs	40-150%	±40%	50-150%	30-150%	10 ng/sample
PBDEs	50-150%	±50%	50-150%	50-150%	2 ng/sample[5]
PCB native congeners[6]	na	na	50-150%	na	0.1 ng/sample
PCB native congeners[7]	50-150%	±50%	na	na	0.1 ng/sample
PCB labeled congeners[7]	30-140%[8]	na	25-150%[9]	na	0.1 ng/sample
Total organic carbon	80-120%	±20%	na	75-125%[10]	1 mg/L
Total suspended solids	80-120%	±20%	na	na	1 mg/L

1. Relative percent difference.
2. Surrogate recoveries are compound or congener specific.
3. Spiked at the extraction lab but analyzed in another lab.
4. RL = reporting limit. Split samples multiply reporting limits.
5. PBDE-47, 49, 66, 71, 99, 100 RL = 2 ng/sample; PBDE-138, 153, 154, 183, 184, 191 RL = 4 ng/sample; PBDE-209 RL = 10 ng/sample.
6. Unlabeled PCB congeners that are spiked into membranes before Environmental Sampling Technologies extraction in addition to the labeled congeners of method 1668A.
7. As prescribed in Method 1668A.
8. LCS: PCB-001L and -003L = 15% - 140% recovery.
9. Sample quality control: PCB-001L and -003L = 15% - 150% recovery.
10. True matrix spike = spiked and analyzed at the analyzing lab.

na: not applicable.

The MQOs for precision and bias correspond to Manchester Laboratory's Action Limits. The MQO for recovery of native and labeled congeners in the PCB analysis is the quality control limit specified in Method 1668A. PCB surrogate recovery is in addition to Method 1668A MQO. Data outside these limits will be evaluated for appropriate corrective action.

Surrogates and Matrix Spikes

Surrogates are compounds with characteristics similar to target compounds. These surrogates will be added to all SPMD membranes prior to extraction. Recovery of surrogate spikes can be used to estimate the recovery of target compounds in the samples.

Environmental Sampling Technologies will provide field quality SPMD membranes for matrix spikes. Manchester Laboratory will provide the matrix spike solution. The matrix spikes may provide an indication of bias due to interferences from components in the sample. To reduce cost, there will be no duplicate matrix spikes, and Manchester will not run a separate matrix spike or matrix spike duplicate (MS/MSD) for their procedure, except for total organic carbon (TOC) as is routinely done.

The PCB analysis for this study is by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) using labeled congeners. The 12 PCBs designated as toxic by the World Health Organization (also known as dioxin-like PCBs), and the earliest and latest eluted congener at each level of chlorination, are determined by isotope dilution quantitation. The remaining congeners are determined by an internal standard quantitation technique.

Surrogates and matrix spikes are not part of the isotopic dilution method for PCB congeners (Method 1668A). Instead, labeled compounds will be added at the extraction laboratory prior to extracting the SPMDs. Previously, recovery of PCBs through the entire procedure (dialysis, cleanup, and analysis) was assessed using selected unlabeled PCB congeners as surrogates. PCB recovery will be assessed with an ongoing precision and recovery (OPR) of selected congeners (see *Quality Control Procedures* section).

Other Quality Control Samples

Check standards and laboratory control samples contain known amounts of analyte and indicate bias due to sample preparation and calibration. These quality-control samples apply to the analyzing laboratories only: Manchester Laboratory and Analytical Perspectives Laboratory.

Precision of the SPMD data for the present study will be assessed with field replicates rather than laboratory duplicates. However, analyzing laboratories will process laboratory control sample duplicates for determining precision in the analyzing procedures. More details are in the *Quality Control Procedures* section.

Blanks are particularly important quality-control samples for low-level analyses where results are expected near detection limits. Various method blanks will be analyzed along with all samples to measure any response in the analytical system for target analytes. Method blanks have an expected theoretical concentration of zero. Field blanks are used to detect contamination which could be interpreted as bias or sampling variability. Sources of contamination include: containers, sample equipment, environmental surroundings, preservatives, transportation, storage, handling, other samples, or laboratory analysis.

The lowest concentrations of interest for the organic analytes are the reporting limits based on the estimated quantitation limits (EQL: lowest validated standard in calibration curve) that Manchester Laboratory or their contractors have achieved in analyzing SPMD extracts in the past. These have been adequate to quantify the target compounds in waterbodies with low levels of contamination.

Sampling Design

Monitoring Sites

During 2010, this study will continue monitoring six of the original 12 waterbodies using SPMDs. The six sites to be sampled during May and September are shown in Figure 1.

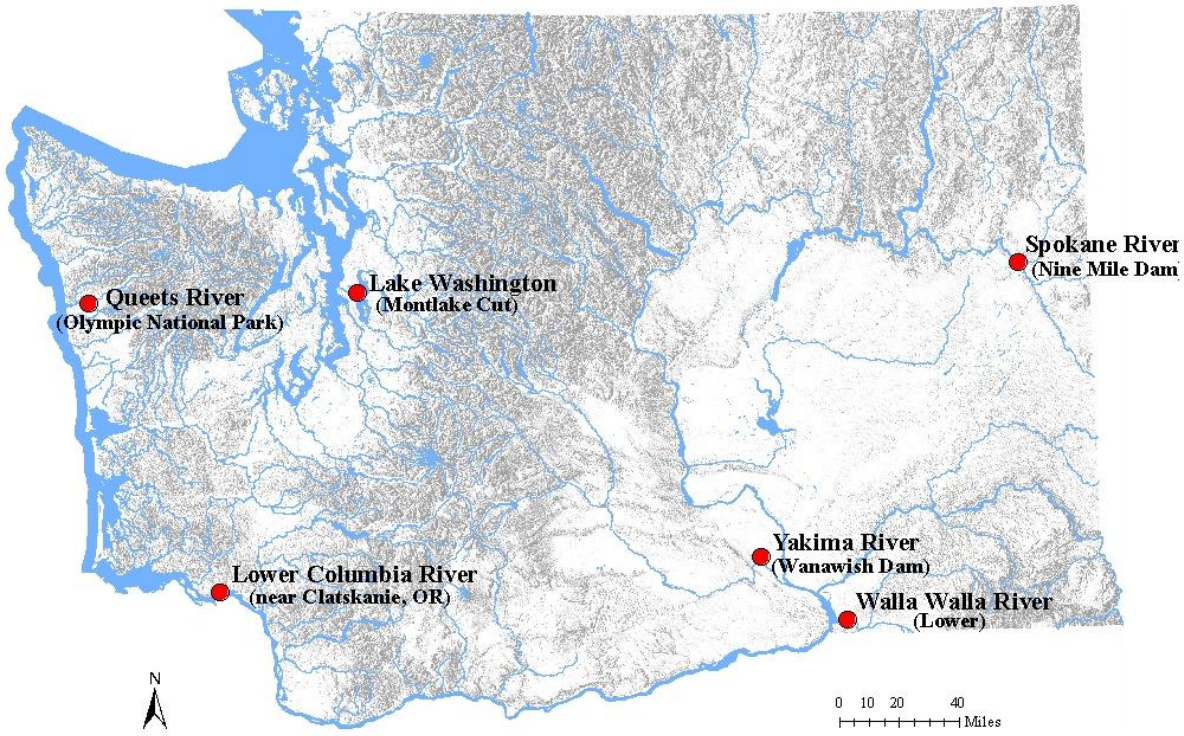

Figure 1. PBT Trends Monitoring Sites for 2010.

These waterbodies were selected based on the following considerations:

- Levels and types of contaminants reported in fish.
- 303(d) listings and TMDL status[1].
- Fish consumption advisories.
- Availability of a secure sampling site.
- Expectation that detectable changes in water quality are deemed likely to occur.
- Representative of statewide distribution of sampling effort.

[1] The 303 (d) listings are federal Clean Water Act required listings of impaired waterbodies. Total maximum daily loads (TMDLs) are cleanup plans for impaired waters.

Sites selected for the 2010 sampling events include: (1) four sites in the Columbia River drainage; the Lower Columbia, Yakima, Walla Walla, and the Spokane Rivers, (2) Lake Washington in the Puget Sound basin, and (3) the Queets River reference site in the Olympic National Park. Most sites are located near the mouths of watersheds to capture an integrated overview of contaminant loading in the watershed.

Location descriptions of the monitoring sites are in Appendix C.

To maintain statewide and analyte representativeness, assessment will be made for site and sampling revisions as new information becomes available. After a minimum of four sampling years (spring and fall sampling periods), results will be assessed on a site- and parameter-specific basis. Statistical trend testing will begin after the fourth year of data collection. Certain sites or analyses will be dropped if ability for trend detection is negligible. Additionally, new sites, different locations in a waterbody, or timing of sample collection may be added to address concerns of toxic chemicals found in other areas or at different times for chemical peaks. Recommendations for changes will be noted in the annual reports prior to implementing a study revision.

Passive Sampling

A passive sampling technique employing SPMDs is used to provide time-weighted (28-day) average concentrations for the chemicals of interest. SPMDs are designed to mimic the bioconcentration of organic pollutants from water by aquatic organisms without the variability introduced by movements, growth, and spawning of fish (Huckins et al., 2006; USGS, 2008). Large chemical residues accumulated in SPMDs give a strong analyte signal, translating into parts-per-trillion detection limits or lower.

In water, the amount of chemical absorbed by an SPMD is proportional to the dissolved concentration in the local water column. Total or whole water chemical concentrations determined from SPMDs are estimates based on organic carbon-water equilibrium partitioning (K_{oc}).

To account for the effects of water temperature, water velocity, and biofouling on SPMD sampling rates, permeability/performance reference compounds (PRCs) are used as an in-situ calibration method. PRCs are (analytically) non-interfering compounds with moderate to high tendency to escape and do not occur in significant concentrations in the environment. The rate of PRC loss while exposed during a sampling period is related to the uptake of the target compound. Based on studies by Huckins et al. (2002), the difference between measured concentrations of an analyte and the PRC-derived estimates should be within a factor of 2.

Details of SPMD theory, construction, and applications can be found at wwwaux.cerc.cr.usgs.gov/SPMD/index.htm and in Huckins et al. (2006).

For this study, PCB-004, PCB-029, and PCB-050 will be used as PRCs. These PCBs are not found in significant amounts in commercial PCB mixtures or environmental samples. Environmental Sampling Technologies will spike each SPMD membrane with PRCs prior to their being deployed in the field, including in the field trip blank and their other quality-control

blanks (see the *Quality Control Procedures / Laboratory* section). Loss rates should be 20-80%. The spiking level will be 10 ng of PCB-004, and 5 ng of PCB-025 and PCB-050 per SPMD membrane resulting in 50 ng (PCB-004) and 25 ng (PCB-025, -050) per sample. (Refer to *Quality Control Procedures / Laboratory* section.)

Sample Timing and Procedures

The SPMDs are deployed for approximately 28 days in May - June (spring) and September - October (fall). Deployments during these periods captured typical seasonal high-flow (spring) and low-flow (fall) conditions for the rivers (Figure 2). For Lake Washington, these sampling events capture the higher water level (pre-stratification beginning in April) and lower water level (strong stratification in the fall) (King County, 2003). Previous studies in Washington have shown that peak levels of the target chemicals tend to occur during these periods (Johnson et al., 2004; Johnson and Norton, 2005).

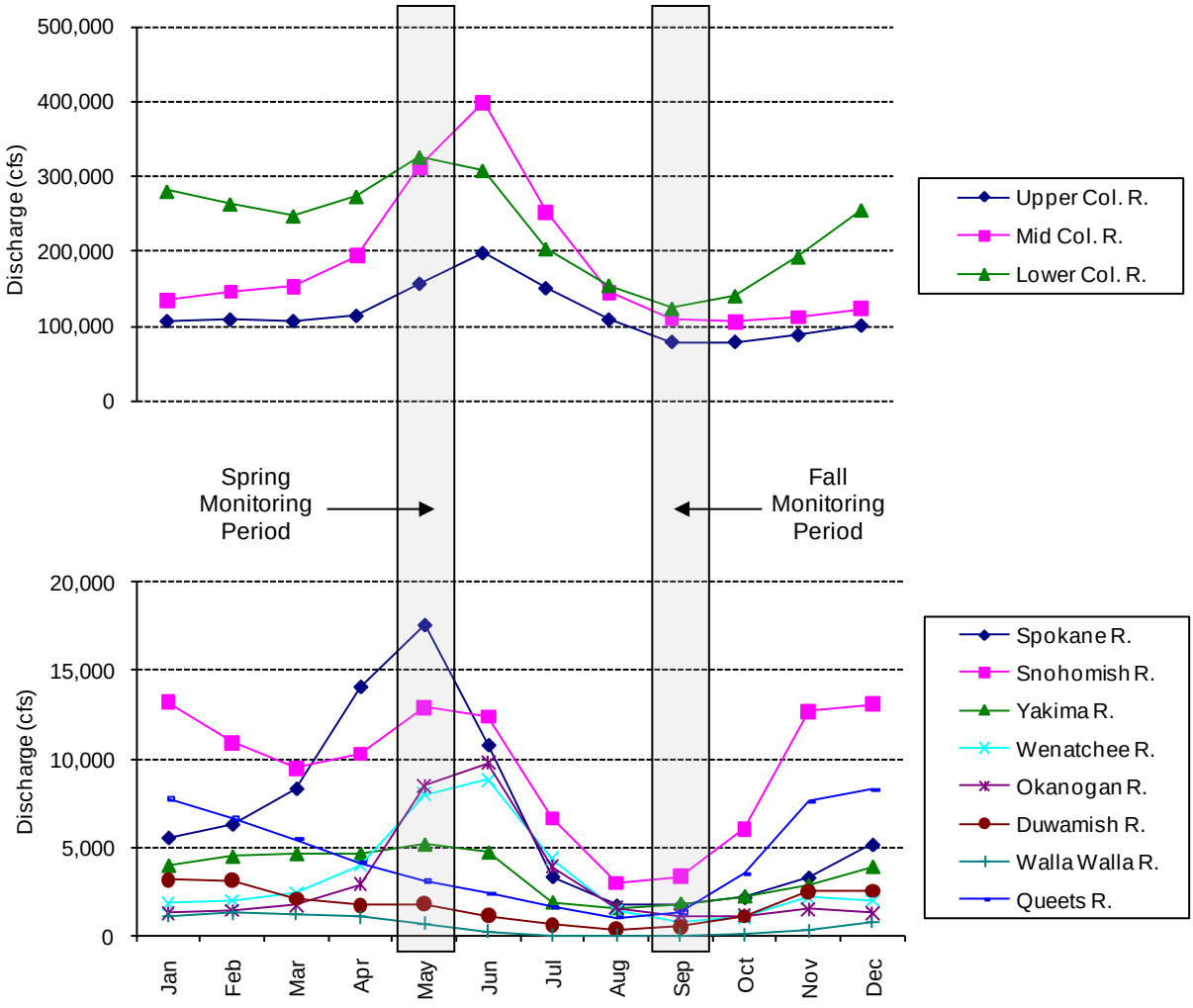

Figure 2. Annual Streamflow Pattern for the 11 River Monitoring Sites.

One SPMD sampler is placed at each monitoring site in a well-mixed location and away from known point sources of the chemicals of interest. For deepwater sites, the SPMDs are positioned in the top 20 feet of the water column, above the summer thermocline. For shallow water, the SPMDs are placed approximately one foot above the bottom.

During each monitoring period, field-replicate samplers are deployed and field trip blanks are exposed to ambient air at selected sampling sites. The replicate site is chosen after reviewing results from previous years and needs for additional data at particular sites. Field trip blanks are exposed during deployment and retrieval to assess background air contamination. Replicates and blanks are further discussed below in the *Quality Control Procedures* section.

Chemical Analyses

Table 5 shows the target analytes, sampling methods, and timing of collection. Appendix D lists all individual target compounds.

Table 5. Parameters Monitored.

<table>
<tr><th rowspan="2">Parameter</th><th rowspan="2">Sampling Method</th><th colspan="3">SPMD Sampling Timeframe</th></tr>
<tr><th>Deployment</th><th>Midcheck[1]</th><th>Retrieval[2]</th></tr>
<tr><td>Chlorinated pesticides</td><td rowspan="4">SPMDs[3]</td><td colspan="3" rowspan="5">Continuous[4]</td></tr>
<tr><td>PCB congeners</td></tr>
<tr><td>PBDEs</td></tr>
<tr><td>PAHs</td></tr>
<tr><td>Water temperature</td><td>TidbiTs[5]</td></tr>
<tr><td>Total organic carbon</td><td rowspan="2">Grab[6,7]</td><td>X</td><td>X</td><td>X</td></tr>
<tr><td>Total suspended solids</td><td>X</td><td>X</td><td>X</td></tr>
<tr><td>Water temperature</td><td rowspan="2">Field measurement[6,7]</td><td>X</td><td>X</td><td>X</td></tr>
<tr><td>Conductivity</td><td>X</td><td>X</td><td>X</td></tr>
</table>

1. Midcheck: checking on SPMDs approximately two weeks after deployment.
2. Retrieval: retrieving SPMDs from sampling site approximately four weeks after deployment.
3. SPMD: semipermeable membrane devices.
4. Passive monitoring: continuous sample collection.
5. TidbiTs: Onset Computer Corporation Hoboware temperature loggers.
6. Active monitoring: instantaneous sample collection such as a grab sample.
7. Samples collected at or near SPMD locations and at or near the same time period.

The PBT chemicals are sampled using the SPMD passive sampler. Whole-water grab samples are collected at the beginning, middle, and end of the SPMD deployment period. The grab samples are analyzed for TOC and total suspended solids (TSS). Field measurements include conductivity and temperature. Streamflows are determined from data bases such as USGS real-time gaging stations and online hydro-power discharge information.

Sampling Procedures

Ecology's most current standard operating procedures (SOPs) will be used for collecting and processing samples, processing results, and for minimizing the spread of invasive species from areas of moderate or extreme concern (Table 6). The SOP for SPMD data reduction is under development and is scheduled for completion in early 2011. Any new or updated SPMD SOPs will incorporate the guidance in Huckins et al. (2006). Ecology's SOPs are located at www.ecy.wa.gov/programs/eap/quality.html.

Table 6. Standard Operating Procedures for Sample Collection and Processing.

Method	Parameters	Reference to Ecology SOPs[1]
SPMDs Planning and Deployment	Chlorinated pesticides, PAHs, PBDEs, PCB congeners	Johnson 2007b, Sandvik and Seiders 2010
Grab Sample	TOC, TSS grab samples	Joy 2006
	Water temperature	Nipp 2006
	Conductivity	Ward 2007
TidbiTs	Water temperature	Bilhimer and Stohr 2009
GPS, GIS, or EIM	Sample site coordinates	Janisch 2006 (GPS)
Invasive Species Prevention	Minimizing the spread of invasive species	Parsons et al. 2010, Ward et al. 2010

1. The most current SOPs will be incorporated with this QA Project Plan.

SPMDs will be purchased from Environmental Sampling Technologies. Standard SPMD membranes are composed of a thin-walled, lay-flat polyethylene tube (91.4 x 2.5 cm x 70-95 µm thickness) filled with 1 mL of neutral lipid triolein (purity 99.9%) and mounted onto a spider carrier device in a clean room environment (Figure 3). Five membranes will be used for each sample to ensure that sufficient residues are obtained for chemical analysis. Mounted membranes are stored, shipped, and kept frozen in solvent-rinsed metal cans filled with argon gas until deployed. SPMDs are transported to the field on ice.

Field Deployment

At the sampling site, equipment is prepared for suspension of the SPMD device from a surface structure or anchored to the bottom. The SPMDs will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for anticipated fluctuations in water level. For deep-water sites, the SPMDs are positioned in the top 20 feet of the water column, above the summer thermocline. During preparation, a TidbiT™ temperature monitoring logger is attached to the SPMD canister to log water temperature every two minutes. Another TidbiT™ is secured nearby to measure ambient air temperature.

Figure 3. Standard SPMD Membrane Mounted on a Spider Carrier.

The cans containing the SPMDs will be carefully opened, and five SPMD membrane carriers will be slid into each canister. Field personnel will wear nitrile gloves and not touch the membranes. The canister lid will be screwed on and secured with a zip tie. Field personnel will wear nitrile gloves and not touch the membranes. Because SPMDs are potent air samplers, this procedure should be done as quickly as possible.

When sampling for PAHs, an additional shade mechanism will be employed to protect the SPMD membranes from loss of PAHs due to photo degradation (Figure 4). Canisters loaded with the SPMDs are quickly secured in the shade device before deployed into the water. All canisters and shade devices will be cleaned and solvent (acetone) rinsed before field deployment following Ecology's *Chemical Hygiene Plan* (Ecology, 2006).

The SPMDs will remain submerged for approximately 28 days as recommended by the U.S. Geological Survey (USGS) and by Environmental Sampling Technologies. During a 28-day deployment, chemical uptake by an SPMD is linear and there are no significant losses of residues.

The retrieval procedure is essentially the opposite of deployment. The cans holding the SPMDs must be carefully sealed, and the SPMDs must be maintained at or near freezing until they arrive at Environmental Sampling Technologies for dialysis and cleanup.

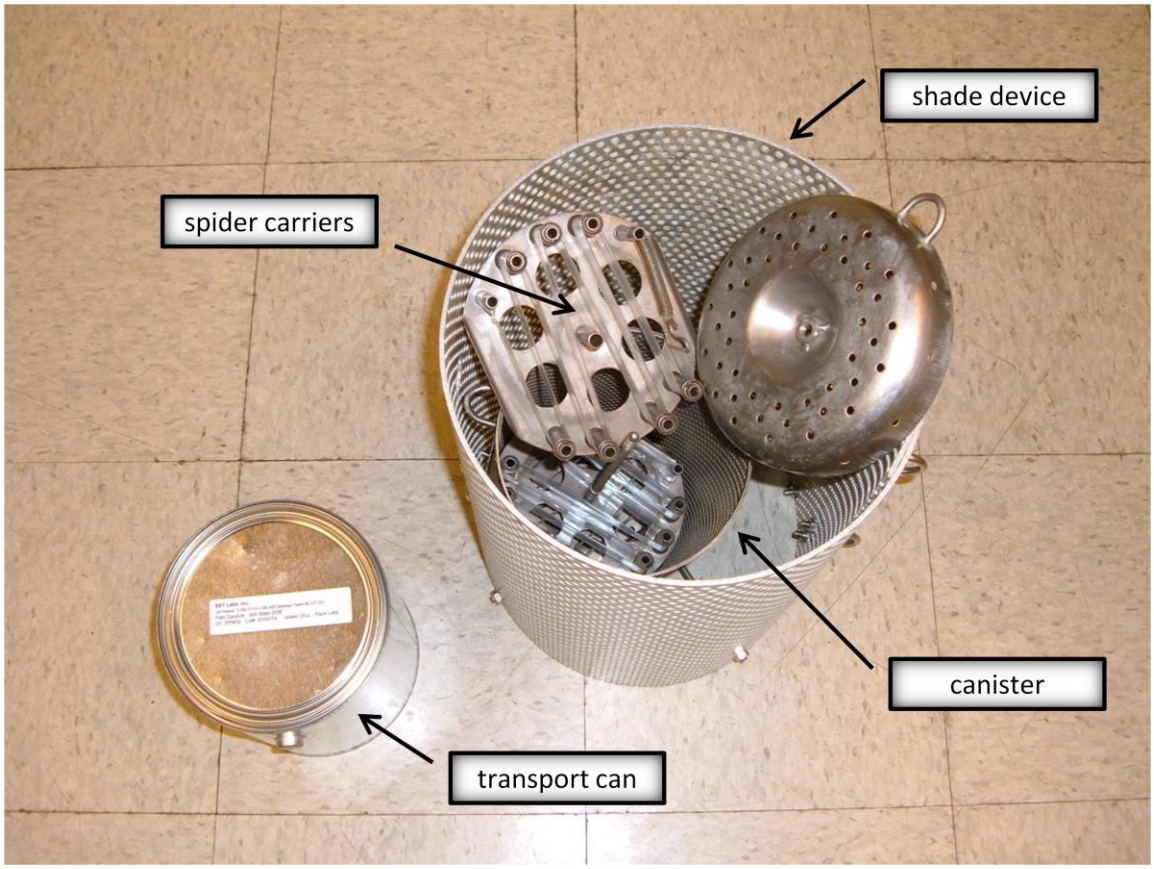

Figure 4. SPMD Sample Equipment.

At deployment, retrieval, and in the middle of the deployment cycle (midcheck), TOC and TSS grab samples as well as conductivity and temperature measurements, are collected from each sample site. TOC and TSS grab samples are collected at least six inches below the water surface, being careful not to disturb bottom sediments in shallow water. In deep water deployments, grab samples are collected at the depth of the SPMD sampler using a Kemmerer or Niskin sampler. Samples will be placed on ice in a cooler immediately following collection. Table 7 list the containers for TOC and TSS obtained from Manchester Laboratory, which are cleaned to analytic-specific standards (MEL, 2008).

Table 7. Container and Holding Times for Water Samples.

Parameter	Minimum Sample Size	Container	Preservation	Holding Time
Total organic carbon	50 mL	60 mL poly bottle	1:1 HCl to pH <2; Cool to ≤4°C	28 days
Total suspended solids	1000 mL	1 L poly bottle	Cool to ≤4°C	7 days

Samples will be identified and labeled with a lab sample number consisting of an assigned work order number from Manchester Laboratory hyphenated with a unique identifying number. Sample location (field station identification name), date, time of sample collection, and parameters will also be noted on the sample tag.

Field log entries include the same information as the sample tags plus manual measurements and observations as outlined on pre-prepared forms. Annual briefings of procedures, equipment handling, and field logs will be done with field staff before the sampling begins or whenever needed.

Current sample site locations for this project are recorded in Ecology's Environmental Information Management (EIM) database. Any sites added in the future will be located by a Global Positioning System (GPS) or Geographic Information System (GIS) and added into EIM. Sites dropped from sampling will remain in EIM.

SPMD membranes will be shipped to Environmental Sampling Technologies by overnight Federal Express, in coolers packed in blue ice. Water samples will be returned to Ecology Headquarters to be transported to Manchester Laboratory the following day. Samples must be kept frozen or near freezing on ice during storage and while being transported. Custody will be maintained at all times for all samples; this is known as chain-of-custody.

Measurement Procedures

Success of this project depends on consistent application and documentation of field and laboratory procedures. The project manager must coordinate the work of field crews and services from three laboratories. Each step of the sampling and analytical process must be documented and communicated accurately to the project manager, laboratories, and among field staff.

After deployment, Environmental Sampling Technologies processes and extracts the SPMDs. Sample extracts are then shipped to Manchester Laboratory for in-house analysis or sent to a laboratory contracted by Manchester. For SPMDs, sample extraction occurs at a different location (Environmental Sampling Technologies) from the actual analysis (by Manchester or contract laboratory).

Table 8 shows target analytes, numbers of samples, reporting limits, and methods used for this 2010 study. Method selection was based on the lowest detection limits available for the proposed analysis.

Table 8. Laboratory Procedures for PBT Trend Monitoring with SPMDs.

Analysis	Number of Field Samples[1]	Expected Range of Results	Reporting Limit (per Sample)	Sample Preparation Method	Analytical Method
Chlorinated pesticides	14	1 - 1,000 ng	10 ng	Dialysis/GPC[2]	EPA 3620, 3665, 8081[3]
PBDEs	14	1 - 1,000 ng	2 ng	Dialysis/GPC[2]	EPA 8270[4]
PAHs	14	1 - 1200 ng	10 ng	Dialysis/GPC[2]	EPA 3630B/8270[4]
PCB congeners	14	1 - 500 ng	0.1 ng	Dialysis/GPC[2]	EPA 1668A[5]
Total organic carbon	36	1 - 10 mg/L	1 mg/L	-	SM5310B
Total suspended solids	36	1 - 10 mg/L	1 mg/L	-	SM2540D

1. Per monitoring period, i.e. spring or fall.
2. Environmental Sampling Technologies SOPs E14, E15, E19, E21, E32, E33, E44, E48.
3. Modifications of EPA SW-846.
4. GC/MS SIM: gas chromatography / mass spectrometry applying selective ion monitoring.
5. HRGC/HRMS: high-resolution gas chromatography / high-resolution mass spectrometry.

After the membranes arrive at Environmental Sampling Technologies, conditions of the membranes are documented as they are cleaned and prepared to process. Membranes are then spiked with PCB extraction standards and pesticide, PBDE, and PAH surrogates. Environmental Sampling Technologies then extracts (also known as dialysis) and performs gel permeation chromatography (GPC) cleanup according to a patented procedure described in Huckins et al. (2006). Environmental Sampling Technologies procedures are documented in SOPs which are on file at Ecology.

Following dialysis and GPC cleanup, the extracts are divided 50:50 (except for single membrane quality-control samples) and sealed in glass ampoules. The ampoules are shipped overnight Federal Express to Manchester Laboratory, where Manchester keeps half of each sample and sends the other half to the contracted laboratory for PCB congener analysis. Single quality-control samples are made for specific analysis and are sent along with samples designated for the same analysis. Laboratories will report SPMD residue results as total (ng/sample) by multiplying the results by the total number of sample portions created from splits: e.g., multiply results by 2 for 50:50 split. Homologue totals or total PCBs (T-PCBs) will be re-calculated by the project manager.

Residue results are then examined with quality-control data, and if blank contamination is present, the Ecology QA Officer will be consulted before correcting any data.

The blank-corrected residue results for each analyte are then translated into a dissolved water concentration using USGS's Estimated Water Concentration model. Currently, this model is version 5. The major inputs to the model include the residue results, results from PRC compounds, Log K_{ow}s (octanol-water partition coefficient constant), and volume of SPMD (volume determined by number of standardized membranes).

Monitoring Costs

The total laboratory cost of analyzing samples for this project is estimated at $36,839 per monitoring period or $73,677 annually (Table 9).

Table 9. Estimated Laboratory Costs for PBT Trends Monitoring with SPMDs.

Lab	Analyses	Field Samples	Field Trip Blanks	EST Quality Control Blanks	Matrix Spike	Number of Analyses	Cost/ Sample	Subtotal
MEL	Chlorinated pesticides	6	0	1	1	8	$249	$1,992
	PBDE	8	3	2	1	14	$170	$2,380
	PAH	8	3	2	1	14	$348	$4,872
EST	Dialysis+GPC	-	-	-	-	-	$542	$10,835
AP	PCB congeners[a]	8	3	3	1	15	$1,063	$15,938
MEL	Total organic carbon[b]	18	0	-	3[c]	18	$34.26	$617
	Total suspended solids[b]	18	0	-	na	18	$11.42	$206
							Estimated Lab Cost per Monitoring Period:	$36,839
							Estimated Annual Lab Cost:	$73,677

MEL: Manchester Environmental Laboratory.
EST: Environmental Sampling Technologies.
AP: Analytical Perspectives Laboratory.
a. Cost/sample is $850 + 25% MEL surcharge: $850 + 212.5 = $ 1062.50.
b. Three samples per station.
c. Matrix spike - no charge.
na: not analyzed.
GPC: gel permeation chromatography.
Costs include 50% discount for analyses done by MEL.
Not included is approximately 5-10% equipment expense.

Approximately 50% of the cost of the project is directed to QA. Because SPMDs are potent air samplers and the results for some chemicals are expected near the reporting limits, many quality-control blank samples are essential to preserve the certainty of the data as much as possible. These include field-replicate samples, field trip blanks, as well as manufacturing, processing, and analyzing blanks.

Quality Control Procedures

The goal for completeness of data is 100%. Data gaps may occur due to various reasons, such as lost samplers, unmanageable contamination of the sampling system, or analytical laboratories not meeting goals for quality control or reporting limits. Minimizing data gaps includes measures such as (1) redeploying a sampler if lost in the field, (2) locating and minimizing sources of contamination, and (3) constant coordination with laboratories to ensure quality control and other goals are being met. Where data gaps do occur, their impact on trend analyses will be considered and addressed.

Comparability of the data will be facilitated through the use of SOPs for field deployments, sample collections, analytical methods, and SPMD data reduction. All procedures will be examined to determine their potential impact on trends analyses. Changes in some analytical procedures may introduce a bias which must be considered in viewing trends.

Field

Field quality-control samples will provide estimates of variability and potential for bias due to contamination during SPMD preparation, deployment, and retrieval. Variability will be measured using replicate field samples. Field and laboratory contamination will be assessed using field trip blanks. Table 10 shows the field quality-control samples for this project.

Table 10. Field Quality Control Samples (per sampling event).

Sample Type	Analysis	Replicates	Field Trip Blanks
SPMD	Chlorinated pesticides	1	0
	PBDEs	2	3
	PAHs	2	3
	PCB congeners	2	3
Water	Total organic carbon	na	na
	Total suspended solids	na	na

na: not analyzed.

Two field-replicate SPMDs will be deployed for each sampling period (spring and fall) to estimate total variability in the field and laboratory. Each replicate contains five SPMD membranes like the field samples and is deployed in a nearby location. Sites that are likely to have the widest variety and highest concentrations of target compounds are selected for replication. Two sites have been chosen for continued replicate sampling (each sampling period): Lower Columbia River and Spokane River. A third site may be included for replication on a rotational basis if the budget allows.

Field Trip Blanks

SPMDs are known to be potent air samplers, and a certain "background level" of contamination appears to exist for PBDEs, PAHs, and PCBs (Huckins et al., 2006; Sandvik, 2010). Field trip

blanks are used to assess sources and levels of contamination as well as correct SPMD residue results for such contamination. Suspected sources of contamination include the polyethylene membrane, lipid inside the membrane, extraction process, and ambient air where SPMD membranes are handled. A variety of blank-correction procedures have been used in the past which makes comparability of results challenging. One effort to standardize blank correction is an SOP for SPMD data reduction as mentioned earlier.

Field trip blanks consist of SPMD membranes manufactured and shipped in airtight cans with the field samples from Environmental Sampling Technologies. These blanks are prepared the same way as the field samples. The five membranes will either be mounted on spider rays like the field-sample membranes or placed loosely in the bottom of a can (membranes are not mounted on spider arrays like the field-sample membranes). The blanks are transported, processed, and analyzed with the field samples.

During or shortly after deployment of the field sample, the field trip blank membranes are exposed to ambient air for the approximate average time the field SPMDs are exposed to air during deployment and retrieval. For mounted membranes, each SPMD is taken out and set on an aluminum foiled tray. For membranes not mounted, the lid of the can is removed and the opened can will be gently moved back and forth to increase air exposure. The amount of time SPMDs are exposed to ambient air during deployment and retrieval is recorded in field logs. Average time exposed has been between 60 and 120 seconds. After exposure, the field trip blank SPMDs are returned and resealed and then stored frozen until retrieval. During retrieval of the samples, the field trip blank is taken back into the field and exposed to the air for the same amount of time (or estimated averaged sample exposure time).

Three field trip blanks will be exposed at selected sites:

1. A site likely to have wide variability and high chemical concentrations (e.g., the Spokane).
2. A site likely to have low variability and low chemical concentrations (e.g., the Queets River).
3. An annual rotational location among the remaining sample sites.

TidbiTs™

Onset StowAway TidbiTs™ are used to measure water and air temperature during the deployment period. These data are used to determine if the SPMDs remain submerged during deployment. One TidbiT™ is attached to the top of each SPMD canister holding the membranes in the water, and another TidbiT™ is secured out of the water nearby. Each TidbiT™ is programmed to record temperature every two minutes. The date and time of deployment and retrieval is recorded to capture the exact monitoring period.

Upon retrieval, the data from the TidbiTs™ are downloaded and charted for comparing the water and air temperature. If the SPMDs were out of the water during the sample period, a spike in the water temperature appears on the graph and follows the same temperature values as the air during the time the SPMDs were exposed to the air. The data from the exposed SPMDs would be rejected.

Other Field Quality Control

All efforts will be made to avoid cross-contamination. Field staff will wear non-talc nitrile gloves throughout the sample collection process. Samples will be identified, recorded, and custody maintained at all times. Guidance can be found in Ecology's SOPs as referred to above.

Any equipment used in collection or processing samples (e.g., canisters, shade devices) will be decontaminated prior to going to the field. Sample equipment will be pressure washed or washed thoroughly with hot tap water and Liquinox detergent. Pesticide grade acetone will follow washing. After decontamination, sampling equipment will be air dried and placed in a new plastic bag until used.

Laboratory

Three laboratories are involved in SPMD preparation, extraction, and analysis. A variety of quality-control procedures are employed by the different laboratories, some of these coordinated while others done independently. The project manager heads the coordination process among the laboratories.

Environmental Sampling Technologies will perform the manufacturing preparation of SPMDs and their subsequent spiking and extraction. Manchester Laboratory will conduct all laboratory analyses except for PCB congeners. The PCB congener analysis will be conducted by a laboratory contracted by Manchester. The contract laboratory must show the ability to produce results with specified reporting limits (as described in the MQOs above) and method blanks with T-PCBs below 1 ng/sample. Details for contracted laboratory services are documented in the *Request for Lab Services* developed between Manchester Laboratory and the contract laboratory.

Table 11 summarizes laboratory quality-control samples to be analyzed for this project. Discussion of SPMD blank samples and spiking solutions follow.

Table 11. Laboratory Quality Control Samples.

Analysis	Method Blanks[1]	Check Std./LCS	Surrogate Spikes[2]	Matrix Spikes	OPR	PCB Extraction Standards	Analytical Duplicates
Chlorinated pesticides	2/batch	1/batch	all samples	1/batch[2]	na	na	na
PBDEs	1/batch	1/batch	all samples	1/batch[2]	na	na	na
PAHs	1/batch	1/batch	all samples	1/batch[2]	na	na	1/batch
PCB congeners	1/batch	1/batch	all samples[3]	na	1/batch	all samples	na
Total organic carbon	1/batch	1/batch	na	1/batch	na	na	1/batch
Total suspended solids	1/batch	1/batch	na	na	na	na	1/batch

1. See text for Environmental Sampling Technologies method blanks.
2. To be spiked at Environmental Sampling Technologies.
3. PCB surrogates may be replaced with ES.

LCS: laboratory control sample.
OPR: ongoing precision recovery.
na: not analyzed.

Manchester Laboratory routinely runs laboratory control samples for TOC and TSS, which will be adequate for the purposes of this study. Manchester will follow SOPs as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2006).

SPMD Blank Samples

The analyzing laboratory will analyze one method blank per batch of sampling parameters to assess potential laboratory contamination. Laboratory check standards will also be analyzed to evaluate analytical precision and bias. Conducting matrix spikes will help determine specific matrix interferences and the effect on the analyte recovery.

For SPMDs, Environmental Sampling Technologies will prepare the following method blanks for each sampling period:

- *Day-zero dialysis* blank is to serve as a reference point for chemical compound loss and to represent background contamination during preparation of SPMDs for field, storage, post-field processing, spiking of membranes, dialysis and gel permeation chromatography (GPC) cleanup. This blank will contain the same amount of membranes as in the field samples (5), and manufactured at the same time.
- *Day-zero method* blank is identical to the field samples in number of membranes (5), prepared at the same time, and spiked the same. It is specifically prepared as the PCB analysis method blank.
- *Ongoing precision and recovery* (OPR) blank consist of five (5) membranes and spiked with labeled and unlabeled PCBs for determining PCB recovery. It is prepared after field deployment along with the matrix spike membranes and processed with the samples.
- *Fresh day-zero* blank is prepared just prior to dialysis. It contains five (5) membranes and serves as a control during extraction and dialysis. This blank may help in determining sources and levels of contamination.
- *Spiking* blank is a single membrane for Manchester Laboratory and another single membrane for PCB analysis if requested. This blank helps to assess contamination of membranes exposed while they are spiked with PRCs, surrogates, and extraction standards at Environmental Sampling Technologies. It is prepared and spiked first and exposed to the laboratory environment during the preparation of the other samples.
- *Solvent* blank is to assess contamination independent of the solvent used in GPC. This blank is prepared at the same time the exposed SPMDs are processed. It is spiked with PRCs and surrogates and goes through GPC along with the samples.

Only the day-zero dialysis blank, day-zero method blank, and OPR will be analyzed. The remaining blanks will be saved frozen at the laboratories and analyzed in the event there is evidence of significant contamination in the samples or other problems needing further investigation. Manchester Laboratory and Analytical Perspectives laboratories will also analyze their own method blanks with each batch of SPMD samples.

Spiking Solutions

Environmental Sampling Technologies will spike PRC, surrogate, and matrix spike compounds into each sample as shown in Table 12. Detailed information will be sent with the spiking solution table to Environmental Sampling Technologies to provide a guide for spiking and laboratory processing of the samples from each sampling event. An example of their bench-sheet guide with sample information can be found in Appendix E.

Table 12. Spiking Solutions.

Spiking Solution	Analysis	Supplier	Compounds	Conc. (ng/uL)	Spiking Amount (per 1 membrane) (uL)	Spiking Level (per extract before splitting) (ng)
PRCs	PCB	EST	PCB--004	0.2	50	50
			PCB-029, -050	0.1		25
Surrogates	Chlorinated Pesticides	MEL	tetrachloro-m-xylene, 4,4-dibromooctafluorobiphenyl	8.0	50	400
	PBDE		Hexabromobiphenyl	8.0	50	400
	PAH	EST	pyrene-D10, acenaphthylene-D8	40	50	2000
	PCB		PCB--014, -078, -186	0.10	50	5.0
ES	PCB	CL	PCB labeled compounds	na	50	2.0
Matrix Spikes	Chlorinated Pesticides	MEL	various compounds	0.8	100	80
	PBDE		various PBDEs	1.0	50	50
	PAH		various PAHs	20	50	1000
OPR	PCB[1]	CL	labeled PCBs	na	100	2.0
			unlabeled PCBs	na		1.0

1. PCB concentrations: 0.02 ng/uL for labeled compounds and 0.01 ng/uL for native compounds.
ES: extraction standards.
EST: Environmental Sampling Technologies.
MEL: Manchester Environmental Laboratory.
CL: contract laboratory for PCB congeners.
na: not available. Solution prepared by contract lab.

PRCs will be spiked into each membrane prior to deployment. PRC compounds will be PCB-004, -029, -050. Surrogates will be spiked into one membrane per sample after deployment but before dialysis. The surrogates for PCB analysis will be PCB-014, -078, and -186 representing the low, middle, and high PCB congener range. Surrogates for chlorinated

pesticides, PBDEs, and PAHs are listed in Table 12. No PRCs or surrogates will be spiked into the matrix spike or OPR membranes.

Environmental Sampling Technologies will do a matrix spike and OPR in two separate SPMD membranes to avoid having PCBs interfere with analysis of chlorinated pesticides. The matrix spiking solutions contain various compounds supplied by the analyzing laboratories. Unlabeled PCBs in the OPR are at half the concentration as the labeled PCB compounds. Matrix spike and OPR extracts will not be split, but instead sent to the respective laboratories.

Data Management Procedures

Data management is a large and critical part of this study. The project manager must keep careful record of each step of the process by documenting or collecting documents for:

- Sampling plans.
- Laboratory contracts.
- Spiking solutions and strategy.
- Field sampling log.
- Sample chain of custody and management.
- TidbiT™ data.
- PRC and surrogate recoveries.
- Quality control sampling and results.
- Blank correction process.

Field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets (Microsoft, 2007) after returning from the field. Data entries will be independently verified for accuracy by another member of the project team.

Environmental Sampling Technologies will provide documentation of the manufacturing and processing, membrane conditions, spiking process, and any deviations that occur.

The data package from Manchester Laboratory will include a case narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the requested analytical method, and an explanation of data qualifiers. Laboratory quality-control results will also be included in the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, check standards/laboratory control samples (LCS) blanks, and ongoing precision and accuracy (ORP) standards/labeled compounds included in the sample batch. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Data from the analyzing contract laboratory will be submitted in electronic format per contract. Manchester Laboratory will give a complete data package as described above to the project manager after it completes a quality-control review.

Results from the project will be published in an annual report. Laboratory data for TOC and TSS will be downloaded directly into EIM from Manchester's data management system. Data entered into EIM follow a formal data review procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

The bulk of project data will be stored in an electronic depository at Ecology. These data include SPMD residue results, laboratory case narratives, quality-control results, membrane manufacturing and processing history, spiking history for each membrane, extract splits and multipliers for results, PRC results, log K_{ow}s used, TidbiT^{TM} data, temperature and conductivity grab sample results, date and time of deployments, field trip blank exposure records, and other field or laboratory notes.

Audits and Reports

Audits

Manchester Laboratory participates in performance and system audits of their routine procedures. Results of these audits are available on request.

Environmental Sampling Technologies has patented and proprietary procedures for the manufacture, preparation, post-deployment processing, and extraction of SPMDs. They have made SOPs available. Questions about their procedures have been addressed satisfactorily by Ecology and, therefore, they are deemed to not require accreditation and audits under Ecology's Environmental Laboratory Accreditation Program.

The PCB analyses are contracted out to a laboratory accredited by Ecology for Method 1668A. The Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports and establishes that the laboratory has the capability to provide accurate, defensible data. Results of on-site assessments and proficiency tests are available from Ecology on request.

Reports

Ecology will prepare an annual report approximately one year after sample collection. A draft report will be prepared for review by the client and other interested parties approximately nine months after sample collection (e.g., 2010 data would be in draft by September 2011). Ecology will finalize the report within one to two months (e.g., November 2011), depending on when review comments are received and editing turnaround.

The annual report will include:

- Maps of the study area showing monitoring stations.
- Coordinates and detailed descriptions of each station.
- Descriptions of field and laboratory methods.
- Discussions of data quality, blank-correction, other data reduction procedures, and the significance of any problems encountered in the analyses.
- Summary tables of the chemical and ancillary data.
- Descriptions of methods used to calculate water column concentrations.
- Evaluations of evidence for temporal trends in the data.
- Recommendations for the next year of monitoring.

Project data will be stored in an organized structure and EIM as previously described. Some project results will be entered into EIM. Access to the final report and data in EIM will be available through Ecology's internet homepage (www.ecy.wa.gov). Access to other project records and data will be made available upon request.

Data Verification

Environmental Sampling Technologies will provide documentation describing the spiking, dialysis, and GPC procedures used on project samples. PRC spikes, pre-dialysis condition, identification, dialysis, clean-up, and any problems encountered with SPMD processing will be described for each sample. A copy of the chain-of-custody form will be returned to Manchester Laboratory along with the SPMD extracts.

Manchester Laboratory will conduct a review of all laboratory data and case narratives. Manchester will verify that:

1. Methods and protocols specified in the QA Project Plan were followed.
2. All calibrations, checks on quality control, and intermediate calculations were performed for all samples.
3. Data are consistent, correct, and complete, with no errors or omissions.

Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. Manchester Laboratory will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

To determine if project MQOs have been met, the project manager will compare results on field and laboratory quality-control samples to the MQOs. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

The project manager will also review the laboratory data packages and Manchester's data verification reports. The project manager will work with Manchester Laboratory to address any concerns with the data, such as errors or omissions. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered. Data verification will be documented in the annual progress reports.

Data Quality (Usability) Assessment

Once the data have been verified, the project manager will determine if the data can be used to make the calculations, determinations, and decisions for which the project was conducted. If the results are satisfactory, data analysis will proceed and include, but not necessarily be limited to, the following.

Dissolved Concentrations

Prior to calculating dissolved water concentrations, sample results are evaluated for usability. If blank contamination appears to be an issue, the Ecology QA Officer will be consulted before correcting any data. Corrected data will be flagged accordingly.

Water column concentrations of dissolved results from SPMD residue will be estimated using the most recent version of the SPMD Water Concentration Calculator model developed by USGS. Currently, this is version 5 dated 11/15/06 and can be found at the USGS website: www.cerc.usgs.gov/Branches.aspx?BranchId=8. The equations will be used for estimating SPMD chlorinated pesticide, PBDE, PCBs, and PAH water concentrations. Total concentrations for these compounds will be estimated using the relationship with TOC developed by Meadows et al. (1998).

The user will verify that the most current version of the calculator is being used and be certain to lock the spreadsheet to prevent accidental changes to underlying formulae. Before each use, the spreadsheet will be tested with a set of verified SPMD parameters and results to ensure that consistent, accurate data are being obtained throughout the project.

Data Analysis

Data analysis for this project continues to be straightforward. For the first several years, the analysis will be limited to examining simple statistical summaries and time-series plots of either the residue (ng/SPMD) or dissolved concentration data (ng/L) for qualitative evidence of increasing or decreasing trends over time. Box-and-whisker plots can be used to identify seasonal differences at each station. A contaminant scoring index for ranking sites was developed for the 2008 SPMD data and will be adjusted annually.

Trends in contaminant levels at a particular site can be assessed with SPMDs by directly comparing absorbed amounts or by estimating water column concentrations. As more data accumulate, the Mann-Kendall trend test for small sample sizes ($N<10$) and the Wilcoxon Rank Sum test will be used to test the null hypothesis that there is no temporal trend in the data vs. the alternate hypothesis of either an upward or downward trend over time. The Wilcoxon Rank Sum is not as robust with respect to outliers as Mann-Kendall, but it has more statistical power. A minimum of four sampling events (four years for each monitoring period) are required for testing.

Total Concentrations

Total concentrations will be compared to Washington State water quality criteria (WAC 173-201A) and EPA national recommended water quality criteria. Federal and state agencies and tribes adopt water quality criteria to protect designated uses (e.g., public water supply, protection of fish and wildlife, and recreational or agricultural purposes). Although the focus of this study is to determine trends, comparing the results with criteria helps put the water quality of the study sites in perspective. At this time, Ecology does not use results derived from SPMDs for the 303(d) Water Quality Assessment.

Using the total concentration of a contaminant is a conservative approach for comparing to water quality standards. The dissolved form is usually considered the chemical fraction for bioconcentration by fish (EPA, 2000). Water quality criteria, however, are framed in terms of the total amount of a chemical. Total chemical concentrations are estimated from the dissolved data as referred to earlier.

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Appendices

Appendix A. Ecology's PBT List

Table A-1. Chemicals and Chemical Groups on Ecology's PBT List (Ecology, 2007).

Metals	Flame Retardants	Banned Pesticides	Organic Chemicals
Methyl-Mercury	PBDE Tetrabromobisphenol A Hexabromocyclododecane Pentachlorobenzene	Aldrin/Dieldrin Chlordane DDT/DDD/DDE Heptachlor Epoxide Toxaphene Chlordecone Endrin Mirex	1,2,4,5 Tetrachlorobenzene Perfluoro-octane Sulfonates Hexachlorobenzene Hexachlorobutadiene Short-chain Chlorinated Paraffins Polychlorinated Naphthalenes

Combustion By Products	Banned Flame Retardants	Banned Organic Chemicals	Metals of Concern
PAHs PCDDs PCDFs PBDD/PBDFs	Hexabromobiphenyl	PCBs	Cadmium Lead

Appendix B. Historical Contamination of Sites Monitored for PBT Trends

Following is an overview of contaminant data for 12 sites monitored from 2007 to 2010.

1. Lower Columbia River near Clatskanie, Oregon

Elevated levels of chlorinated pesticides and PCBs have been reported in the Lower Columbia River (EPA, 2009a; Johnson and Norton, 2005; McCarthy and Gale, 1999). Increasing concentrations of PBDEs were found in Ecology's statewide PBDE (Johnson et al., 2006). Fish consumption advisories or water quality violations for chlorinated pesticides, PCBs, DDT, DDE, dieldrin, and PAHs are listed by Oregon and Washington.

2. Middle Columbia River at McNary Dam

Elevated levels of chlorinated pesticides (p,p' DDE, aldrin, chlordane), PCBs, and dioxins have been reported in fish tissue which have led to 303(d) listings in the area between Rock Island Dam and McNary Dam.

3. Upper Columbia River at Rock Island Dam

The WSTMP found elevated concentrations of PCBs and DDT in fish tissue near Rock Island Dam. 303(d) listings for the upper Columbia River area are for DDTs and PCBs. Sources of chlorinated pesticides and PCBs entering the Columbia River above Rock Island Dam include the outflow from Lake Chelan and the Wenatchee, Okanogan, Spokane Rivers. Concentrations of PBDEs have also been reported (Rayne et al., 2003; Seiders et al., 2007; Johnson et al., 2006).

4. Lower Green/Duwamish River

The Lower Duwamish Waterway (LDW) and the Duwamish River are on the 2004 303(d) list for DDT compounds, alpha-BHC, PCBs, and PAHs in edible fish tissue. The heavily industrialized LDW has been under remedial investigation for some of the highest PCB levels in the state as well as other detected PBTs, since 1996. The EPA Superfund Program has placed a 5-mile portion on the National Priority List in 2000 (EPA, 2009b). The Washington State Department of Health has issued a fish consumption advisory for fish and shellfish from the Duwamish Waterway (WDOH, 2006).

5. Lake Washington

Highly developed and urbanized, Lake Washington was historically degraded through discharge of sewage and wastewater until 1968. Currently, all sewage effluent is treated before discharging into Puget Sound except for combined sewer overflows (CSOs). CSOs may discharge untreated sewage during large storm events.

Even with improvements, human impacts continue to influence the quality of the lake's water. PCBs, DDTs, chlordane, and TCDD in fish were found above NTR criteria (Seiders et al., 2007). The Washington State Department of Health (WDOH, 2006) issued a fish consumption advisory (2004) for PCBs in different fish species. Additionally, Lake Washington ranked as the fourth most contaminated among the waterbodies surveyed for PBDEs (Johnson et al., 2006).

6. Snohomish River

In 2004, the WSTMP found elevated PCBs and PBDEs in fish from the Snohomish River compared to other western Washington rivers (Seiders et al., 2007; Johnson et al., 2006). PBDE concentrations in the Snohomish River were ranked among the highest in the five waterbodies sampled during the Johnson study.

7. Wenatchee River

Concentrations of PCBs in Wenatchee River fish were reported by the 2004-05 WSTMP as among the highest in the state, at greater than 1300 ug/kg (Seiders et al., 2007). Similar high levels of PCBs were reported in previous studies (Era-Miller, 2004; McCarthy and Gale, 1999; Davis et al., 1995; and Hopkins et al., 1985).

The Wenatchee River has a fish consumption advisory for PCBs in mountain whitefish. The river is listed on the 303(d) list for p,p' DDE and PCBs for fish tissue.

8. Okanogan River

Ecology has consistently found high levels of DDT in fish tissue from the Okanogan River. A TMDL evaluation was conducted for DDT and PCB compounds in 2004, and a cleanup plan is in place (Peterschmidt, 2004). Ecology developed a TMDL effectiveness plan for monitoring total DDT and PCBs in fish tissue from the lower Okanogan River starting in 2008 (Coffin, 2009).

9. Yakima River at Wanawish Dam

The Yakima River has been studied intensely for over 30 years. Very high levels of DDT and PCBs have been repeatedly found in fish tissue. 303(d) listings include PCBs, DDT, DDD, DDE, alpha-BHC, chlordane, dieldrin, and dioxins. TMDLs have been established for suspended sediment to reduce, DDE, DDT, and dieldrin (Joy and Patterson, 1997; Joy, 2002). Ecology is currently conducting a TMDL for pesticides and PCBs throughout the river (Johnson et al., 2010). Fish consumption advisories have been issued for DDT and DDE in this river (WDOH, 2006).

10. Walla Walla River

Elevated levels of DDT compounds, dieldrin, toxaphene, chlordane, hexachlorobenzene, heptachlor epoxide, and PCBs were reported in fish tissue (Davis et al., 1995; Johnson et al., 2004). A TMDL was completed and a cleanup plan developed for chlorinated pesticides and

PCBs (Johnson et al., 2004; Gray et al., 2006). Fish consumption advisories currently exist for PCBs in this river (WDOH, 2006).

11. Spokane River at Nine Mile Dam

Some of the highest PCB levels in Washington State freshwater fish have been reported in the Spokane River (Johnson, 2001). Recent studies also report elevated PCBs, PBDEs, and metals in fish tissue (Serdar and Johnson, 2006). The Spokane River has 303(d) listings for PCBs and TCDD in tissue. Fish consumption advisories are listed for all fish in this river. A TMDL evaluation and a stormwater loading analysis for PCBs were recently conducted (Serdar et al., 2006 draft; Parsons, 2007).

The highest PBDE levels in fish from Washington were detected in the Spokane River during Ecology's PBDE statewide survey (Johnson et al., 2006).

12. Queets River

This site was chosen for a reference site. It was also used as reference for the 2005-2006 PBDE survey (Johnson et al., 2006). In 2007 and 2008, no water quality criteria were exceeded at the Queets River site, and concentrations of all chemicals were among the lowest for all sites.

Appendix C. Monitoring Site Descriptions

Table C-1. Sample Site Descriptions for PBT Trends.

Site Name	County	Site Description	Latitude[1]	Longitude[1]	WBID[2]	WRIA Number	EIM "User Location ID" [3]
			Decimal Degrees				
Lower Columbia R.	Wahkiakum	Columbia River, RM 54	46.1849	-123.1876	WA-CR-1010	25	SPMDTR-LCR2
Queets R.	Jefferson	Queets River, RM 11.5	47.5522	-124.1978	WA-21-1030	21	SPMDTR-QUEETS
Spokane R.	Spokane	Spokane River, Nine Mile Dam, RM 58.1	47.7747	-117.5444	WA-54-1020	54	SPMDTR-SPOK
Walla Walla R.	Walla Walla	Walla Walla River, RM 9	46.0709	-118.8268	WA-32-1010	32	SPMDTR-WALLA
Washington L.	King	Lake Washington, outlet	47.6475	-122.3019	WA-08-9350	8	SPMDTR-LKWA2
Yakima R.	Benton	Yakima River, Wanawish Dam, RM 18.0	46.3783	-119.4181	WA-37-1010	37	SPMDTR-YAK

1 - North American Datum 1983 is horizontal datum for coordinates.
2 - Ecology's Water Body Identification Number (WBID).
3 - Site identification as used in Ecology's Environmental Information Management (EIM) database.
RM: River mile.

Appendix D. Chemicals Analyzed in SPMD Samples

Table D-1. Chemicals Analyzed in SPMD Samples for PBT Trends.

Chlorinated Pesticides (MEL PEST2)	DDMU
alpha-BHC	Cis-nonachlor
beta-BHC	Toxaphene*
gamma-BHC (lindane)	Trans-nonachlor
delta-BHC	Mirex*
Heptachlor	Chlordane (technical)*
Aldrin*	Hexachlorobenzene*
Chlorpyriphos	Dacthal (DCPA)
Heptachlor epoxide*	Pentachloroanisole
trans-chlordane (gamma)*	
cis-chlordane (alpha)*	Polychlorinated Biphenyls*[1]
Endosulfan I (Alpha-endosulfan)	
Dieldrin*	Polybrominated Diphenyl Ethers*
Endrin*	PBDE-47
Endrin Ketone	PBDE-49
Endosulfan II (Beta-endosulfan)	PBDE-66
Endrin Aldehyde	PBDE-71
Endosulfan Sulfate	PBDE-99
4,4'-DDE*	PBDE-100
4,4'-DDD*	PBDE-138
4,4'-DDT*	PBDE-153
2,4-DDE	PBDE-154
2,4'-DDD	PBDE-183
2,4'-DDT	PBDE-184
Methoxychlor	PBDE-191
Oxychlordane	PBDE-209

*PBTs as defined by Ecology

1. Approximately 170 PCB congeners and remainder PCBs as co-eluting groups.

Table D-1 (continued).

Polycyclic Aromatic Hydrocarbons*
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
2-Chloronaphthalene
Acenaphthylene
Acenaphthene
Dibenzofuran
Fluorene
Phenanthrene
Anthracene
Carbazole
Fluoranthene
Pyrene
Retene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene

*PBTs as defined by Ecology

Appendix E. Sample Information Benchsheet

Table E-1. Detailed Information Benchsheet for Spiking and Processing SPMD Samples.

Field ID ("Field Station Identification" on LAR)	MEL Sample Number on LAR	Sample Description	PRCs: PCB 4, 29, 50 (spike each membrane)?	Surrogates: PCB 14, 78, 186 (spike 1 membrane per sample)?	Surrogates: PBDE, PAH, & CP (spike 1 membrane per sample)?	Extraction Standards: PCBs (spike 1 membrane per sample)?	Extract split by EST?	Comment	Lab doing analyses
LCR	1006021-01	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
LCR-CP	1006021-02	Field sample	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
WASH	1006021-03	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
WASH-CP	1006021-04	Field sample	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
QUEETS	1006021-05	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
QUEETS-CP	1006021-06	Field sample	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
YAK	1006021-07	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
YAK-CP	1006021-08	Field sample	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
WALLA	1006021-09	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
WALLA-CP	1006021-10	Field sample	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
SPOK	1006021-11	Field sample	yes	yes	yes	yes	yes	--	MEL + AP
SPOKBD	1006021-12	Field sample	yes	yes	yes	yes	yes	--	MEL + AP

Field ID ("Field Station Identification" on LAR)	MEL Sample Number on LAR	Sample Description	PRCs: PCB 4, 29, 50 (spike each membrane)?	Surrogates: PCB 14, 78, 186 (spike 1 membrane per sample)?	Surrogates: PBDE, PAH, & CP (spike 1 membrane per sample)?	Extraction Standards: PCBs (spike 1 membrane per sample)?	Extract split by EST?	Comment	Lab doing analyses
REPLCR	1006021-13	Field replicate	yes	yes	yes	yes	yes	--	MEL + AP
REPLCR-CP	1006021-14	Field replicate	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL
REPSPOK	1006021-15	Field replicate	yes	yes	yes	yes	yes	--	MEL + AP
TBLKLCR	1006021-16	Field/Transport blank	yes	yes	yes	yes	yes	Prepare field trip blank on spider carriers.	MEL + AP
TBLKQUEET	1006021-17	Field/Transport blank	yes	yes	yes	yes	yes	Prepare field trip blank on spider carriers.	MEL + AP
TBLKSPOK	1006021-18	Field/Transport blank	yes	yes	yes	yes	yes	Prepare field trip blank on spider carriers.	MEL + AP
DAYODIAL	1006021-19	QC sample: "day zero dialysis blank."	yes	yes	yes	NO	yes	Do NOT spike with PCB extraction standards.	MEL + AP
DAY0-MB	1006021-20	QC sample: PCB method blank spiked with PRCs, surrogates, and PCB extraction standards.	yes	yes	yes	yes	yes	PRCs are spiked pre-field and surrogates and ES post-field.	MEL + AP
FRDAY0	1006021-21	QC sample: fresh day zero blank.	yes	yes	yes	yes	yes	Prepare 5 membranes.	Hold at MEL
SPIKEBLK	1006021-22	QC sample: spiked environment blank.	yes	yes	yes	yes	NO	Spike 1/2 the amount (25 uL) of each surrogate solution in each membrane. One membrane for MEL and 1 membrane for contract lab.	Hold at MEL
SPKSOLVNT	1006021-23	QC sample: spiked solvent run through dialysis and GPC.	yes	yes	yes	yes	yes	Split sample: 1/2 of the extract for MEL and 1/2 for contract lab.	Hold at MEL
MSCLPBDPH	1006021-24	QC sample: a matrix spike for chlorinated pesticides, PBDEs, and PAHs.	NO	NO	NO	NO	NO	Spike into a single membrane separate from field samples.	MEL

Field ID ("Field Station Identification" on LAR)	MEL Sample Number on LAR	Sample Description	PRCs: PCB 4, 29, 50 (spike each membrane)?	Surrogates: PCB 14, 78, 186 (spike 1 membrane per sample)?	Surrogates: PBDE, PAH, & CP (spike 1 membrane per sample)?	Extraction Standards: PCBs (spike 1 membrane per sample)?	Extract split by EST?	Comment	Lab doing analyses
RECVRYPCB	1006021-25	QC sample: OPR for PCB congener analysis. (Five SPMD membranes, one of which is spiked with certain labeled and native PCB congeners then run through the dialysis and GPC process.)	NO	NO	NO	NO	NO	Contract lab supplies spiking solution.	AP
PRCSOLN	1006021-26	QC sample: PRC solution (PCB congeners 4, 29, 50).	NO	NO	NO	NO	NO	Send in sealed ampoule.	Hold at MEL
SURROSOLN	1006021-27	QC sample: surrogate solution (PCB congeners 14, 78, 186).	NO	NO	NO	NO	NO	Send in sealed ampoule.	Hold at MEL

CP: chlorinated pesticides.

ES: PCB extraction standards from contract laboratory.

MS: PBDE, PAH, and CP matrix spike from MEL.

OPR: PCB ongoing performance and recovery.

PAH: polycyclic aromatic hydrocarbons.

PBDE: polybrominated diphenyl ethers.

PCB: polychlorinated biphenyls.

PRCs: PCB-004, 029, -050 from EST.

Surrogates: PCB-014, 078, 186 from EST; PBDEs and chlorinated pesticides (in 1 solution) from MEL; and PAHs in separate solution from MEL.

LAR: Laboratory analysis required.

QC: Quality control

EST: Environmental Sampling Technologies.

MEL: Manchester Environmental Laboratory.

AP: Analytical Perspectives Laboratory (contract lab).

Appendix F. Glossary, Acronyms, and Abbreviations

Glossary

Accuracy: An estimate of the closeness of a measurement result to the true value.

Aliquot: Consisting of equal quantities.

Ambient: Background or away from point sources of contamination.

Bias: The difference between the population mean and the true value.

Bioaccumulative pollutants: Pollutants that build up in the food chain.

Blank: A sample prepared to contain none of the analyte of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample.

Check standard: A quality-control sample prepared independently of calibration standards and analyzed along with the samples to check the precision of the measurement system. A check standard can also be used to check for bias due to the way calibration is done. It is sometimes called a lab control sample (LCS) or spiked blank.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Detection limit (limit of detection)**:** The concentration or amount of an analyte which, on an "a priori" basis, can be determined to a specified level of certainty to be greater than zero.

Duplicates: Two samples collected or measurements made at the same time and location, or two aliquots of the same sample prepared and analyzed in the same batch.

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport.

Laboratory control sample (LCS): See "Check standard."

Matrix spike: A quality-control sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects.

Measurement quality objectives (MQOs)**:** The performance or acceptance criteria for individual data quality indicators, including precision, bias, and sensitivity.

Method blank: A blank prepared to represent the sample matrix and analyzed in a batch of samples.

Parameter: A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Precision: A measure of the variability in the results of replicate measurements due to random error.

Relative percent difference (RPD): The difference between two values divided by their mean and multiplied by 100.

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Thermocline: A temperature gradient in a thermally stratified, or temperature divided, body of water. Commonly associated with solar heating of the upper layers of a waterbody while the cooler layers remain on the bottom.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): Portion of solids retained by a filter.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

Acronyms and Abbreviations

BHC	Benzene hexachloride (alpha-, beta-, gamma- (gamma- also known as Lindane))
DDD	Dichlorodiphenyldichloroethane (o,p’ and p,p’: 2,4’ and 4,4’)
DDE	Dichlorodiphenyldichloroethylene (o,p’ and p,p’: 2,4’ and 4,4’)
DDMU	1-chloro-2, 2-bis (p-chlorophenyl) ethane (a breakdown product of DDE)
DDT	Dichlorodiphenyltrichloroethane (o,p’ and p,p’: 2,4’ and 4,4’)
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency

et al.	And others
GC-ECD	Gas chromatography – electron capture detection
GC-MS	Gas chromatography –mass spectrometry
GIS	Geographic Information System software
GPC	Gel permeation chromatography
GPS	Global Positioning System
HPAH	High molecular PAHs
i.e.	In other words
K_{oc}	Carbon-water partition coefficient
K_{ow}	Octanol-water partition coefficient
LPAH	Low molecular PAHs
MQO	Measurement quality objective
MS/MSD	Matrix spike and matrix spike duplicate
NTR	National Toxics Rule
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and -furans
PRC	Permeability/performance reference compounds
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedure
SPMD	Semipermeable membrane device
TCDD	Tetrachlorodibenzo-p-dioxin (most toxic of PCDD/Fs)
T-PCB	Total PCBs (sum of detected congeners)
TMDL	(See Glossary above)
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WBID	Ecology's Water Body Identification Number
WRIA	Water Resources Inventory Area
WSTMP	Washington State Toxics Monitoring Program

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft	feet
mg/L	milligrams per liter (parts per million)
mL	milliliters
ng	nanogram
ng/uL	nanograms per microliter (parts per million)
pg/L	picograms per liter (parts per quadrillion)
uL	microliter