Washington State Toxics Monitoring Program

Evaluation of SPMDs for Trend Monitoring of PBTs in Washington Waters, 2010-2011

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Cover photo: Osprey over nest at Lower Columbia River near river mile 54

Washington State Toxics Monitoring Program

Evaluation of SPMDs for Trend Monitoring of PBTs in Washington Waters 2010-2011

by

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Environmental Assessment Program
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Waterbody Numbers

Lower Columbia River near Clatskanie	WA-CR-1010
Lake Washington	WA-08-9340
Queets River	WA-21-1030
Walla Walla River	WA-32-1010
Yakima River	WA-37-1010
Spokane River	WA-54-1020
Spokane River	WA-57-1010

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Abstract

In 2007, the Washington State Department of Ecology initiated a trend monitoring component for selected organic chemicals as part of the Washington State Toxics Monitoring Program. The study used semi-permeable membrane devices (SPMDs) to estimate concentrations of chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs). Six waterbodies were sampled during 2010 and five during 2011.

This document reports the results from the 2010 and 2011 sampling. In addition, all results from 2007-2011 were assessed for usability in detecting trends. The assessment found bias in the measurement system, inconsistency in methodology, and high uncertainty with detecting analytes. Environmental levels of most target analytes were low in Washington waters relative to background levels at most sites.

Recommendations are made for improving the reliability and accuracy of the SPMD system. In addition, an analysis is presented of minimum thresholds of contaminant levels necessary to conduct long-term trend monitoring in ambient waters.

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Introduction

Background

The Washington State Department of Ecology (Ecology) began the Washington State Toxics Monitoring Program (WSTMP) in 2000 to investigate the occurrences and concentrations of toxic chemicals in the state's waterbodies. Persistent, bioaccumulative, and toxic (PBT) chemicals were targeted. These chemicals degrade slowly, tend to build up in tissues, and can have adverse health effects on humans, fish, and wildlife. A total of 27 substances are on the PBT list at this time. Information about Ecology's PBT initiative can be found at www.ecy.wa.gov/programs/swfa/pbt/.

As one of the objectives of the WSTMP, a trend monitoring program began for PBT chemicals in fish and surface water. Johnson (2007) developed a Quality Assurance (QA) Project Plan for monitoring organic chemicals in surface water, and sampling began in 2007 for this PBT Trends Study. Target analytes included chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). In 2008, polycyclic aromatic hydrocarbons (PAHs) were added to the program. Information about the WSTMP can be found at www.ecy.wa.gov/programs/eap/toxics/wstmp.htm.

Monitoring for the PBT Trends Study involves sampling twice a year (spring and fall) at waterbodies throughout Washington State. Initially, 12 sites were sampled in 2007 and 2008: 11 major rivers and one large urban lake. Standardized passive samplers called semi-permeable membrane devices (SPMDs) are used in this program to concentrate and quantify chemicals over time. Although passive samplers can reduce the variability associated with measuring concentrations in conventional water and biological samples, contamination in the sampling system threatened to compromise the usefulness of results. The ability of SPMDs to detect low concentrations of bioaccumulative chemicals was documented from the results of the first two sampling years. Those results were published (Sandvik, 2009; 2010b) as part of the PBT Trends Study.

Additional quality control (QC) measures and corrective actions were initiated in 2009 to help define sampling and laboratory variability. To accommodate for additional QC measures, targeted waterbodies were reduced to eight in 2009. Sampling was suspended in the fall except for one site in 2009, which was part of another study.

An abbreviated QA Project Plan was developed for the spring sampling in 2009 (Sandvik and Seiders, 2009) to guide development of standard operating procedures (SOPs) for processing, reporting, and better characterizing contamination of, and variability with, SPMD data. Results were also used to update the project plan for this long-term trends monitoring project (Sandvik, 2010a).

The recommendations from the 2009 report (Sandvik and Seiders, 2011) guided this PBT Trend Study in 2010 and 2011. Six waterbodies were sampled in 2010 (spring and fall) and five in 2011 (spring only). The results from 2010 and 2011 are presented in this report, along with an assessment for data usability for the purpose of detecting trends.

Monitoring Design

Monitoring Sites

Figure 1 shows locations of the seven sampling sites for the 2010 and 2011 PBT Trends Study.

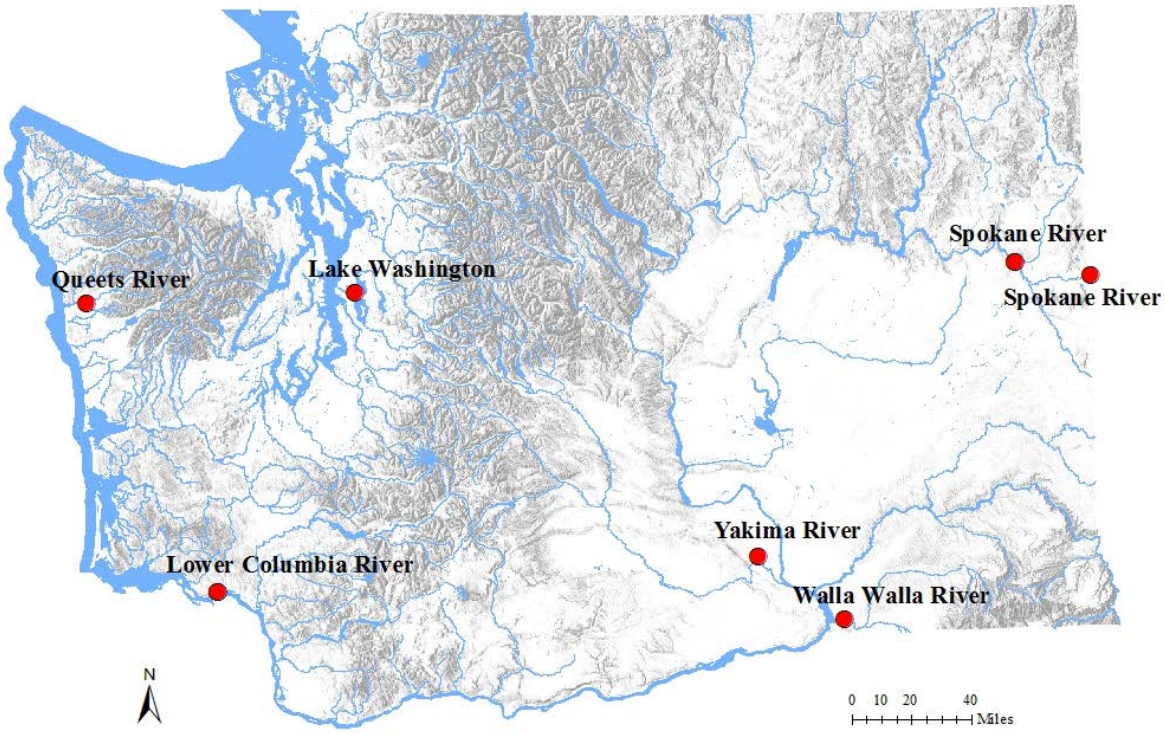

Figure 1. PBT Trend Monitoring Sites in 2010 and 2011.

Considerations for selecting these monitoring sites included review of historical data such as toxics in fish and freshwater samples, potential for water quality improvement, and availability of a secure sampling site. Details of the selection process can be found in the QA Project Plan for this study (Johnson, 2007; Sandvik, 2010a).

The locations selected in 2010 and 2011 were a subset of the sites monitored in the previous years with a couple of exceptions. Sampling from Lake Washington was discontinued in 2011. One waterbody (the Spokane River) was sampled in the spring of 2010 at two locations as part of a focused study for that river: Spokane River Baseline Effectiveness Monitoring for Toxics study (Sandvik, 2011). The two locations were at Nine Mile Dam and upstream near the border of Idaho.

Descriptions of the monitoring sites are included in Appendix A.

Passive Sampling with SPMDs

Passive sampling technology for monitoring chemicals in the environment is becoming widely accepted worldwide. SPMDs are passive samplers made of polyethylene tubes containing ultra pure neutral lipid. They mimic the bioconcentration (uptake) of organic pollutants from water by aquatic organisms (e.g., fish) without the variability introduced by movements, growth, and spawning of fish (Huckins et al., 2006; USGS, 2011). Large chemical residues accumulated in SPMDs give a strong analyte signal, translating into parts-per-trillion detection limits or lower. Residues from SPMDs are used to model time-weighted average dissolved concentrations for the chemicals of interest.

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) and Alvarez (2010b).

Chemicals analyzed for this study included over 30 CPs or breakdown products, 209 individual PCBs or congeners, 22 PAHs, and 13 PBDE congeners. A complete list of target analytes is in Appendix B.

Other parameters collected to supplement SPMD chemical assessment include total suspended solids (TSS) and total organic carbon (TOC), which were determined at the beginning, middle, and end of each sampling period at each site. Water temperature was monitored continuously during deployment at all sites.

Timing and Placement of SPMDs

The SPMDs were deployed for approximately 28 days: from April 27 – May 28 (spring) and September 8 – October 7 (fall) for 2010 and from May 3 – June 2 (spring) for 2011 with one exception. The Walla Walla River site was deployed later, May 25 – June 20 in 2011, due to limited access because of flooding. Deployments aimed to capture the high-flow (spring) and low-flow (fall) conditions for the rivers when peak levels of the target chemicals tend to occur (Johnson et al., 2004; 2005). For Lake Washington, these sampling events capture the higher water level (pre-stratification beginning in the spring) and the lower water level (strong stratification in the fall) (King County, 2003).

One SPMD sampler was placed in the same location as in previous years at each monitoring site. Two field replicate samplers were deployed in each sampling event to provide an estimate of variability in the field samples: one in the Lower Columbia River and one in the Spokane River.

During each sampling event, field blanks were taken at three sites; the Lower Columbia, Queets, and Spokane Rivers. In 2011, extra field blanks were taken at the same sites for comparing two methods of field blank exposure described below.

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Methods

Field Procedures

Standard SPMDs were prepared by Environmental Sampling Technologies (EST), St. Joseph, Missouri (www.est-lab.com/index.php). SPMDs are composed of a thin-walled, layflat polyethylene tube (91.4cm x 2.5cm x 70-95µm thickness) filled with 1 mL of neutral lipid triolein (purity 99.9%).

EST prepared and spiked each membrane with performance reference compounds (PRCs) consisting of 5 ng of PCB-004 and 10 ng of PCB -029 and -050. EST preloaded the SPMD membranes onto carriers then shipped them frozen in solvent-rinsed metal cans filled with argon gas.

SOPs were followed to deploy and retrieve the SPMDs (Sandvik et al., 2011 (in review)). An overview of the procedures is given below.

Ecology staff transported the cans with SPMDs to the field on bottled ice. Upon arriving at the sampling site, an anchoring and tethering system was constructed for securing the SPMD canisters. The cans were carefully opened; five carriers were slid into a 30 cm x 16 cm stainless-steel canister. In 2010, additional shade devices were employed to protect against photo degradation of light-sensitive compounds such as PAHs. PAHs were not sampled in 2011. The device was secured in the water as quickly as possible to limit air contamination. Field personnel wore nitrile gloves and avoided touching the membranes.

Ecology staff checked the SPMDs midway through the month-long deployment. At midcheck, the SPMD samplers were gently moved back and forth under water to remove loose sedimentation or biofouling. Retrieval procedure was essentially the reverse of deployment. All SPMDs were successfully retrieved during 2010 and 2011. The cans holding the SPMDs were sealed and kept at or near freezing for shipping to EST for extraction. Samples were identified and recorded, and custody was maintained at all times following Ecology's chain-of-custody procedures.

To confirm that SPMDs remained submerged throughout the sampling period, an Onset StowAway® TidbiTs™ temperature monitor was attached to each SPMD canister. Another TidbiT™ was secured out of the water near the site. These TidbiTs™ recorded water and air temperature every two minutes. Examination of the charted water and air temperature data showed that all samples remained submerged during deployment.

Grab samples for TOC and TSS were collected at the beginning, middle, and end of each deployment sampling period according to Ecology SOPs (Joy, 2006; Ward, 2007) (Table 1). These samples were held on ice and shipped within the holding time (MEL, 2008) to Ecology's Manchester Environmental Laboratory (MEL) with a chain-of-custody record.

Table 1. Field Procedures for Ancillary Water Quality Parameters.

Parameter	Minimum Sample Size	Container	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4ºC	7 days
TOC	50 mL	123 mL poly bottle	HCL to pH<2, 4ºC	28 days

HCL = hydrochloric acid.

Water temperature and conductivity were measured in-situ during each collection using a temperature/conductivity probe (Hanna DIST 5 pH/EC/TDS meter) or a hydrolab. Use of these instruments followed Ecology's SOP (Swanson, 2007 for hydrolabs) or manufacturer's instructions (for Hanna meter). Flow information and data were obtained from Ecology's Environmental Assessment Program Freshwater Monitoring Unit, the U.S. Geological Survey (USGS), and other sources.

Laboratory Procedures

Analysis

After retrieving the SPMD membranes from the field, Ecology staff sent the SPMD membranes to EST for preparation and extraction (described below) before further analyses by other laboratories. MEL analyzed CPs, PAHs, and PBDEs in 2010 and CPs and PBDEs in 2011. Analytical Perspectives Laboratory (Wilmington, NC) and AXYS Analytical Services, LTD (Sidney, BC) analyzed PCB congeners in 2010 and 2011 respectively. MEL also analyzed conventional water quality samples. Analytical methods are shown in Table 2.

For PCB congeners, extraction internal standards (EIS) were added before the extraction process as directed in Method 1668A. PCBs analyzed in 2007, 2008, and 2009 deviated from this method by adding the extraction standards into the extracts after the extraction process rather than into the SPMDs before extraction.

Table 2. Laboratory Procedures.

Analysis	Sample Matrix	Sample Preparation Method	Analytical Method
CPs	SPMD extract	Dialysis/GPC[1]	EPA 3620, 3665, 8081[2]
PBDEs			EPA 8270[3]
PAH			EPA 3630B/8270[3]
PCBs			EPA 1668A[4]
TOC	Whole water	NA	SM5310B
TSS			SM2540D

1. EST SOPs E14, E15, E19, E21, E32, E33, E44, E48.
2. Modifications of EPA SW-846.
3. GC/MS SIM = gas chromatography / mass spectrometry applying selective ion monitoring.
4. HRGC/HRMS = high resolution gas chromatography / high resolution mass spectrometry.

NA = not analyzed.

SPMD Preparation, Extraction, and Cleanup

Upon receiving the SPMDs, EST inspected and cleaned all membranes. For the 2010 samples, each sample was spiked with surrogate compounds prior to extraction. Surrogates included 50 ng each of PCB-014, PCB-078, and PCB-186 which were prepared by EST, as well as surrogates prepared by MEL which were 2000 ng of PAH and 400 ng of pesticide and PBDE surrogates. The 2011 samples did not receive PCB or PAH surrogates because the spiked PCB EIS standards were determined to suffice and no PAHs were analyzed. Recovery of the surrogates provides estimates of recovery of target compounds in each sample.

EST extracted the membranes from each SPMD sample using dialysis. The extracts from each membrane were combined into a single sample and solvent exchanged to methylene chloride for gel permeation chromatography (GPC) cleanup. After GPC, the extracts were solvent exchanged into hexane, split 50:50, and each fraction sealed in a 5-mL ampoule for transport to the laboratories. One ampoule was sent to MEL. The other ampoule was sent to Analytical Perspectives (2010 samples) or AXYS (2011 samples) (via MEL). EST's extraction and cleanup methods are documented in SOPs on file at Ecology headquarters.

In 2010, a set of samples was used only for pesticide analysis. The extracts were split (50:50) at EST and analyzed at MEL. Another set of samples were used for PBDEs, PAHs, and PCB congeners. After dialysis and the second set of extracts were split (50:50) at EST, half was analyzed for PBDEs and PAHs at MEL and the other half for PCBs at Analytical Perspectives.

In 2011, the MEL ampoule that was a split sample (50%) from EST was further split 50:50 for pesticide and PBDE analysis, resulting in 25% fraction for each. The other half of the split ampoule (50%) was sent to AXYS for PCB congener analysis.

The PBDE/PAH extract was solvent exchanged into iso-octane prior to analysis. No additional cleanup was performed on the samples for PAH analysis. A dual column GC-ECD was used for analyses.

The pesticide ampoule was concentrated and then eluted through a macro Florisil® column. Following a solvent exchange concentration, the pesticide extracts were split and one portion was treated with concentrated sulfuric acid to remove interferences. Both portions were analyzed by dual column GC-ECD.

Analytical Perspectives and AXYS analyzed the extracts for PCB congeners (2010 and 2011 respectively). A multi-column cleanup step was performed, and each extract was brought to a fixed volume. Cleanup and injection standards were spiked into each extract at various steps for measuring the analytical performance throughout the cleanup and analytical procedures.

All results were corrected for all dilutions, and laboratories reported them as ng/sample (mass of chemical found in the sample), the sample being 100% of the extract. The analyte found in the extract from the sample is referred to as the "residue".

Data Reduction

The SPMD residue data were evaluated for use in models that estimate dissolved and whole-water (total) concentrations of individual analytes. The dissolved and whole water estimates were then reported and used in other evaluations, such as summing operations and comparisons among results from different sites or sample events.

Background Contamination

Sample residue results were examined for background contamination and censored following the concepts in Method 1668A (EPA, 1999), USGS (Alvarez, 2010b), and Keith (1991). These concepts were used in Ecology's SOP for Conducting Studies using SPMD (Sandvik et al., 2011 (in review)) and are discussed in the Data Quality section below and in detail in Appendix C. This process is briefly described below.

- Results that were above the limit of quantitation (LOQ) were used as reported. The LOQ is defined as the mean of the field blanks plus ten standard deviations per Keith (1991) and the SOP for SPMD data reduction (Seiders and Sandvik, 2012 (in review)).
- Results that were at or below the limit of detection (LOD) were censored as nondetects (U) at the associated LOD value. The LOD is defined as the mean of the field blanks plus three standard deviations (Keith, 1991 and Sandvik and Seiders, 2012 (in review)).
- Results that were greater than the LOD, but less than or equal to the LOQ, were reported as nondetects at the result value.
- The correction of results by subtracting the values of contamination found in the field or lab blanks, also known as "blank-correction", was not used because blank-correction does not reduce the high uncertainty of a true detection found in results between the LOD and LOQ.

All data qualifiers were retained for residue results in the appendices.

Methods for Estimating Chemical Concentrations in Water

SPMDs absorb only the dissolved form of a chemical. The concentrations of absorbed residues are determined from laboratory analyses. These concentrations can be converted to a time-weighted average dissolved water concentration by using a USGS model. These dissolved concentrations can then be used in another model to estimate the corresponding time-weighted average whole water concentrations.

Dissolved Water Concentrations

Dissolved concentrations for the chemicals of interest were estimated using the most current version of the USGS Estimated Water Concentration Calculator model. This model was developed by USGS at the Columbia Environmental Research Center (CERC) for integrative passive samplers (Alvarez, 2010a; USGS, 2011) and can be found at their website: www.cerc.usgs.gov/Branches.aspx?BranchId=8.

Ecology entered the data collected on chemical residues, exposure times, and PRC recoveries in this present study into the USGS model for the available analytes. Residue data are available from the authors of this report. Exposure times and PRC data are listed in Appendices D and E.

In this study, the uncertainty factors (standard deviations) ranged from 1.1 to 1.9 among the 2010 and 2011 samples, which are within a factor of 2 recommended for the model (Huckins et al. 2002).

The USGS model uses the octanol-water partition coefficient constant (log K_{ow}) for each analyte to estimate dissolved water concentrations. Generally, the higher the compounds log K_{ow}, the greater the capacity of the SPMD for that chemical, although falling diffusion rates with increased molecular weight (around log K_{ow} 6) and potential solubility and sorption limitations significantly reduce the sampling rates (Huckins et al., 2006).

The model provides log K_{ow} values for many bioaccumulative chemicals. For those analytes missing log K_{ow}s in the model, literature values were used. If multiple log K_{ow} values were found, a mean was selected using the t-test at 95% confidence for rejection of outliers (Alvarez, 2010a; USGS, 2011).

Where log K_{ow}s could not be found in the literature, K_{ow}s were calculated using an atom/ fragment calculation developed by Syracuse Research Corporation (Meylan et al., 1995). Log K_{ow}s for analytes PBDE-49, -71, -184, -191 were estimated using similar chemicals (PBDE-47, -69, -183, -190, respectively). This approach seemed reasonable based on other PBDE congeners that are consecutive to each other and have similar log K_{ow}s. USGS estimated the log K_{ow} for chlorpyrifos from endrin because of endrin's proximity in log K_{ow} values (Alvarez, 2010a). Log K_{ow}s used in estimating these concentrations can be found in Appendix F.

In view of the uncertainties previously stated, all chemical concentrations in water calculated in this report should be considered estimates and are qualified accordingly.

Total Water Concentrations

Organic compounds in water partition between dissolved and particulate fractions. The "total" (whole water) concentration is the sum of dissolved and particulate fractions.

In this study, total water column concentrations were estimated from the dissolved data using an equation from Meadows et al. (1998):

$C_{w\text{-}tot} = C_w (1 + TOC (K_{oc}/M_w))$

where:

- $C_{w\text{-}tot}$ is the total water concentration (total pg/L).
- C_w is the dissolved concentration (pg/L).
- TOC is total organic carbon (mg/L) (average of three samples per deployment period).
- K_{oc} is the organic carbon-water equilibrium partition coefficient.
- Mw is the mass of water (1g/mL).

TOC is critical in determining chemical uptake rates of compounds with high log K_{ow}s because of TOC's effect on the dissolved fraction. The higher the K_{ow}, the greater the affinity of the compound has for suspended organic matter. There is therefore a lower tendency for these compounds to be transported in the dissolved phase. Limited water solubility, coupled with increased binding to TOC, limits the amount of the compound in contact with the SPMD membrane (Meadows et al., 1998). K_{oc} values were derived using Karickhoff's (1981) approximation $K_{oc} = 0.411K_{ow}$.

Analytes Expressed as Sums

Several analytes are reported here as summed values of detected compounds that belong to a group having similar characteristics. For example, total DDT is the sum of o,p'- and p,p'- isomers of DDD, DDE, and DDT. Total chlordane is the sum of *cis* and *trans* chlordane, *cis* and *trans* nonachlor, and oxychlordane. Endosulfan, unless specified, is the sum of alpha (endosulfan I) and beta endosulfan (endosulfan II). Total PCB is the sum of the individual congeners. Total PBDE is the sum of the 13 congeners analyzed in this study.

Low molecular weight PAH (LPAH) represents the sum of the following low molecular weight PAH (< 4 rings):

- Naphthalene.
- Acenaphthylene.
- Acenaphthene.
- Fluorene.
- Phenanthrene.
- Anthracene.

High molecular weight PAH (HPAH) represents the sum of the following high molecular weight PAH (4 or more rings):

- Fluoranthene.
- Pyrene.
- Benz(a)anthracene.
- Chrysene.
- Total benzofluoranthene ("B," "J," and "K" isomers).
- Benzo(a)pyrene.
- Indeno(1,2,3,-c,d)pyrene.
- Dibenzo(a,h)anthracene.
- Benzo(g,h,i)perylene.

Total PAH is the sum of LPAH and HPAH.

Nondetect results were treated as zero when summing compounds for total DDT, total chlordane, total PAH, total PBDE, and total PCB. All summed compounds were calculated from water concentration values (as opposed to the residue concentration).

Data Quality

The QA Project Plan developed for this study established data quality requirements for accuracy, bias, and reporting limits with measurement quality objectives (MQOs). A new QA Project Plan (Sandvik, 2010a) replaced earlier editions (Johnson, 2007; Sandvik and Seiders, 2009) in order to revise sample sites and analytes, update analytical methods for some analytes, include additional QC and QA procedures, and incorporate standardized data management and reporting practices.

The project lead compared results from field and laboratory QC samples to the MQOs to determine if the MQOs were met. Based on these assessments and reviews of laboratory data verification reports, the data were accepted, accepted with appropriate qualifiers, or rejected. Laboratory and field data quality are summarized below. Data quality related to the preparation, spiking, and extraction of SPMD membranes are included in Field section below: the Laboratory section addresses the analysis of the SPMD extracts. A more detailed description of data quality is in Appendix C.

Laboratory

All sample extracts were prepared and analyzed within the method holding times for the various parameters. Analytical laboratory method blanks (from MEL and contract laboratories) showed no significant contamination for any of the chemicals analyzed. Most QC procedures and corresponding samples fell within acceptable limits.

Most results met MQO requirements of this study. Over 80% of PCB, close to 70% of PAH, over 50% of CP, and around 25% of PBDE results were considered detected with no qualifications. All other results were appropriately qualified (detected and nondetected).

Field

Sample Integrity

The SPMDs were checked midway (two weeks) through the month-long deployment period. During this check, SPMD samplers were gently moved back and forth under water to remove loose sediment or biofouling. All samplers remained submerged based on data from continuous temperature monitoring devices (TidbiT™) which were attached to the sampler and attached on shore nearby. All SPMDs were retrieved for the 2010 and 2011 sampling events.

Membrane Spike, PRC, and Surrogate Recoveries

Various spiking practices were used in the preparation and processing of SPMDs to help define the quality of results. All recoveries for the membrane spike analytes fell within the acceptable 50% - 150% recovery limits with several exceptions. Yet no sample results were qualified based on the membrane spike recoveries.

The PRC recoveries were within an acceptable range (20-80%) with several exceptions. High PRC recoveries were found in about 40% of the field samples. The highest PRC percent recovery for individual samples was not used in calculations if the uncertainty factor (standard deviation) was above 2.

Most surrogate recoveries were within an acceptable range (25-150%). One low surrogate recovery (2%) was found in a sample that suffered loss due to a laboratory accident in 2010. That sample was rejected.

Replicates

Replicate SPMDs were deployed at two locations in each sampling event: the Lower Columbia and Spokane Rivers. These were independent samples deployed within a few feet of each field sample. Although one replicate (Spokane River) was compromised in the spring of 2010 due to a laboratory accident, the others showed fairly good precision.

Precision was measured by comparing residue results of the replicates using relative percent differences (RPDs): lower RPDs had better precision. In most cases, over 75% of the chemicals analyzed had RPDs of 30% or less. Higher variability was observed for PAHs in 2010, ranging from 18-59% of residue results with RPDs of 25% or less. No PAHs were analyzed in 2011.

Lower variability was observed in the Spokane River replicates compared to the Lower Columbia River replicates. For Spokane River replicates, 91% of results had RPDs of <=25% in 2010 and 2011, whereas Lower Columbia River showed RPDs of 71% and 64% for spring and fall replicates, respectively, in 2010 and 83% in 2011. Results are listed in Appendix G.

Where replicates were deployed, the water concentration values were averaged and are used in the remainder of this report.

Blanks

The quality of blank results is reported in more detail in Appendix C. Certain background levels of PCBs, PBDEs, and PAHs exist in the preparation, extraction, and deployment of the SPMDs as seen in EST laboratory blanks and in field blanks.

EST Laboratory Blanks

EST prepared various QC samples and solutions such as blanks, spikes, and spiking solutions to help assess contamination during manufacturing, preparation, spiking, and extraction of SPMDs. These were: Day0-dialysis blank, Fresh Day0 blank, spiking blank, solvent blank, and membrane blank. In addition, EST prepared a method blank and an Ongoing Precision and Recovery (OPR) blank to meet method requirements for isotopic dilution using HRMS methods (e.g., PCB congeners with EPA 1668A). Descriptions about these blanks can be found in Appendix N and in more details in the SOP for Conducting Studies using SPMDs (Sandvik et al., 2011 (in review)).

In 2011, the spiking blank was split (50:50). Half of the spiking blank went through the GPC cleanup process while the other half did not, in order to assess PCB congener contamination from the GPC cleanup process. PCB congener results from the spiking blanks show the spike blank using GPC had higher residue concentrations than the spike blank that did not use GPC (42 versus 30 ng/sample ,respectively). Significance was not determined from this small sample size.

Four Day0-dialysis blanks were analyzed in 2011; three were spiked with EIS before extraction, while one was spiked before analysis in order to assess method differences between pre-2010 and post-2010. These blanks have not yet been assessed.

Field Blanks

Results from various field and lab blanks can help determine the sources, magnitude, and relative significance of contamination.

Field blanks consisted of the same number of SPMD membranes used in the samples. These blanks were prepared at the same time and spiked identically as the field samples. The levels of contamination in the field blank are assumed to represent the sum of all contamination and de-contamination effects from the varied steps involved in using SPMDs.

During each sampling event, three field blanks were exposed to air during deployment and retrieval to assess background air contamination at three sampling sites: the Lower Columbia, Queets, and Spokane Rivers. These SPMD membranes are typically loose in a can and exposed to air by removing the lid for approximately the same amount of time the field samples are exposed to air during deployment and retrieval; this method is the practice adopted by USGS. This study exposed the field blanks to air at the sampling site about two minutes during deployment and two minutes during retrieval.

In 2011, an additional method of exposing the field blanks was added to help evaluate the representativeness of the commonly used method. These added blanks consisted of membranes mounted on carriers, the same as the field samples. At each site, the mounted field blank was exposed on a foiled tray out of direct sun for the same amount of time as the blank consisting of membranes in the can. In all, six field blanks were used: two at each of three sites.

Results from field blanks can be found in Appendix H.

Field blanks were used to censor results. The impact of censored results varied among the chemical groups. Table 3 shows the percent of the results above the LOD and LOQ for each sampling period in 2010 and 2011. Detail discussion of LOD and LOQ can be found in Appendix C.

Table 3. Percent of Results above LOD and LOQ for 2010 and 2011 Samples.

Chemical	Year	Spring / Fall	>LOD	>LOQ
CPs	2011	S	35%	35%
PBDEs	2010	S	16%	8%
	2010	F	20%	16%
	2011	S	14%	10%
PCBs	2010	S	34%	13%
	2010	F	51%	38%
	2011	S	61%	<1%
PAHs	2010	S	12%	5%
	2010	F	46%	34%

Pesticide results were deemed usable; all detected results were above the LOQ in 2011. Since there was no contamination found in the pesticide blanks, the LOD and LOQ were the same, which was the detection limit. Even though the LOD and LOQ were not calculated (no field blanks were analyzed) in 2010, the pesticide results were deemed usable because no contamination was found in the other laboratory blanks.

Results above the LOQ for the other chemical groups ranged from <1% to 38% and varied considerably between sampling periods. This is a result of a combination of the low levels in the sampling environment and high blank contamination at these detection limits. To correct results within this noise would be risky for trend analysis. Therefore, only levels high enough above the noise (>LOQ) were assessed for 2010 and 2011.

Results and Discussion

Streamflow Conditions

Above normal precipitation events during the spring sampling events in both 2010 and 2011 kept many streamflow levels toward the upper end of their normal historical ranges. One exception was the Spokane River during the 2010 spring sampling (last of April – first of June). Flows in the Spokane River remained below the median of the past 115 year's record period during this time (Ecology, 2010 and 2011). Half of the historical streamflows for the record time period fall above this level and half below. Another exception was the Walla Walla River which reached new maximum flow levels for the past 54 years in the spring of 2011 (Ecology, 2010 and 2011).

Low temperatures and above normal precipitation in the fall of 2010 kept most rivers near the median of their historical flows. The Spokane River was below the 20th percentile of historical flow at the beginning of the sampling period (end of August 2010) but reached above historical median flows by the end of September when samples were retrieved (Ecology, 2010 and 2011). In the fall of 2011, wetter than normal conditions pushed most rivers towards the upper end of their normal historical flow level ranges, although no sampling was done at this time.

Flow data and charts are provided in Appendix I.

Ancillary Water Quality Parameters

Results for TSS, TOC, and conductivity measurements taken during SPMD deployment at all sites are listed in Appendix J.

For TSS and TOC, higher values were generally seen in the spring than in the fall. Averaged TSS ranged from 1 – 190 mg/L. One of three TSS samples taken in the Walla Walla River during spring of 2010 was high (508 mg/L) compared to the other two samples (<50 mg/L), which averaged to 190 mg/L overall. The high TSS result was due to fast settling sand, and therefore, qualified as an estimate. TOC for all sites averaged 1.0 – 2.5 mg/L.

Conductivity was generally higher in the fall, probably due to lower flows. Average conductivity ranged from 20 us/cm in the Queets River (2010 spring) to 283 us/cm in the Walla Walla River (2010 fall).

Dissolved Chemicals

Concentrations of CPs, PCBs, and PBDEs

Summary statistics for dissolved CPs, PCBs, and PBDEs are shown in Table 4 for 2010 spring and fall and in Table 5 for 2011 (spring only). A total of 16 field samples were analyzed in 2010 and 7 in 2011. The type of chemical analyses performed varied among samples. The concentrations are in picograms per liter (parts per quadrillion) and are considered estimates. For analytes that were not detected, the limit of detection (LOD) was used in calculating the statistics. The data are in Appendices K and L. These data and SPMD residue data are also available upon request through Ecology.

DDT or its breakdown products (DDE and DDD) were detected in 92% of the 2010 samples and in 80% of the 2011 samples. This is consistent with other studies detecting DDT in over half the samples (Sandvik, 2010b; Sandvik and Seiders, 2011; Johnson et al., 2004, 2005).

Although chlorpyrifos and endosulfan were found in many samples (over half), results varied between sampling events. Detection may reflect the application period of these current-use pesticides.

Other pesticides had varied results, but generally were detected more frequently in 2010 than in 2011. The pesticide results may be skewed since sampling took place twice in 2010 (spring and fall) and only once in 2011 (spring).

Pesticides not detected in 2010 or 2011 were heptachlor, alpha-benzenehexachloride (a-BHC), beta-benzenehexachloride (b-BHC), delta-benzenehexachloride (d-BHC), aldrin, endrin, endrin ketone, endrin aldehyde, mirex, and methoxychlor. Additionally, gamma-benzenehexachloride (Lindane) was not detected in the 2010 and 2011 samples.

PCBs were detected in 94% of the samples in 2010, but were considered undetected above the LOQ in 2011. Both sample and data sets (2010 and 2011) were handled and censored the same, but the 2011 results were analyzed by a different laboratory than in 2010. The low PCB results found in 2011 may reflect higher reporting limits, some unknown differences in laboratory analysis, may be part of the natural variability, or may include some other factor. The small sample set, results near the detection limit, and results censored for blank contamination make it difficult to sort out true differences.

PBDEs were detected in all samples. Total PBDEs ranged from 6.4 to 810 pg/L with an average of 120 pg/L in 2010. PBDEs were lower in 2011 ranging from 16 to 95 pg/L and averaging 42 pg/L, which probably reflect bias due to not sampling in the fall when the Spokane River site has higher concentrations.

Table 4. Summary Statistics (pg/L, dissolved) for 2010 CPs (n = 12), Total PBDEs (n = 16), and Total PCBs (n = 16).

Parameter	Number of Detections	Detection Frequency	Min	Max	Median	Mean	Std Dev	90th % ile
Total PBDEs	16	100%	6.4	810	38	120	220	280
Total PCBs	15	94%	<0.10	578	76	180	220	540
Total DDT[1]	11	92%	<4.7	460	92	150	140	330
Total Chlordane[3]	11	92%	4.3	140	25	32	37	42
Hexachlorobenzene	12	100%	7	51	17	21	12	34
Pentachloroanisole	10	83%	<4.4	56	22	28	19	51
Chlorpyrifos	8	67%	<11	2100	45	330	62	750
Dieldrin	8	67%	<6.5	183	20	44	54	110
Endosulfan I	8	67%	<110	1400	170	290	36	390
Endosulfan Sulfate	5	42%	<160	600	230	280	160	580
Dacthal (DCPA)	5	42%	<10	38	14	17	7.9	23
Toxaphene	4	33%	<57	2400	120	380	680	810
Endosulfan II	2	17%	<230	<880	230	450	280	830
DDMU[2]	2	17%	<4.1	<36	6	12	11	29
Heptachlor Epoxide	1	8%	<7.3	<18	9.1	11	3.6	16
Gamma-BHC (Lindane)	0	0%	<34	<38	35	35	1.1	36

1. Total DDT is the sum of 2,4'- and 4,4' isomers of DDD, DDE, and DDT.
2. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethylene) is a breakdown product of DDE.
3. Total chlordane is the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane.

< = below LOQ.
Std Dev = Standard Deviation.

Table 5. Summary Statistics (pg/L, dissolved) for 2011 CPs (n = 5), Total PBDEs (n = 7), and Total PCBs (n = 7).

Parameter	Number of Detections	Detection Frequency	Min	Max	Median	Mean	Std Dev	90th % ile
Total PBDEs	7	100%	16	95	25	42	31	82
Total PCBs	0	0%	<111	<111	<111	<111	0	<111
Total DDT[1]	4	80%	<12	630	270	290	220	510
Total Chlordane[3]	2	40%	8.3	41	14	19	13	32
Hexachlorobenzene	4	80%	<11	48	34	32	16	47
Pentachloroanisole	4	80%	<11	41	35	28	14	40
Chlorpyrifos	4	80%	<23	3100	360	940	1300	2200
Dieldrin	2	40%	<16	27	18	19	4.5	24
Endosulfan I	2	40%	<220	3100	220	870	1300	2100
Endosulfan Sulfate	0	0%	<320	<320	320	320	0.00048	320
Dacthal (DCPA)	3	60%	<24	44	26	32	9.2	42
Toxaphene	4	80%	<140	2100	440	680	790	1400
Endosulfan II	0	0%	<460	<690	460	540	120	680
DDMU[2]	2	40%	<11	<23	19	18	4.9	23
Heptachlor Epoxide	0	0%	<13	<20	17	16	3	19
Gamma-BHC (Lindane)	0	0%	<68	<72	70	70	1.7	71

1. Total DDT is the sum of 2,4'- and 4,4' isomers of DDD, DDE, and DDT.
2. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethylene) is a breakdown product of DDE.
3. Total chlordane is the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane.

< = below LOQ.
Std Dev = Standard Deviation.

Concentrations of PAHs

Table 6 shows summary statistics for dissolved PAHs collected in 2010. Except for summary statistics below, no further discussion for PAHs is reported.

Table 6. Summary Statistics for 2010 PAHs (n = 15) (dissolved, pg/L).

Parameter	Number of Detections	Detection Frequency	Min.	Max.	Median	Mean	Std Dev	90th % ile
Acenaphthene	6	40%	<45	620	180	210	140	330
Anthracene	5	33%	<25	206	36	61	55	140
Acenaphthylene	2	13%	<60	<160	110	99	34	140
Phenanthrene	1	7%	<810	<3200	2200	1900	890	2900
Fluorene	1	7%	<120	<440	330	290	110	400
Naphthalene	0	0%	<6200	<6400	6400	6300	100	6400
Total LPAH[1]	7	47%	40	3500	220	640	1300	1600
Indeno(1,2,3-cd)pyrene	7	47%	<32	250	80	96	64	160
Fluoranthene	6	40%	<150	3600	1700	1600	990	2400
Benzo(b)fluoranthene	6	40%	<18	560	58	140	180	420
Pyrene	5	33%	<110	5000	800	1200	1300	2400
Chrysene	5	33%	<18	640	140	180	170	390
Benzo(k)fluoranthene	5	33%	<15	130	30	49	43	130
Dibenzo(a,h)anthracene	4	27%	<23	120	42	52	28	94
Benzo(a)pyrene	3	20%	<21	130	41	49	30	82
Benzo(a)anthracene	2	13%	<83	600	220	240	130	360
Benzo(ghi)perylene	2	13%	<29	110	46	52	24	89
Total HPAH[2]	9	60%	46	11000	1600	3100	3800	7500
Total PAH[3]	10	67%	40	14000	1100	3300	4600	7500
Retene	6	40%	<63	<2600	1400	1200	860	2200
Carbazole	2	13%	<510	5100	510	890	1200	1100
Dibenzofuran	1	7%	<360	<470	420	410	30	450
1-Methylnaphthalene	0	0%	<1700	<2000	1900	1900	76	2000
2-Methylnaphthalene	0	0%	<3300	<4200	3800	3800	300	4100
2-Chloronaphthalene	0	0%	<100	<120	110	110	4.5	120

1. Total LPAH is the sum of low molecular weight PAHs: naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, and fluorene.
2. Total HPAH is the sum of high molecular weight PAHs: 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.
3. Total PAH is the sum of LPAH and HPAH.
< = below LOQ. Std Dev = Standard Deviation.

PAHs were detected in 67% of the samples and ranged from 40 to 14,000 pg/L for total PAH. Higher concentrations were found in the fall with the Lower Columbia River having the highest concentrations overall. The next highest was found in Lake Washington followed by the Spokane River, but generally at half of that found in the Lower Columbia River.

Spatial and Seasonal Patterns

Some seasonal patterns were observed among the sites. Table 7 compares 2010 and 2011 waterbodies where the highest detected (above the LOQ) concentrations were recorded. The apparent seasonal differences could be due to normal seasonal differences rather than a pattern. The low levels found in the samples are near or in the area of high uncertainty (background noise), make discerning these differences difficult.

Table 7. Locations of Maximum Detected Concentrations Observed in 2010 and 2011.

Parameter	2010		2011	
	pg/L[1]	Location	pg/L[1]	Location
Spring				
Total PBDEs	-	-	95	Spokane R.
Total PCBs	-	-	nd	
Total DDT[2]	-	-	630	Yakima R.
Total Chlordane[3]	-	-	41	Walla Walla R.
Hexachlorobenzene	51	Walla Walla R.	48	Walla Walla R.
Pentachloroanisole			41	Yakima R.
Chlorpyrifos	2100	Walla Walla R.	3100	Walla Walla R.
Dieldrin	-	-	27	Yakima R.
Endosulfan I	1400	Yakima R.	3100	Walla Walla R.
Endosulfan Sulfate	600	Yakima R.	nd	
Dacthal (DCPA)	38	Yakima R.	44	Lower Columbia R.
Toxaphene	-	-	2100	Walla Walla R.
Endosulfan II	650	Walla Walla R.	nd	
DDMU[4]	5.9	Walla Walla R.	19	Lower Columbia R.
Heptachlor Epoxide	12	Walla Walla R.	nd	
Fall				
Total PBDEs	810	Spokane R.	na	na
Total PCBs	580	Spokane R.	na	na
Total DDT[1]	460	Yakima R.	na	na
Total Chlordane[2]	140	Walla Walla R.	na	na
Pentachloroanisole	56	Lake Washington	na	na
Dieldrin	180	Yakima R.	na	na
Toxaphene	2400	Walla Walla R.	na	na

1. Estimated dissolved concentrations.
2. 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.
3. Total chlordane is the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane.
4. DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethylene) is a breakdown product of DDE.

- means maximum concentration found in the other sampling period; spring versus fall.

na = not analyzed.

The highest pesticide concentrations were generally found in the Walla Walla and Yakima Rivers in the spring. Maximum concentrations of total PBDEs, total PCBs, and total chlordane were found in the Spokane River predominantly in the fall. The Lower Columbia River also had elevated concentrations of PCBs in the fall of 2010. Elevated concentrations of toxaphene and dieldrin were found in the Walla Walla and Yakima Rivers during the fall of 2010 respectively.

Figures 2-4 compare 2010 with 2011 levels of T-DDT, total PCBs, and total PBDEs at locations common to both sampling years. Sites are ordered from the highest to lowest concentrations observed in the spring of 2011.

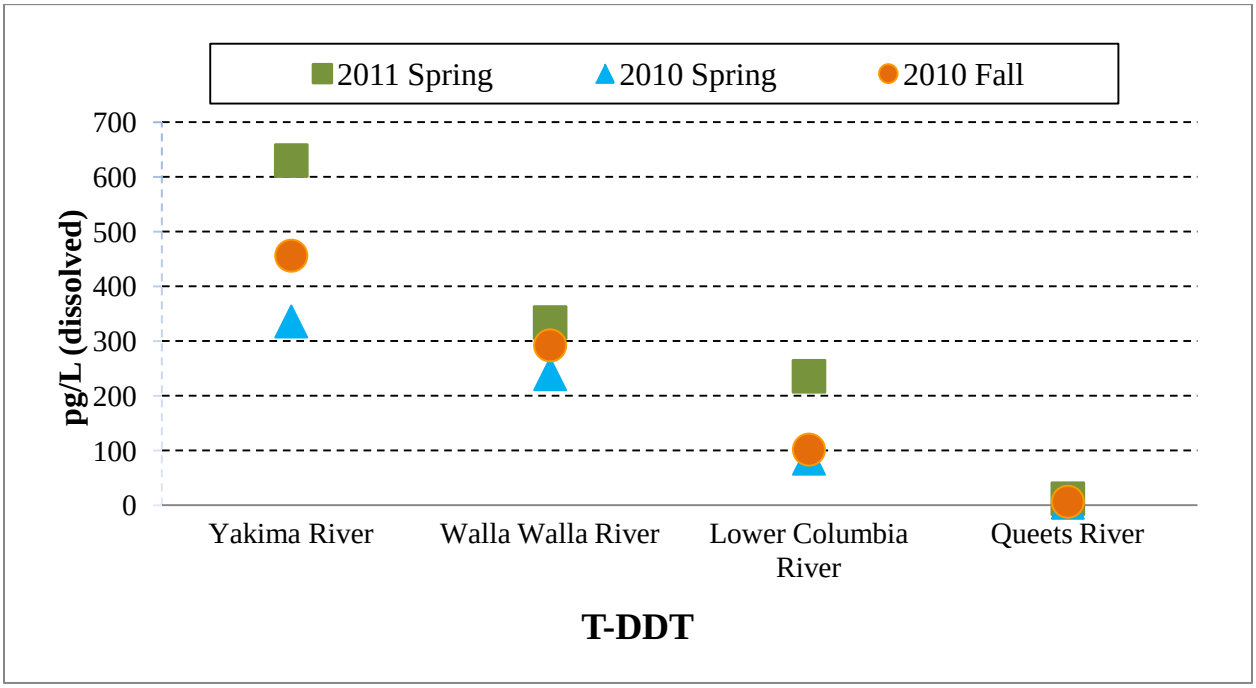

Figure 2. Estimated Dissolved Concentration of Total DDT (T-DDT) in 2010 and 2011.

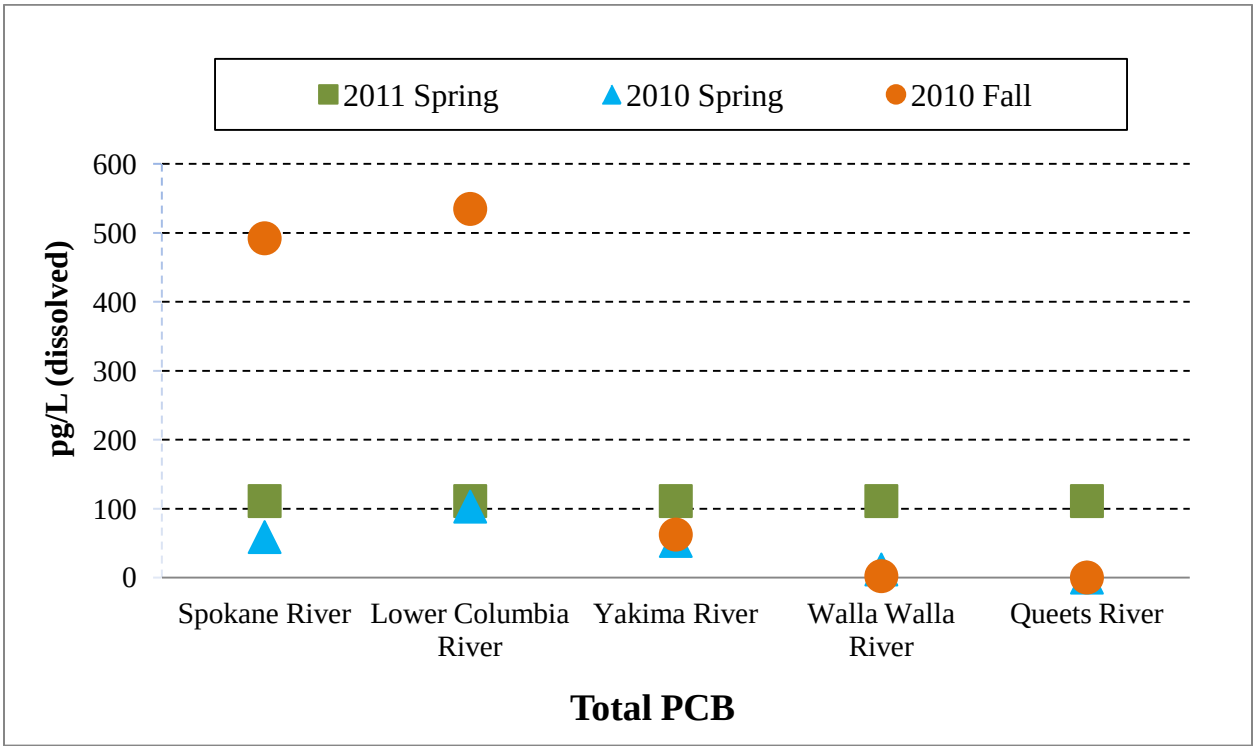

Figure 3. Estimated Dissolved Concentration of Total PCBs in 2010 and 2011.

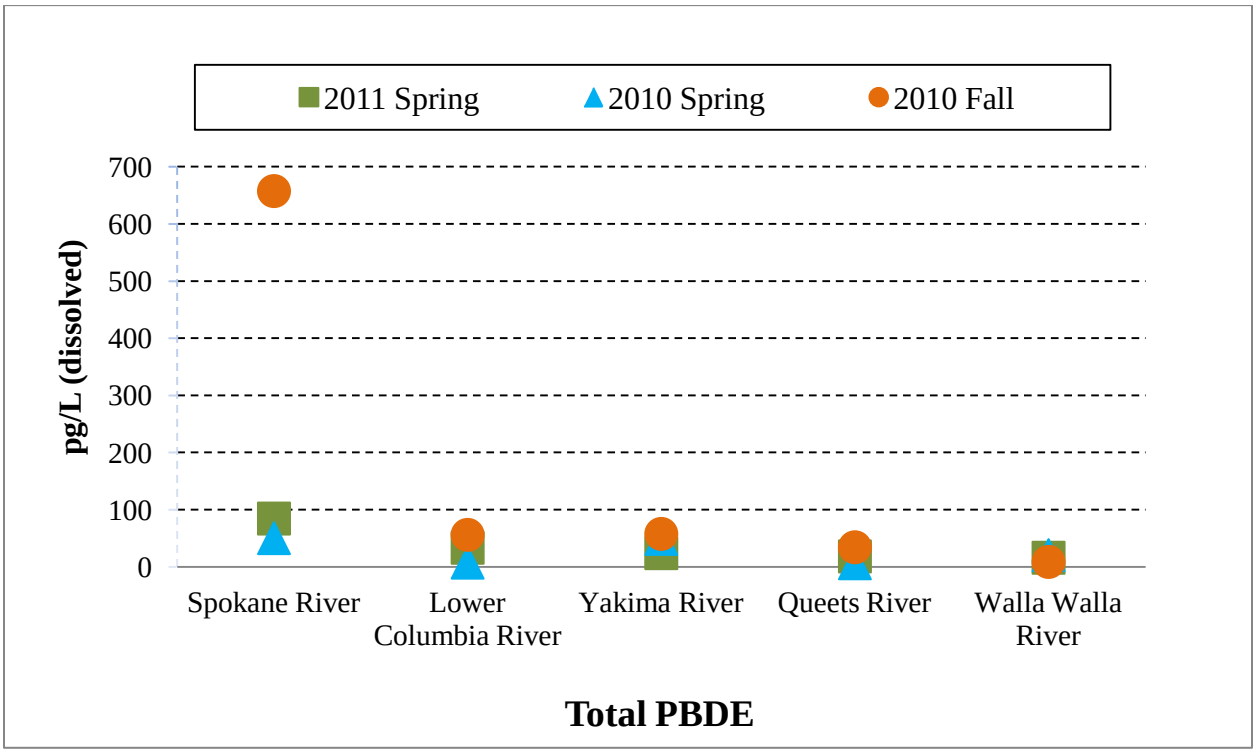

Figure 4. Estimated Dissolved Concentration of Total PBDEs in 2010 and 2011.

Data Usability

We reviewed all aspects of this study since it began in 2007 to determine whether the data collected are suitable for detecting temporal trends at sample sites. The 2010-2011 effort focused on sites and analytes likely to provide the most useful data to meet the goal of detecting trends. The ability to detect trends depends on:

- Sample results that are unbiased by noise in the measurement system. In this project, the greatest noise is manifested in contamination of blank samples.
- Methodology that remains consistent. Even small changes in sampling, laboratory, and analytical procedures can introduce bias.
- The initial and final levels of target analytes are high enough to be discerned from the noise of the measurement system.

Noise in the Measurement System

Contamination of a measurement system is commonly determined by using various blank samples. These samples help identify sources of contamination and help guide actions to reduce or eliminate the problem. Various practices of blank-correcting results are controversial and often add uncertainty to corrected results. Ideally, the signal that is measured is much higher than the level of noise in the system, and the noise is not an important factor. This study found that the signals measured in the environment were often similar to the level of noise in the measurement system. Additional QA efforts were made in 2009 - 2011 to help address concerns about contamination found in various blanks in this and other Ecology studies using SPMDs. Results are summarized below.

2009 QA

Some major findings from 2009 can be found in Sandvik and Seiders (2011) and include:

- Fabrication, storage, dialysis, and GPC processes for SPMDs accounted for most of the contamination (60% - 90%), while spiking processes and air exposure during deployment and retrieval accounted for 10% - 30% and 0% - 15%, respectively.
- The level of contamination varied among analytes as well as among sampling events.
- The ability to measure spatial or temporal trends with SPMDs at many sites is compromised because contaminant levels are low relative to the noise in the sampling system.
- The level of confidence in results that were blank-corrected using previously recommended techniques is poor, which reduces the sensitivity and credibility of any analyses for trends.
- Individual PBDE congeners found in the environment were also found in the blanks including the most prevalent congeners of -047 and -099. Therefore this background contamination must be accounted for when analyzing for PBDEs.
- About a fourth of the PCB congeners were consistently found in blanks yet varied slightly depending on which laboratory analyzed them. Future analyses might be able to tease out congeners unaffected by contamination, but studies should not depend on a congener

subgroup long term because of the uncertainty of finding a consistent group free from contamination issues.

Certain analyses such as for PAHs were recommended to be discontinued (starting in 2011) because the levels found posed little environmental risk and were low relative to contamination.

2010 – 2011 QA

In 2010, field blanks were constructed and exposed to ambient air as were the field samples rather than sitting loose in a can as is typically done. These were not paired with other blanks, which limited comparisons.

In 2011, additional blanks were analyzed to identify additional sources of contamination within the sampling system. These included: (1) the EST laboratory spiking blank split 50:50 with half using GPC cleanup process and the other half not, (2) four Day0-dialysis blanks—three spiked with EIS before extraction and one spiked before analysis (after extraction), and (3) three field blanks constructed and exposed to ambient air as were the field samples paired with three blanks exposed in an open can as is typically done.

Residue results showed the following:

- The spiking blank using GPC cleanup processes had higher total PCB concentrations than the blank not using GPC (42 versus 30 ng/sample respectively). The GPC instrument is suspect in this contamination since it is difficult to clean for these low levels.
- Three Day0-dialysis blanks showed no CP contamination, less than LODs for detected PBDEs, and ranged from 95 – 130 ng/samples for total PCBs. Further assessment is needed for comparing the impact of spiking EIS before or after extraction.
- Results from the different methods of field blank exposure for PBDEs and PCBs are difficult to discern since the levels among these blanks are relatively similar. Figures 5 and 6 show the 2011 paired field blanks levels. More paired samples would be needed for statistical evaluation.

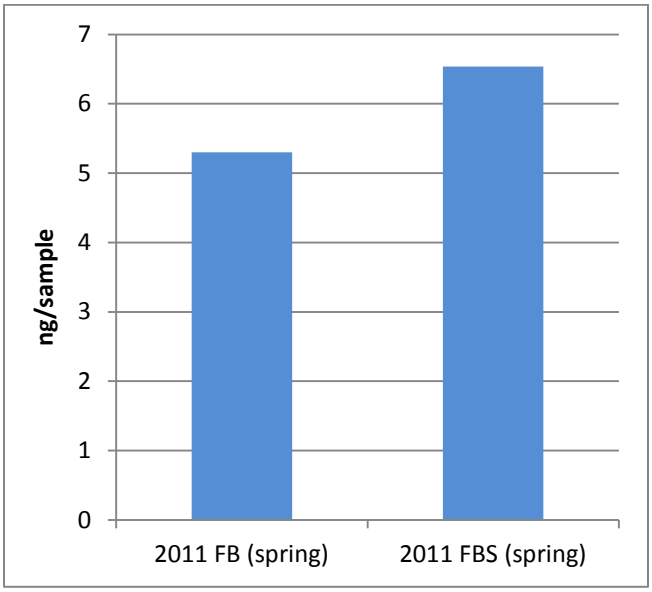

Figure 5. Averaged Residue Results in Paired Field Blanks for Total PBDEs in 2011. (ng/sample).

FB = field blanks in can; FBS = field blanks specially mounted like field samples.

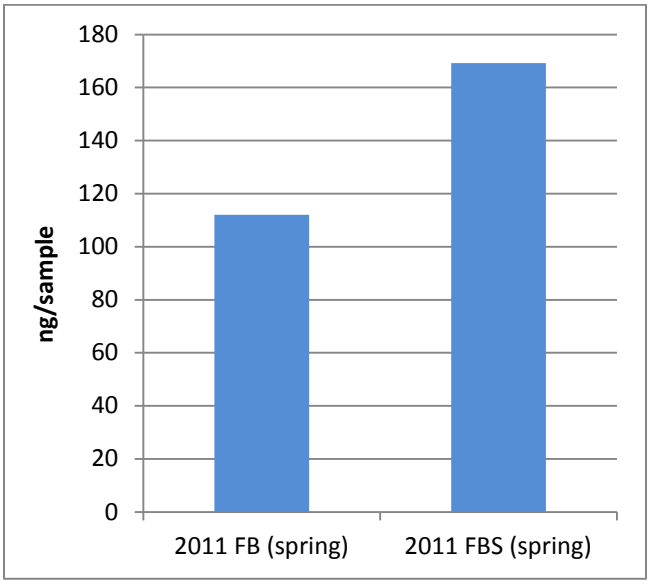

Figure 6. Averaged Residue Results in Paired Field Blanks for Total PCBs in 2011. (ng/sample).

FB = field blanks in can; FBS = field blanks specially mounted like field samples.

Further assessment of the above QA results is needed for significance of these findings and will be reviewed for future SPMD studies conducted at Ecology.

Methodology Changes

Changes in methods can introduce unwanted bias in the data from a long-term monitoring project. Bias that is consistent in a data set may have a small effect on trend analysis. However, if a bias is corrected (or introduced) at some mid-point during sampling and result processing, then the statistical analysis will be compromised. The potential effect of bias due to changes in procedures can be assessed by overlapping the new and old procedures for several sampling events prior to abandoning the old method. This was not done in most cases due to the nature of the changes (e.g., method corrections) and expense.

The increased QA efforts in 2009-2011 helped evaluate some changes in methodology and are discussed below. Appendix M details the historical changes in sampling and laboratory procedures, as well as large-scale environmental changes, that potentially affect this project by introducing bias.

2007, 2008, and 2009 Method Differences

There were two main differences in how results were processed in 2007, 2008, and 2009:

1. Blank correcting all results versus blank correcting only results that were deemed acceptable for blank correction.
2. Using summed PCB values (e.g., total PCBs) versus individual congeners as inputs into the USGS model used for estimating PCB concentrations in water.

Differences in blank correction techniques were assessed by comparing results from the two techniques on PCB and PBDE results from 2008 and 2009. RPDs generally were (1) <10% in results above the reporting limits, but much higher in results near or at the reporting limits particularly in PBDEs, (2) up to 27% for PCBs, and (3) >50% for PBDEs (Sandvik and Seiders, 2011). Results near or at the reporting limit were within the noise of the system, which clouded comparability.

Differences in results from using summed versus individual PCB congeners as inputs into the USGS models were compared using the results from 2008 and 2009. RPDs were less than 10% overall, which is deemed adequate for considering the results comparable (Sandvik and Seiders, 2011).

Sampling procedures (i.e., field deployment, sampling processing) were the same, and data reduction processes were very similar.

Pre- and post-2009 Method Differences

In 2010 and 2011, there were two major changes from pre-2009 methodology:

1. The PCB extraction internal standards (EIS) were spiked into the SPMD samples before extraction (dialysis) at the processing laboratory (EST) instead of afterward at the analytical laboratory (contract lab) as was done from 2007-2009. Further evaluation should be done to assess the impact of this change.

2. The initial concentration of PRCs was the value measured in the blanks rather than the documented amount spiked into the SPMD membranes. The initial concentration of PRC is used in the USGS model for estimating water concentrations.

The full magnitude and direction of a bias can likely be estimated by re-working all the historical data, but that is beyond the scope of this report. A separate study would be needed to answer the QC questions about data comparability before trends can be assessed using results from 2007-2009.

Thresholds

Ideally the noise of the sampling and analytical system would be well below the levels of contaminants in the environment to allow for high confidence in the measured values. Unfortunately, the levels of contaminants measured in the majority of samples thus far are close to the level of noise in the measurement system, thus confounding attempts to determine true change in the environment. The ability to detect trends in this project requires ambient levels of target analytes to be high enough that they can be discerned from noise in the measurement system with confidence.

Estimation of thresholds needed for beginning a trend monitoring effort was discussed in an earlier report (Sandvik and Seiders, 2011). The report suggested that ambient levels of target analytes in SPMD residues should be at least 50 to 100 times greater than what is measured in the blanks. The thresholds needed at the start of a trend monitoring effort were estimated to be: 2300-4600 ng/sample for total PBDEs, 3250-6500 ng/sample for total PCBs, and 50-100 ng/sample for most CPs. Since PAH monitoring was discontinued starting in 2011, they were not considered here. Note that the threshold for continued monitoring for CPs was set at only 5 to 10 times the reporting limit since contamination was not found in blanks. All sample results (2007-2011) were under these thresholds except for some CPs.

These thresholds were re-examined using the 2010-2011 results because the many changes in this project have led to poor confidence in the 2007-2009 results. Thresholds for continued monitoring were based on multiples of the limit of quantitation (LOQ) for dissolved water concentrations.

1. First, the concentration *after* some decrease over time should be well above the noise of the measurement system. This would be, at a minimum, the LOQ. A more conservative level would be 2 to 5 times the LOQ for some analytes where the variability of blank contamination over time is poorly understood (e.g., PCBs and PBDEs).
2. Second, the initial concentrations measured *before* decrease over time should be high enough that a decrease is detectable and can be attributed to actual change over time. Such a decrease would need to be a strong signal for this project because of the low frequency of sampling (1-2 samples per year) and high variability of the data. A strong signal would be a large reduction, such as a change by a half to a full order of magnitude. Thus, the pre-trend value would need to be 5 to 10 times greater than the post-trend value. Using the LOQ as a post-trend value (from #1 above), the pre-trend value would then need to be 5 to 10 times the LOQ. A more conservative approach would use a post-trend value that is 2 to 5 times the LOQ, which corresponds to a pre-trend value of 10-50 times the LOQ.

The ability to detect a trend with a weaker signal, such as a reduction by a factor of 2-5, seems less likely given the variability associated with using SPMDs. A weaker signal will be obscured by uncertainty from a combination of factors: the sample collection system (SPMDs), analytical methodologies for organic chemical, and variability associated with the inputs for the model used for estimating water concentrations.

For this project then, continued monitoring for trends using SPMDs might be worthwhile where the ambient levels of target analytes are 10 to 50 times greater than the LOQs determined from the 2010-2011 results. Table 8 shows LODs, LOQs, and threshold values for selected analytes. Note that the CPs in Table 8 have not been detected in blanks, so the threshold for continued monitoring could be only 5 to 10 times the LOQ.

Table 8. Thresholds for Trend Monitoring with SPMDs Using the 2010-2011 Results (pg/L).

Analyte →	t-PBDEs		t-PCBs		t-DDTs	Dieldrin	Chlor-pyriphos	Endo-sulfan I	Toxa-phene
Threshold	Low	High	Low	High	Uses single result				
LOD	18	29	10	17	9	13	22	220	120
LOQ	23	29	29	110	9	13	22	220	120
2x LOQ (post-trend lo)	46	59	58	220	18	26	44	440	230
5x LOQ (post-trend hi)	120	150	150	560	46	66	110	1100	580
10x LOQ (pre-trend lo)	230	290	290	1100	91	130	220	2200	1200
50x LOQ (pre-trend hi)	1200	1500	1500	5600	460	660	1100	11000	5800

Sample Locations

Monitoring for trends involved a minimum of four years of sampling twice a year at waterbodies throughout Washington State. As this study progressed and more information became available, it became apparent that low contaminant levels at certain sites made trend detection unlikely; therefore, some sites were excluded. As previously described, six sampling locations were selected in 2010 and five sites in 2011, a reduction from 12 sites initiated in 2007. Continued monitoring at all or some of the five 2011 sites would be necessary to begin to assess for trends.

Table 9 summarizes the possibility of detecting trends at the sites monitored in 2011. In a qualitative assessment, high chemical levels in samples would be at least 50 x LOQ, medium levels would be approximately 20-30 x LOQ, and low levels would be 10 x LOQ.

Selected pesticides in the Yakima and Walla Walla Rivers are the most promising for trend detection because ambient levels are high relative to reporting limits. While levels of PCBs and PBDEs in the Spokane River do not regularly meet the 10x-50x threshold, the interest in this site may warrant continued monitoring, even though detection of a true trend will be challenging. The Lower Columbia River site shows a medium possibility for detecting trends in most analytes, so it may be worthy of continued monitoring. The Queets River site can be considered a reference site, with all analytes found at low levels.

Table 9. Qualitative Summary of the Possibility of Detecting Trends at Monitored Sites.

Site	t-PBDEs	t-PCBs	t-DDTs	Dieldrin	Chlor-pyriphos	Endo-sulfan I	Toxa-phene
Yakima R	u	u	H	L	H	L	u
Walla Walla R	u	u	H	L	M	L	H
Spokane R @ Ninemile Dam	M	L	-	-	-	-	-
Lower Columbia R	u	M	M	u	M	u	u
Queets R	R	R	R	R	R	R	R

H, M, L = high, medium, and low possibility for detecting decreasing trend. R- reference site
u = unlikely to detect decreasing trend
- = not analyzed.
R= reference.

This study recommends continued monitoring efforts for those sites with medium to high possibilities for detecting trends. These include the Lower Columbia, Spokane, Walla Walla, and Yakima Rivers. The Lower Columbia River is also used by other monitoring programs for focus studies (e.g., USGS, Oregon Department of Environmental Quality), which could supplement this monitoring effort. The Spokane River has other monitoring efforts underway that this monitoring effort may add value to.

Other SPMD Uses

SPMDs continue to be a good tool for detecting certain chemicals when substantial effort to ensure useful data is assured with strict QC practices (i.e., SOPs). Data collected could be used as a tool for locating sources (screening) within a waterbody or for identifying the time of highest concentrations. Sites with appropriate characteristics could then be added to a long-term trend monitoring effort.

This study found several areas where SPMD data could be a useful screening tool. For example, toxaphene was found in high concentrations in the Walla Walla River during all sampling events (2007-2011). Therefore, SPMDs could be used to aid the current studies aimed at locating the

source of the toxaphene in the Walla Walla River or tributaries. Likewise, PBDEs have been found at moderate concentrations in the Spokane River, specifically in the fall. SPMDs may be useful in identifying certain reaches of the river and certain times of the year where PBDE concentrations were the highest, aiding in identifying the source.

Summary

The 2007-2011 data from this project are currently inadequate for use in detecting temporal PBT trends. Various factors contribute to this situation, with the most important being:

- Changes in analytical procedures, particularly for PCB congeners whose results are also used for critical model inputs such as the SPMD sampling rates.
- Large variability and uncertainty in results from the lower end of the analytical range, particularly for PCBs, PBDEs, and PAHs. The levels of background contamination have exhibited large variability, suggesting that sources of contamination have not been fully identified or corrected.
- The levels of target analytes at selected sites are low relative to the ability of the SPMD system to accurately measure them on a consistent basis. This is an issue more for PCBs, PBDEs, and PAHs than it is for CPs.

Continued use of SPMDs for long-term monitoring should be given careful consideration. The use of SPMDs still requires substantial resources, even though corrective actions have improved the reliability of data from the SPMD system since this project began. Results from SPMDs are still considered to be estimates based on models, and are not yet acceptable for use in regulatory contexts, such as for Ecology's Water Quality Assessment and 303(d) listing process.

Other sampling and analytical procedures should be investigated to see if the goals of trend detection and broader use of results could be met. The detection and reporting limits described above may be achievable with other techniques.

Objectives for other studies, such as source tracking or screening for presence/absence, could be met from the ability of SPMDs to accumulate certain chemicals over time. Chemical concentrations found above the thresholds described above could be included in a longer-term monitoring effort.

Conclusions

This report presents the fourth and fifth year (2010-2011) results as well as an assessment of data collected from 2007 through 2011 for usability in detecting temporal trends.

The study results support the following conclusions:

- Results from the 2010 and 2011 monitoring included:
  - A similar spatial and seasonal pattern was seen in previous sampling years (2007-2009) although the concentrations were not comparable.
    - Pesticide concentrations were generally highest in the Walla Walla and Yakima Rivers in the spring.
    - PBDEs were highest in the Spokane River in the fall.
    - PCBs were highest in the Spokane and Lower Columbia Rivers.
    - Toxaphene levels continue to be elevated in the Walla Walla River.
    - Lower Columbia River, Lake Washington, and the Spokane River had the highest level of PAHs in 2010.
  - Results continue to be inconclusive regarding seasonal patterns for PBDEs, except for elevated PBDE concentrations in the Spokane River observed in the fall sampling event.

- Usability assessment of the 2007-2011 Data for Temporal Trend Analyses found:
  - Sample results since the start of this study have been biased by noise in the measurement system which makes trend detection not feasible at this time. The greatest noise is manifested in changes in analytical methods and contamination of the analytical process as found in blank samples.
    - From the 2009 study, most of the contamination was found within the SPMD laboratory procedures involving membrane fabrication, storage, dialysis, GPC cleanup, and spiking processes.
  - Methodology has not remained consistent throughout the past five years (2007-2011). This inconsistency introduced bias, which hampers the ability to detect trends. The major differences in methods were: changes in the PCB congener analysis (the spiking of extraction internal standards after extraction versus spiking before extraction), changes in addressing background noise (blank-correcting versus censoring data), and selecting the initial PRC values used in modeling dissolved water concentrations (using reported spiked values versus measured spike values from blanks). Since there were large method changes, only 2010 and 2011 results could be considered comparable.
  - Environmental levels of most target analytes in ambient waters in Washington were low relative to background noise in the measurement system at most sites, resulting in high uncertainty in quantifying levels of analytes and assessing trends.

- Minimum contaminant levels for long-term monitoring for temporal trend detection are suggested in the report. Levels of PCBs, PBDEs, and PAHs do not meet these thresholds in most waters, hindering the ability to detect trends. Levels of some CPs appear more suitable for long-term monitoring and trend detection.

- SPMDs could be a valuable tool used by other studies for source tracking and screening for presence/absence of certain chemicals within a waterbody.

Recommendations

Based on an analysis of results collected since 2007, the following recommendations are made:

- Evaluate whether continued monitoring with SPMDs for trend detection is a cost-effective endeavor. An evaluation-and-recommendation document for continued monitoring is currently being developed.
- If cost effective, continue monitoring at selected sites where levels of target analytes meet the thresholds for high and moderate probability for detecting trends as described in this report.
  - Sites and analytes with high probability for detecting trends are:
    - Yakima River for chlorinated pesticides (CPs).
    - Walla Walla River for CPs.
  - Moderate probability sites and analytes include:
    - Lower Columbia River for PBDEs, PCBs, and CPs.
    - Spokane River at Nine Mile for PBDEs.
- Use SPMDs as a tool for locating sources (screening) or for identifying the time of highest concentrations.
- Determine whether to improve the reliability and accuracy of the SPMD system through actions Ecology could take, such as:
  - To limit analytical bias, analyze PCB congeners by the same laboratory each year.
  - Explore other options for a passive sampling system which could include an in-house technique that would have the benefit of full control and consistency in QC and analytical methods.
  - Determine if the use of PRCs is cost effective, especially in PCB congener analyses, which uses the expensive HRMS method. This assessment would compare outputs of different models (version 4 versus version 5) and determine whether collection of this information is worth the added cost.

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Appendices

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Appendix A. Monitoring Site Descriptions

Table A-1. Sample Site Descriptions, 2010 and 2011 PBT Trends Study.

Site Name	County	Sampling Dates		Site Description	Latitude[1]	Longitude[1]	WBID[2] WA-	WRIA Number	EIM "User Location ID"[3]
		Deployed	Retrieved		Decimal Degrees	Decimal Degrees			
Lower Columbia R.	Wahkiakum	4/30/10 9/8/10 5/4/11	5/27/10 10/6/10 6/1/11	Columbia River, RM 54.	46.1849	-123.1876	WA- CR-1010	25	SPMDTR-LCR2
Lower Columbia R. Replicate	Wahkiakum	4/30/10 9/8/10 5/4/11	5/27/10 10/6/10 6/1/11	Columbia River, RM 54.	46.1849	-123.1876	WA- CR-1010	25	SPMDTR-REPLCR
Queets R.	Jefferson	4/30/10 9/9/10 5/5/11	5/28/10 10/7/10 6/2/11	Queets River, RM 11.5.	47.5522	-124.1978	WA- 21-1030	21	SPMDTR-QUEETS
Queets R. Replicate	Jefferson	4/30/10 9/9/10	5/28/10 10/7/10	Queets River, RM 11.5.	47.5522	-124.1978	WA- 21-1030	21	SPMDTR-QUEETS
Spokane R.	Spokane	4/28/10 9/9/10 5/3/11	5/27/10 10/7/10 5/31/11	Spokane River, Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA- 54-1020	54	SPMDTR-SPOK
Spokane R. Replicate	Spokane	4/28/10 9/9/10 5/3/11	5/27/10 10/7/10 5/31/11	Spokane River, Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA- 54-1020	54	SPMDTR-REPSPOK
Spokane R.	Spokane	4/29/10	5/27/10	Spokane River, near Idaho border, RM 98.3.	47.6942	-117.0094	WA- 57-1010	57	SPMDTR-SPOKBD
Walla Walla R.	Walla Walla	4/27/10 9/8/10 5/25/11	5/26/10 10/6/10 6/20/11	Walla Walla River, RM 9.	46.0709	-118.8268	WA- 32-1010	32	SPMDTR-WALLA
Washington L.	King	4/28/10 9/9/10	5/26/10 10/5/10	Lake Washington, outlet.	47.6475	-122.3019	WA- 08-9350	8	SPMDTR-LKWA2
Yakima R.	Benton	4/27/10 9/8/10 5/3/11	5/26/10 10/6/10 5/31/11	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) system.

Appendix B. Chemicals Analyzed in SPMD Samples

Table B-1. Chemicals Analyzed in SPMD Samples Collected During 2010 and 2011.

Chlorinated Pesticides (MEL PEST2)
alpha-BHC
beta-BHC
gamma-BHC (lindane)
delta-BHC
Heptachlor
Aldrin*
Chlorpyrifos
Heptachlor epoxide*
trans-chlordane (gamma)*
cis-chlordane (alpha)*
Endosulfan I (Alpha-endosulfan)
Dieldrin*
Endrin*
Endrin Ketone
Endosulfan II (Beta-endosulfan)
Endrin Aldehyde
Endosulfan Sulfate
4,4'-DDE*
4,4'-DDD*
4,4'-DDT*
2,4-DDE
2,4'-DDD
2,4'-DDT
Methoxychlor
Oxychlordane
DDMU
Cis-nonachlor
Toxaphene*
Trans-nonachlor
Mirex*
Chlordane (technical)*
Hexachlorobenzene*
Dacthal (DCPA)
Pentachloroanisole

Polychlorinated Biphenyls*[1]

Polybrominated Diphenyl Ethers*
PBDE-47
PBDE-49
PBDE-66
PBDE-71
PBDE-99
PBDE-100
PBDE-138
PBDE-153
PBDE-154
PBDE-183
PBDE-184
PBDE-191
PBDE-209

*PBTs as defined by Ecology

1. Approximately 170 individual PCB congeners and the remainders as co-eluting groups.

Table B-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 C. Data Quality Summary

Laboratory Case Narrative Summary

Manchester Environmental Laboratory (MEL) prepared written case narratives assessing the quality of the data collected during 2010 (spring and fall) and 2011 (spring) sampling events. Case narratives are available upon request.

The project lead compared results from field and laboratory QC samples to the MQOs to determine if the MQOs were met. Based on these assessments and reviews of laboratory data verification reports, the data were accepted, accepted with appropriate qualifiers, or rejected. Results presented here were accepted, and any qualifiers were retained.

All samples were prepared and analyzed within the methods holding times for the various parameters. Analytical laboratory method blanks showed no significant contamination for any of the chemicals analyzed. Most QC procedures and corresponding samples fell within acceptable limits.

PCBs

All calibration standards for PCBs were within the QC limits. However, a number of PCB congeners were qualified as estimates (J qualified) because the concentration was below the lowest calibration standard.

Each congener reported as detected met the isotopic abundance ratio and retention time criteria for positive identification with several exceptions. These exceptions have been qualified to reflect tentative identification, and the associated numerical value represents its approximate concentration: qualified NJ. The values reported for these congeners were not included in the totals for the corresponding homolog.

Recoveries for labeled compounds (aka extraction internal standards (EIS)) in the samples were all within QC limits of 15% - 150% for PCB-001L and PCB-003L, and 25% - 150% for all others, with several exceptions. These limits are consistent with the updates and revisions from 2003 to Method 1668A. Analytes that use the affected labeled compounds for quantification have been qualified as estimates: J for detected and UJ for nondetected.

One laboratory control sample (LCS) known as the on-going precision and recovery (OPR) was spiked with labeled and unlabeled PCB compounds for each sampling period (spring and fall). All labeled compound recoveries were within QC limits of 15% - 140% for PCB-001L and PCB-003L and 30% - 140% for all others. Targeted unlabeled compound recoveries were within QC limits of 50% - 150% with several exceptions. Corresponding sample analytes were not qualified. Unlabeled analytes that were not deliberately spiked into the OPR were also detected in this sample.

PAHs

Overall, PAH results had excellent QA results for 2010. No PAHs were analyzed in 2011. Some 2010 PAH analytes did not meet calibration criteria and were biased high. Detected results were qualified for benzo(b)fluoranthene and benzo(k)fluoranthene in the spring samples and for fluorene, carbazole, benzo(a)anthracene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene in the fall samples. Detected results for one spring sample were qualified for low surrogate recoveries.

A spiked membrane blank was prepared for evaluation of the dialysis process. All analytes recovered within the acceptable range of 50% - 150% except for acenaphthylene. This result may be biased low and was qualified as an estimate (J). No sample results have been qualified based on this spiked membrane blank.

Chlorinated Pesticides

All calibration checks for chlorinated pesticides (CP) were within QC limits with a few exceptions of chlorpyrifos, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, and methoxychlor for 2010 results and toxaphene, endrin, and DDMU for 2011 results. Detected native samples were qualified as estimates (J). Similarly, all degradation check standards met the established criteria of ≤ 15%. CP surrogate and LCS or LCS duplicate recoveries were within the established QC limits of 30% -130% and 50%-150% respectively except a-BHC in 2011. Non detected results were qualified at estimated reporting limits, "UJ," and detected results as estimates, "J".

Positive identification was made for all CP analytes in the 2010 and 2011 sampling periods with a few exceptions. The exceptions were qualified as estimates ("J") for relative percent differences > 40%, or estimated reporting limits ("UJ") for chromatographic interferences.

Most analytes in a spiked membrane blank recovered within the MQO acceptable range of 50%-150% except for a few results. a-BHC, d-BHC, g-BHC (Lindane), endosulfan I, and endrin aldehyde in 2010 spring; for d-BHC, chlorpyrifos, dacthal, endosulfan I, endosulfan II, and methoxychlor in 2010 fall; and for chlorpyrifos, d-BHC, endrin ketone, and methoxychlor in 2011 spring. No sample results have been qualified based on this spiked membrane blank.

Concentrations of technical chlordane and toxaphene were determined using 3 – 10 of the most prominent homologs for averaging and comparing to a commercial standard. Components that appear to be masked by interference are avoided in this calculation. Because these analytes undergo processes in the environment that degrade (or "weather") these components, the pattern of these contaminants rarely show the same ratios as the commercial standards. Therefore, if the homologs exceeded 40% RPD, the detected results were reported as estimated concentrations (J). Three technical chlordane results and three toxaphene results in 2010 were qualified as estimates, and all toxaphene results in 2011 were qualified as estimates.

PBDEs

Both 2010 and 2011 samples had excellent QA results for PBDEs. In 2010 several detected results were qualified estimates (J) because they fell below the lowest calibration point on the

curve or for low calibration response for PBDE-138. Sample 1006021-15 was rejected because a laboratory accident produced low surrogate recoveries.

Field

Sample Integrity

The SPMDs were checked midway (two weeks) through the month-long deployment period. During this check, SPMD samplers were gently moved back and forth under water to remove loose sediment or biofouling. All samplers remained submerged based on data from continuous temperature monitoring devices (TidbiT™) which were attached to the sampler and attached on shore nearby. All SPMDs were retrieved for the 2010 and 2011 sampling events.

Membrane Spike, PRC, and Surrogate Recoveries

Various spiking practices were used in the preparation and processing of SPMDs to help define the quality of results. Although the spiking solutions for the membrane spike contain matrix spike analytes, they are considered more like a spiked blank than a true matrix spike because they are spiked at the processing laboratory, not the analytical laboratory. All recoveries for the membrane spike analytes fell within the acceptable 50% - 150% recovery limits with several exceptions. Yet no sample results were qualified based on the membrane spike recoveries.

The PRC recoveries were within an acceptable range (20 – 80%) with several exceptions. High PRC recoveries were found in about 40% of the field samples. The highest PRC of individual samples was not used in calculations for water concentrations using the USGS model if the uncertainty factor (standard deviation) was above 2.

Most surrogate recoveries were within an acceptable range (25 – 150%). One low surrogate recovery (2%) was found in a sample that suffered loss due to a laboratory accident. That sample (the Spokane River replicate in the spring of 2010) was rejected.

Field Replicate Samples

Field sample replicates were deployed with each sampling event to estimate total variability in the field and laboratory. In 2010 and 2011, two locations had field replicates: the Lower Columbia River and the Spokane River at Nine Mile Dam.

Each replicate contained five SPMD membranes (like the field sample) and was deployed beside the sample within a few feet. Unfortunately, the field replicate in the Spokane River 2010 spring sampling event (sample number 1006021-15) was compromised as mentioned above. Results from the other replicate samples are listed in Appendix G.

The replicates showed good precision in most cases, with over 75% of the residue results having RPDs of 30% or less. CP residue results showed excellent precision for the Lower Columbia River replicates with 88% (2010 spring), 91% (2010 fall), and 82% (2011 spring) RPDs of 25% or less. No CPs were analyzed in the Spokane River samples. PBDEs also showed excellent precision of 25% or less RPDs in nearly 70% in 2010 and over 90% in 2011. PCBs had fairly

good precision with RPDs of 65% or greater in 2010 and over 80% in 2011. Higher variability was seen in PAHs with 45%, 18%, and 59% for the Lower Columbia River (2010 spring and fall) and the Spokane River (2010 fall) respectively having RPDs 25% or less. No PAHs were analyzed in 2011.

Lower variability was observed in the Spokane River replicates compared to the Lower Columbia River replicates. For the Spokane River replicates, 91% of all analyte results had RPDs <= 25% in both 2010 and 2011, whereas Lower Columbia River showed RPDs of 71% and 64% for spring and fall replicates respectively in 2010 and 83% in 2011. Since the 2010 spring sample for the Spokane River was rejected, this may bias the observed difference. Yet, a similar observation was made in 2009 between the Lower Columbia and Spokane River spring replicates (Sandvik et al., 2011). Differences were speculated then to be due to laboratory handling (some extract loss) with the Lower Columbia River samples. Although the laboratory recorded 2 to 3 drops loss for the 2010 Lower Columbia River spring samples, this does not explain the difference seen in the 2010 fall samples and in 2011. Measuring variability differences from the differences in the dynamics of the sampling locations may be clouded by other variables such as field and laboratory handling of the samples.

Variability in the estimated water concentration between replicates reflects the differences in PRC recoveries and has been shown to follow a similar pattern as the residue results (Sandvik, 2010b). These are not reported here because the overall RPDs for CP, PBDE, PCB, and PAH residue concentrations remain generally within 30% or better.

Field and Processing Blanks

Several blanks were used to measure contamination at various stages in the measurement system (Table F-1). All steps in the use of SPMDs, from manufacture to final lab analyses, are represented in the left-hand column. Each step is a potential contributor of contamination to each blank if indicated by an “X”.

Analytical laboratory (MEL or contract laboratory) method blanks showed no significant contamination for any of the chemicals analyzed. Exceptions included benzo(a)anthracene in 2010 fall. Compounds are considered native to the sample if the area counts are greater than five times the blank. Four sample results in 2010 with low area counts (<5 times found in blank) were qualified as nondetects (UJ).

Individual CP, PCB, PBDE, and PAH compounds were detected in processing blanks. Concentrations of individual target chemicals in the blanks were inconsistent. Some of these same compounds (PCB, PBDE, and PAH) were found at similar levels in the field blanks, suggesting a combination of manufacturing and field sources. The background level appears to exist for PCBs, PBDEs, and PAHs and has been documented in previous reports (Sandvik, 2009; Sandvik, 2010b, Sandvik and Seiders, 2011). Handling background contamination is described above in the Methods section.

CPs are typically not found in blanks. An exception for CP contamination was found in one process blank (the Day0-dialysis blank) in the spring of 2010. Although the source of the CP

contamination is not clear, this blank was rejected because it was compromised due to spiking errors.

Table C-1. Types and Characteristics of Field and Processing Blanks.

QC Blanks and Processes	Field Blank	Day0-dialysis Blank	Day0 Method Blank[1]	Recovery Spike of OPR Process[1]	Fresh Day0 Blank[2]	Spiking Blank[3]	Spiked Solvent Reagent[3]
Pre-Field Processing							
Fabrication	X	X	X			X	
Membranes used	5	5	5	5	5	1 per lab	0
Spiking: PRCs	X	X	X			X	
Storage + transport to Ecology	X	X	X			X	
Field Storage & Transport							
Storage + transport to field	X						
Air exposure: deployment	X						
Storage + transport to-from field	X						
Air exposure: retrieval	X						
Storage + transport to EST	X						
Post-Field Processing							
Fabrication				X	X		EST [4]
Storage	X	X	X	X	X	X	X
Spiking: PRCs					X		X
Spiking: PCB congener EIS	X	X			X	X	X
Spiking: PCB congener OPR				X			
Spiking surrogates	X	X	X		X	X	X
Spiking: matrix spike							
Dialysis (extraction)	X	X	X	X	X	X[5]	X
GPC (cleanup)	X	X	X	X	X	X	X
Ampulizing: extract or reagent	X	X	X	X	X	X	X
Storage + transport	X	X	X	X	X	X	X
Analysis							
Analysis of samples	X	X	X[6]	X	X	X	X

1 - Used in isotopic dilution methods for PCB congeners.
2 - Held at Manchester Environmental Laboratory (MEL) for possible future analysis.
3 - Held at Manchester Environmental Laboratory (MEL) for possible future analysis.
4 - Source of the reagent that is used in spiking and/or processing.
5 - Typically goes through dialysis; yet could exclude dialysis if seeking influence of dialysis on contamination.
6 - The PCB congener EIS are spiked by the lab conducting analysis, just prior to analysis.
EST = Environmental Sampling Technologies.
EIS = extraction internal standards.
OPR = ongoing precision and recovery.

Limit of Detection and Quantitation

The censoring of results is to prevent a possible faulty inference being drawn (i.e., an analyte is reported as detected when, in fact, it is not detected or when an analyte is reported not detected when, in fact, it is detected). The data user must interpret the individual data values as sets of data with limitations and uncertainties.

Assuming well characterized blanks have provided background signal response, a real signal (detected analyte) can be distinguished from the blank signal (background noise), and thus true variability is known. This variability corresponds to different multiples of the standard deviation of the blanks. Since the variability is usually determined from a limited data set, considerable uncertainty to the standard deviation is introduced. Therefore, the question is: How much statistical confidence is desired for trends?

Two thresholds were used for censoring the data adopted by Keith (1991) and recommended by Alvarez (2010): the limit of detection (LOD) and the limit of quantitation (LOQ). The LOD is the level a result value was considered detected, and the LOQ is the level above which quantitative results may be obtained with a specified degree of confidence. These criteria were estimated using the mean of the field blanks and standard deviations within each sampling event.

In this study, results reported above the LOQ (field blank mean plus ten standard deviations) were used as reported (no correction). This LOQ corresponds to an uncertainty of ± 30% in the measured result value at the 99% confidence level (Keith, 1991).

For results below the LOD (field blank mean plus three standard deviations), results were censored as nondetects (U) at the associated LOD value. There is 99% confidence that this LOD level has less than a 1% risk of an analyte falsely detected, but a much larger risk arises that an analyte may be falsely labeled not detected (50%) (Keith, 1991). The high false nondetects risk does not impair this study since those results lie within the region of high uncertainty (field blank mean and field blank mean plus three standard deviations).

If the result is greater than the LOD but less than the LOQ, the reported result is used as the associated value for “U”.

Appendix D. Mean Water Temperature and Exposure Times

Table D-1. Mean Water Temperature and Water Exposure Times for SPMD Samples, 2010 and 2011.

Site	April-May 2010		Aug.-Sept. 2010		April-May 2011	
	Temp (ºC)	Time (days)	Temp (ºC)	Time (days)	Temp (ºC)	Time (days)
Lower Columbia River	12.5	26.9	18.6	28.0	11.6	27.9
Lower Columbia River - CP	12.5	26.9	18.6	28.0	-	-
Lake Washington	12.9	27.9	18.2	26.2	-	-
Lake Washington - CP	12.9	27.9	18.2	26.2	-	-
Queets River	9.1	27.9	12.9	28.4	8.4	28.2
Queets River - CP	9.1	27.9	12.9	28.4	-	-
Yakima River	14.9	28.8	18.3	27.9	13.3	28.2
Yakima River - CP	15	28.0	18.4	27.9	-	-
Walla Walla River	13.5	28.9	18.6	27.9	15.7	26.0
Walla Walla River - CP	13.6	28.9	18.5	27.8	-	-
Spokane River at Nine Mile Dam	11.0	29.1	14.3	28.0	9.6	28.0
Lower Columbia River Replicate	12.4	26.9	18.5	28.0	11.5	27.9
Lower Columbia River Replicate - CP	12.4	26.9	18.5	28.0	-	-
Spokane River at Nine Mile Dam Replicate	10.9	29.1	14.4	28.0	9.6	28.0
Spokane River near Idaho Border	10.4	27.9	-	-	-	-

CP = sample used for chlorinated pesticide analysis only.

- = not available. Did not sample. Yakima spring replicate lost.

Appendix E. Performance Reference Compound (PRC) Recovery in SPMDs

Table E-1. 2010 PRC Sample Recovery (spring).

PRCs spiked in each membrane. Samples = 5 membranes.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Lower Columbia River	1006021-01	PCB-004	3.64	37%
		PCB-029	4.06	72%
		PCB-050	4.82	89%
Lake Washington	1006021-03	PCB-004	5.06	52%
		PCB-029	4.34	77%
		PCB-050	4.78	88%
Queets River	1006021-05	PCB-004	4.14	42%
		PCB-029	4.0	71%
		PCB-050	4.22	78%
Yakima River	1006021-07	PCB-004	3.94	40%
		PCB-029	4.24	76%
		PCB-050	4.54	84%
Walla Walla River	1006021-09	PCB-004	2.52	26%
		PCB-029	3.48	62%
		PCB-050	4.14	76%
Spokane River at Nine Mile Dam	1006021-11	PCB-004	4.48	46%
		PCB-029	3.94	70%
		PCB-050	4.82	89%
Spokane River near Idaho Border	1006021-12	PCB-004	7.44	76%
		PCB-029	4.46	80%
		PCB-050	4.84	89%
Lower Columbia River Replicate	1006021-13	PCB-004	3.32	34%
		PCB-029	3.94	70%
		PCB-050	4.38	81%
Spokane River Replicate[3]	1006021-15	PCB-004	2.62	27%
		PCB-029	3.34	60%
		PCB-050	3.68	68%

Table E-1. (continued)

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Field Blank - Lower Columbia R.	1006021-16	PCB-004	10.6	108%
		PCB-029	4.5	80%
		PCB-050	4.64	86%
Field Blank - Queets R.	1006021-17	PCB-004	10.52	107%
		PCB-029	4.3	77%
		PCB-050	4.7	87%
Field Blank - Spokane R.	1006021-18	PCB-004	10.14	103%
		PCB-029	4.28	76%
		PCB-050	4.64	86%
Day0-dialysis Blank	1006021-19	PCB-004	7.5	76%
		PCB-029	6.1	109%
		PCB-050	5.64	104%
Day0-method Blank	1006021-20	PCB-004	10.2	104%
		PCB-029	4.84	86%
		PCB-050	5.02	93%
Spike Blank[4]	1006021-22	PCB-004	9.44	96%
		PCB-029	6.37	114%
		PCB-050	5.83	107%

1. 2010 initial concentrations are based on PRC recovery of mean of the Day0-method and Spike Blanks.
2. 2010 spring PRC initial concentrations: PCB-004 = 9.82 ng/SPMD; PCB-029 = 5.605 ng/SPMD; PCB-050 = 5.425 ng/SPMD.
3. The Spokane River replicate was rejected due to loss of sample in a lab accident.
4. Spike Blank = 1 SPMD membrane.

Table E-2. 2010 PRC Sample Recovery (fall).

PRCs spiked in each membrane. Samples = 5 membranes.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Lower Columbia River	1011010-01	PCB-004	3.46	32%
		PCB-029	4.82	95%
		PCB-050	4.6	88%
Lake Washington	1011010-03	PCB-004	3.92	36%
		PCB-029	4.3	85%
		PCB-050	4.84	93%
Queets River	1011010-05	PCB-004	5.1	47%
		PCB-029	4.26	84%
		PCB-050	4.28	82%
Yakima River	1011010-07	PCB-004	3.88	36%
		PCB-029	4.46	88%
		PCB-050	4.88	94%
Walla Walla River	1011010-09	PCB-004	2.58	24%
		PCB-029	3.9	77%
		PCB-050	4.4	85%
Spokane River at Nine Mile Dam	1011010-11	PCB-004	4.02	37%
		PCB-029	4.5	89%
		PCB-050	4.98	96%
Lower Columbia River Replicate	1011010-12	PCB-004	3.94	36%
		PCB-029	4.58	91%
		PCB-050	5.16	99%
Spokane River Replicate	1011010-14	PCB-004	3.56	33%
		PCB-029	4.04	80%
		PCB-050	4.28	82%

Table E-2. (continued)

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Field Blank - Lower Columbia R.	1011010-15	PCB-004	10.92	101%
		PCB-029	4.74	94%
		PCB-050	4.94	95%
Field Blank - Queets R.	1011010-16	PCB-004	10.2	94%
		PCB-029	3.8	75%
		PCB-050	3.94	76%
Field Blank - Spokane R.	1011010-17	PCB-004	10.32	95%
		PCB-029	4.62	91%
		PCB-050	4.72	91%
Day0-dialysis Blank	1011010-18	PCB-004	5.78	53%
		PCB-029	3	59%
		PCB-050	3.34	64%
Day0-method Blank	1011010-19	PCB-004	11.2	103%
		PCB-029	4.96	98%
		PCB-050	5.3	102%
Spike Blank[3]	1011010-21	PCB-004	10.5	97%
		PCB-029	5.14	102%
		PCB-050	5.11	98%

1. 2010 initial concentrations are based on PRC recovery of mean of the Day0-method and Spike Blanks.
2. 2010 fall PRC initial concentrations: PCB-004 = 10.85 ng/SPMD; PCB-029 = 5.05 ng/SPMD; PCB-050 = 5.205 ng/SPMD.
3. Spike Blank = 1 SPMD membrane.

Table E-3. 2011 PRC Sample Recovery (spring).

PRCs spiked in each membrane. Samples = 5 membranes.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Lower Columbia River	1106028-01	PCB-004	4.08	39%
		PCB-029	5.62	96%
		PCB-050	5.4	87%
Queets River	1106028-02	PCB-004	4.48	42%
		PCB-029	5.14	88%
		PCB-050	4.8	78%
Yakima River	1106028-03	PCB-004	3.14	30%
		PCB-029	3.98	68%
		PCB-050	4.44	72%
Walla Walla River	1106028-04	PCB-004	2.78	26%
		PCB-029	3.76	64%
		PCB-050	2.86	46%
Spokane River at Nine Mile Dam	1106028-05	PCB-004	2.82	27%
		PCB-029	4.78	82%
		PCB-050	4.34	70%
Lower Columbia River Replicate	1106028-06	PCB-004	4.02	38%
		PCB-029	5.26	90%
		PCB-050	5.4	87%
Spokane River Replicate	1106028-07	PCB-004	3.18	30%
		PCB-029	4.28	73%
		PCB-050	4.42	72%
Field Blank Special - Lower Columbia R.	1106028-08	PCB-004	13.48	127%
		PCB-029	7.14	122%
		PCB-050	6.22	101%
Field Blank Special - Queets R.	1106028-09	PCB-004	16.92	160%
		PCB-029	9.5	162%
		PCB-050	8.42	136%
Field Blank Special - Spokane R.	1106028-10	PCB-004	11.74	111%
		PCB-029	6.28	107%
		PCB-050	5.6	91%

Table E-3.

Sample Field ID	Sample Lab ID	Parameter Name	Final Concentration (ng/SPMD)	Recovered[1,2] (%)
Field Blank - Lower Columbia R.	1106028-11	PCB-004	10.1	95%
		PCB-029	6.16	105%
		PCB-050	6.82	110%
Field Blank - Queets R.	1106028-12	PCB-004	10.88	103%
		PCB-029	5.96	102%
		PCB-050	5.98	97%
Field Blank - Spokane R.	1106028-13	PCB-004	10.12	96%
		PCB-029	5.94	101%
		PCB-050	6.36	103%
Day0-dialysis Blank 1	1106028-14	PCB-004	10.54	99%
		PCB-029	5.76	98%
		PCB-050	6.64	107%
Day0-dialysis Blank 2	1106028-15	PCB-004	10.58	100%
		PCB-029	5.9	101%
		PCB-050	5.88	95%
Day0-dialysis Blank 3	1106028-16	PCB-004	10.66	101%
		PCB-029	5.9	101%
		PCB-050	6.02	97%
Day0-dialysis Blank 4	1106028-17	PCB-004	6.08	57%
		PCB-029	4.1	70%
		PCB-050	3.54	57%
Spike Blank A[3]	1106028-24	PCB-004	10.8	102%
		PCB-029	6.3	108%
		PCB-050	4.745	77%
Spike Blank B[3]	1106028-25	PCB-004	10	94%
		PCB-029	5.6	96%
		PCB-050	7.75	125%

1. 2011 initial concentrations are based on PRC recovery of mean of three Day0-dialysis Blanks.
2. 2011 spring PRC initial concentrations: PCB-004 = 10.593 ng/SPMD; PCB-029 = 5.853 ng/SPMD; PCB-050 = 6.18 ng/SPMD.
3. Spike Blank = 2 SPMD membrane composited and then split for Spike Blank A and B.

Appendix F. Log K_{ow}s Used to Estimate Water Concentration.

Table F-1. Log K_{ow}s Used in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2010 and 2011 PBT Trends Study.

Organochlorine Pesticides	Log K_{ow}	Ref.
p,p'-DDT	5.47	a
p,p'-DDE	6.14	a
p,p'-DDD	5.75	a
o,p'-DDT	5.59	a
o,p'-DDE	5.56	a
o,p'-DDD	6.08	a
DDMU	5.50	e
Dieldrin	4.60	a
Chlorpyrifos	4.90	f
Endosulfan I	3.78	a
Endosulfan-II	3.50	e
Endosulfan Sulfate	3.64	e
Hexachlorobenzene (HCB)	5.71	a
Pentachloroanisole (PCA)	5.48	b, e
Toxaphene	4.73	a
Chlordane (technical)	6.29	e
trans-Chlordane	5.38	a, c, d, e
cis-Chlordane	5.38	a, c, d, e
Dacthal	4.26	e
trans-Nonachlor	6.35	c, e
cis-Nonachlor	6.20	c, e
Heptachlor	5.19	a
Heptachlor Epoxide	4.51	a
alpha-Benzenehexachloride (a-BHC)	3.86	a
beta-Benzenehexachloride (b-BHC)	3.86	a
delta-Benzenehexachloride (d-BHC)	4.12	a
Lindane	3.71	a
Aldrin	5.97	e, i
Endrin	4.63	a
Endrin ketone	4.99	e
Endrin aldehyde	4.80	e
Mirex	6.89	a
p,p'-Methoxychlor	4.61	a
Oxychlordane	5.48	e

PAHs	Log K_{ow}	Ref.
Naphthalene	3.45	k
2-Methylnaphthalene	3.86	l
1-Methylnaphthalene	3.86	l
2-Chloronaphthalene	3.81	e
Acenaphthylene	4.08	k
Acenaphthene	4.22	k
Dibenzofuran	4.12	l
Fluorene	4.38	k
Phenanthrene	4.46	k
Anthracene	4.54	k
Carbazole	3.23	e
Fluoranthene	5.20	k
Pyrene	5.30	k
Retene	6.35	e
Benzo(a)anthracene	5.91	k
Chrysene	5.61	k
Benzo(b)fluoranthene	5.78	k
Benzo(k)fluoranthene	6.20	k
Benzo(a)pyrene	6.35	k
Indeno(1,2,3-cd)pyrene	6.75	k
Dibenzo(a,h)anthracene	6.51	k
Benzo(ghi)perylene	6.90	k

Table F-1. (continued)

Individual PBDE Congeners IUPAC No.	Log K_{ow}	Ref.
47	6.02	h, j
49	6.22	f
66	6.25	j
71	6.02	f, j
99	6.81	h, j
100	6.81	h, j
138	7.57	j
153	7.39	h, j
154	7.39	h, j
183	7.71	h, j
184	8.27	f
191	8.36	f, j
209	10.0	j

Table F-2. Log K_{ow}s Used for Individual PBDE and PCB Congeners in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2010 PBT Trends Study.

Individual PCB Congeners Log Kow Ref. g

PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}
1	4.46	28	5.67	56	6.11
2	4.69	29	5.60	57	6.17
3	4.69	30	5.44	58	6.17
4	4.65	31	5.67	59,62,75	5.96
5	4.97	32	5.44	59	5.95
6	5.06	33	5.60	60	6.11
7	5.07	34	5.66	61,70,74,76	6.14
8	5.07	35	5.82	61	6.04
9	5.06	36	5.88	62	5.89
10	4.84	37	5.83	63	6.17
11	5.28	38	5.76	64	5.95
12,13	5.26	39	5.89	65	5.86
12	5.22	40,71	5.82	66	6.20
13	5.29	40	5.66	67	6.20
14	5.28	41	5.69	68	6.26
15	5.30	42	5.76	69	6.04
16	5.16	43	5.75	70	6.20
17	5.25	44,47,65	5.82	71	5.98
18,20	5.34	44	5.75	72	6.26
18	5.24	45	5.53	73	6.04
19	5.02	46	5.53	74	6.20
20,28	5.62	47	5.85	75	6.05
20	5.57	48	5.78	76	6.13
21,33	5.56	49,69	5.95	77	6.36
21	5.51	49	5.85	78	6.35
22	5.58	50,53	5.63	79	6.42
23	5.57	50	5.63	80	6.48
24	5.35	51	5.63	81	6.36
25	5.67	52	5.84	82	6.20
26,29	5.63	53	5.62	83	6.26
26	5.66	54	5.21	84	6.04
27	5.44	55	6.11	85,116	6.32

Table F-2. (continued)

PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}
85	6.30	113	6.54	141	6.82
86,87,97,108,119,125	6.44	114	6.65	142	6.51
86	6.23	115	6.49	143	6.60
87	6.29	116	6.33	144	6.67
88	6.07	117	6.46	145	6.25
89	6.07	118	6.74	146	6.89
90,101,113	6.43	119	6.58	147,149	6.66
90	6.36	120	6.79	147	6.64
91	6.13	121	6.64	148	6.73
92	6.35	122	6.64	149	6.67
93,100	6.14	123	6.74	150	6.32
93	6.04	124	6.73	151	6.64
94	6.13	125	6.51	152	6.22
95	6.13	126	6.89	153,168	7.02
96	5.71	127	6.95	153	6.92
97	6.29	128,166	6.84	154	6.76
98	6.13	128	6.74	155	6.41
99	6.39	129,138,163	6.85	156,157	7.18
100	6.23	129	6.73	156	7.18
101	6.38	130	6.80	157	7.18
102	6.16	131	6.58	158	7.02
103	6.22	132	6.58	159	7.24
104	5.81	133	6.86	160	6.93
105	6.65	134	6.55	161	7.08
106	6.64	135,151	6.64	162	7.24
107,124	6.72	135	6.64	163	6.99
107	6.71	136	6.22	164	7.02
108	6.71	137	6.83	165	7.05
109	6.48	138	6.83	166	6.93
110	6.48	139,140	6.67	167	7.27
111	6.76	139	6.67	168	7.11
112	6.45	140	6.67	169	7.42

Table F-2. (continued)

PCB Congeners IUPAC No.	Log K_{ow}
170	7.27
171,173	7.07
171	7.11
172	7.33
173	7.02
174	7.11
175	7.17
176	6.76
177	7.08
178	7.14
179	6.73
180,193	7.44
180	7.36
181	7.11
182	7.20
183	7.20
184	6.85
185	7.11
186	6.69
187	7.17
188	6.82
189	7.71
190	7.46
191	7.55
192	7.52
193	7.52
194	7.80
195	7.56
196	7.65
197	7.30
198,199	7.41
198	7.62

PCB Congeners IUPAC No.	Log K_{ow}
199	7.20
200	7.27
201	7.62
202	7.24
203	7.65
204	7.30
205	8.00
206	8.09
207	7.74
208	7.71
209	8.18

Table F-3. Log K_{ow}s Used for Individual PBDE and PCB Congeners in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2011 PBT Trends Study.

Individual PCB Congeners Log K_{ow} Ref. g

PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}	PCB Congeners IUPAC No.	Log K_{ow}
1	4.46	28	5.67	55	6.11
2	4.69	29	5.60	56	6.11
3	4.69	30	5.44	57	6.17
4	4.65	31	5.67	58	6.17
5	4.97	32	5.44	59,62,75	5.96
6	5.06	33	5.60	59	5.95
7	5.07	34	5.66	60	6.11
8	5.07	35	5.82	61,70,74,76	6.14
9	5.06	36	5.88	61	6.04
10	4.84	37	5.83	62	5.89
11	5.28	38	5.76	63	6.17
12,13	5.26	39	5.89	64	5.95
12	5.22	40,41,71	5.78	65	5.86
13	5.29	40	5.66	66	6.20
14	5.28	41	5.69	67	6.20
15	5.30	42	5.76	68	6.26
16	5.16	43	5.75	69	6.04
17	5.25	44,47,65	5.82	70	6.20
18,20	5.34	44	5.75	71	5.98
18	5.24	45,51	5.58	72	6.26
19	5.02	45	5.53	73	6.04
20,28	5.62	46	5.53	74	6.20
20	5.57	47	5.85	75	6.05
21,33	5.56	48	5.78	76	6.13
21	5.51	49,69	5.95	77	6.36
22	5.58	49	5.85	78	6.35
23	5.57	50,53	5.63	79	6.42
24	5.35	50	5.63	80	6.48
25	5.67	51	5.63	81	6.36
26,29	5.63	52	5.84	82	6.20
26	5.66	53	5.62	83,99	6.33
27	5.44	54	5.21	83	6.26

Table F-3. (continued)

PCB Congeners IUPAC No.	Log K_{ow}
84	6.04
85,116,117	6.36
85	6.30
86,87,97,108,119,125	6.44
86	6.23
87	6.29
88,91	6.10
88	6.07
89	6.07
90,101,113	6.43
90	6.36
91	6.13
92	6.35
93,95,98,100102	6.14
93	6.04
94	6.13
95	6.13
96	5.71
97	6.29
98	6.13
99	6.39
100	6.23
101	6.38
102	6.16
103	6.22
104	5.81
105	6.65
106	6.64
107,124	6.72
107	6.71
108	6.71
109	6.48

PCB Congeners IUPAC No.	Log K_{ow}
110,115	6.49
110	6.48
111	6.76
112	6.45
113	6.54
114	6.65
115	6.49
116	6.33
117	6.46
118	6.74
119	6.58
120	6.79
121	6.64
122	6.64
123	6.74
124	6.73
125	6.51
126	6.89
127	6.95
128,166	6.84
128	6.74
129,138,160,163	6.87
129	6.73
130	6.80
131	6.58
132	6.58
133	6.86
134,143	6.58
134	6.55
135,151,154	6.68
135	6.64
136	6.22

PCB Congeners IUPAC No.	Log K_{ow}
137	6.83
138	6.83
139,140	6.67
139	6.67
140	6.67
141	6.82
142	6.51
143	6.60
144	6.67
145	6.25
146	6.89
147,149	6.66
147	6.64
148	6.73
149	6.67
150	6.32
151	6.64
152	6.22
153,168	7.02
153	6.92
154	6.76
155	6.41
156,157	7.18
156	7.18
157	7.18
158	7.02
159	7.24
160	6.93
161	7.08
162	7.24
163	6.99
164	7.02

Table F-3. (continued)

PCB Congeners IUPAC No.	Log K_{ow}
165	7.05
166	6.93
167	7.27
168	7.11
169	7.42
170	7.27
171,173	7.07
171	7.11
172	7.33
173	7.02
174	7.11
175	7.17
176	6.76
177	7.08
178	7.14
179	6.73
180,193	7.44
180	7.36
181	7.11
182	7.20
183,185	7.16
183	7.20
184	6.85
185	7.11
186	6.69
187	7.17
188	6.82
189	7.71
190	7.46
191	7.55
192	7.52
193	7.52
194	7.80
195	7.56
196	7.65
197,200	7.29
197	7.30
198,199	7.41
198	7.62
199	7.20
200	7.27
201	7.62
202	7.24
203	7.65
204	7.30
205	8.00
206	8.09
207	7.74
208	7.71
209	8.18

IUPAC = International Union of Pure and Applied Chemistry; a systematic method of naming organic chemical compounds.
Ref. = Reference.
If multiple log K_{ow} values were found in the literature, a mean value was selected using the t test at 95% confidence for rejection of outliers (USGS 2011 and Alvarez 2010a).

(See references for Appendix F on the following page.)

References for Appendix F.

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Appendix G. Field Replicate Results

This appendix is available only electronically, attached as a zip file to this report on the internet.

Appendix H. Pesticide, PCB, PBDE, and PAH Residues in SPMD Extracts

This appendix is available only electronically, attached as a zip file to this report on the internet.

Appendix I. Streamflow Data

Table I-1. Flow Data for the PBT Monitoring Study, Spring 2010.

Site Location	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River	54	USGS	14246900	Columbia River at Beaver Army Terminal near Quincy, OR	4/30/2010 - 5/27/2010	250,000-330,000	285,138
Queets River	11.5[a]	USGS	12040500	Queets River near Clearwater, WA	4/28/2010 - 5/28/2010	1,817-11,242	2,914
Yakima River	18	USGS	12510500	Yakima River at Kiona, WA	4/27/2010 - 5/26/2010	1,700-6,780	2,831
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	4/27/2010 - 5/26/2010	446-1,330	864
Spokane River	58.1[b]	USGS & Spokane	12422500 12424000 City of Spokane 2008	Spokane River at Spokane, WA Hangman Creek at Spokane, WA RPWRF Spokane WWTP	4/28/2010 - 5/27/2010	6,676-15,615	9,696
Spokane River	98.3	USGS	12419000	Spokane River near the Idaho border	4/29/2010 - 5/27/2010	6,470-16,400	9,722
Lake Washington	na	King Co.	King County, 2005	controlled water level: fluctuation ~ 2 ft	4/28/2010 - 5/26/2010	Flushing Rate 0.43 / year	-

a. Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.
b. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Waste Water Treatment Plant (WWTP). Historical (1995-2011) WWTP monthly mean contribution ranged from .29-8.62%.
RPWRF = Riverside Park Water Reclamation Facility (Spokane, WA).

Table I-2. Flow Data for the PBT Monitoring Study, Fall 2010.

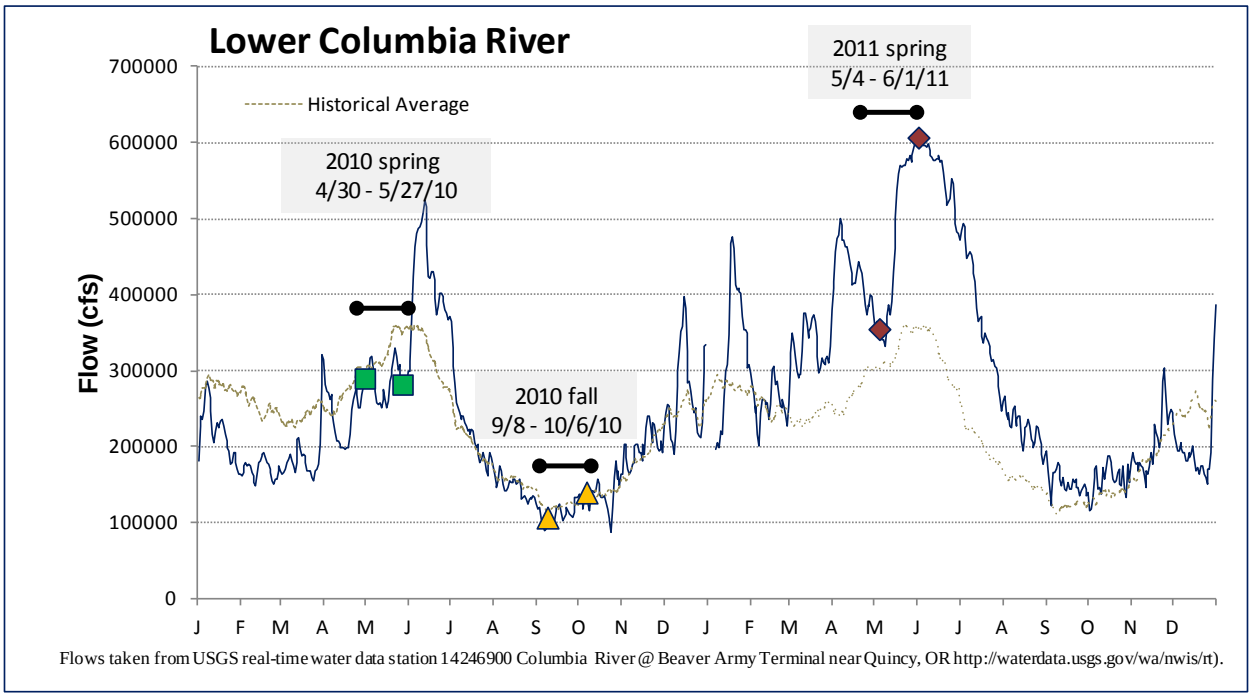
Site Location	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River	54	USGS	14246900	Columbia River at Beaver Army Terminal near Quincy, OR	9/8/2010 - 10/6/2010	98,300-139,000	117,126
Queets River	11.5[a]	USGS	12040500	Queets River near Clearwater, WA	9/9/2010 - 10/7/2010	434-7,584	1,385
Yakima River	18	USGS	12510500	Yakima River at Kiona, WA	9/8/2010 - 10/6/2010	1,970-2,870	2,136
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	9/8/2010 - 10/6/2010	43-128	69.4
Spokane River	58.1[b]	USGS & Spokane	12422500 12424000 City of Spokane 2008	Spokane River at Spokane, WA Hangman Creek at Spokane, WA RPWRF Spokane WWTP	9/9/2010 - 10/7/2010	1,412-2,039	1,730
Lake Washington	na	King Co.	King County, 2005	controlled water level: fluctuation ~ 2 ft	9/9/2010 - 10/5/2010	Flushing Rate 0.43 / year	-

a. Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.
b. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Waste Water Treatment Plant (WWTP). Historical (1995-2011) WWTP monthly mean contribution ranged from .29-8.62%.
RPWRF = Riverside Park Water Reclamation Facility (Spokane, WA).

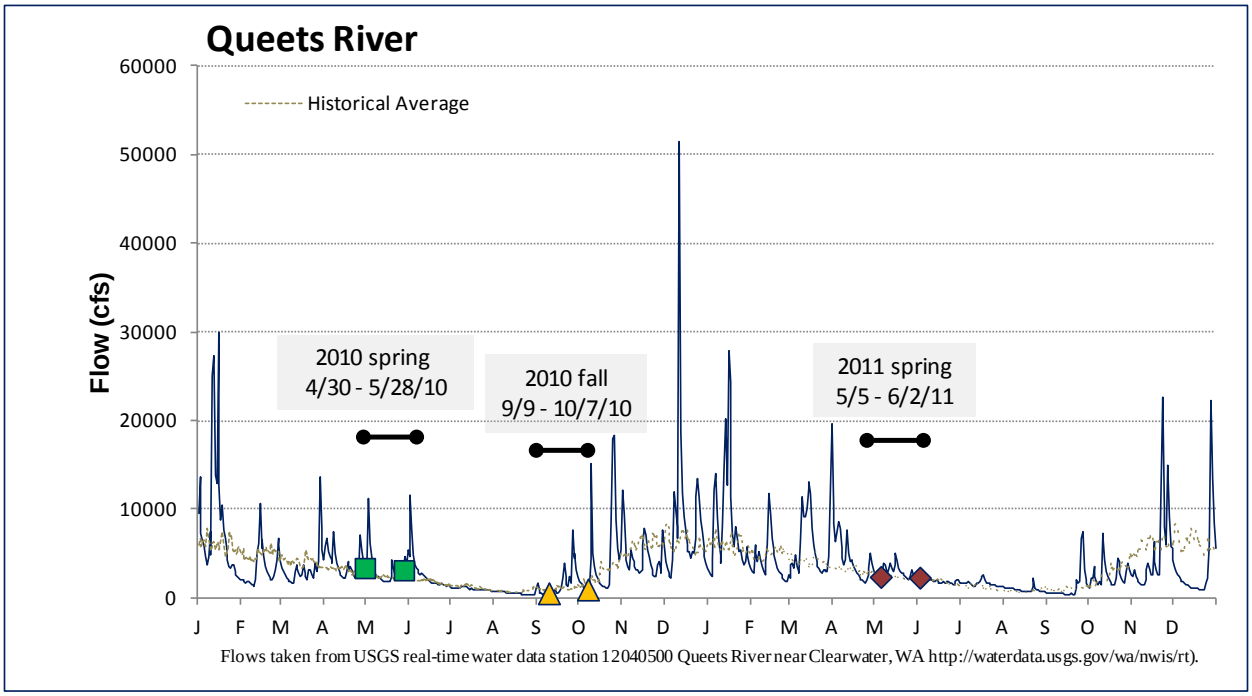
Table I-3. Flow Data for the PBT Monitoring Study, Spring 2011.

Site Location	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River	54	USGS	14246900	Columbia River at Beaver Army Terminal near Quincy, OR	5/4/2011 - 6/1/2011	329,000-562,000†	418,234†
Queets River	11.5[a]	USGS	12040500	Queets River near Clearwater, WA	5/5/2011 - 6/2/2011	2,102-5,105	2,923
Yakima River	18	USGS	12510500	Yakima River at Kiona, WA	5/3/2011 - 5/31/2011	3,790-24,100	8,591
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	5/25/2011 - 6/20/2011	765-3,400	1,540
Spokane River	58.1[b]	USGS & Spokane	12422500 12424000 City of Spokane 2008	Spokane River at Spokane, WA Hangman Creek at Spokane, WA RPWRF Spokane WWTP	5/3/2011 - 5/31/2011	15,828-34,261	25,123

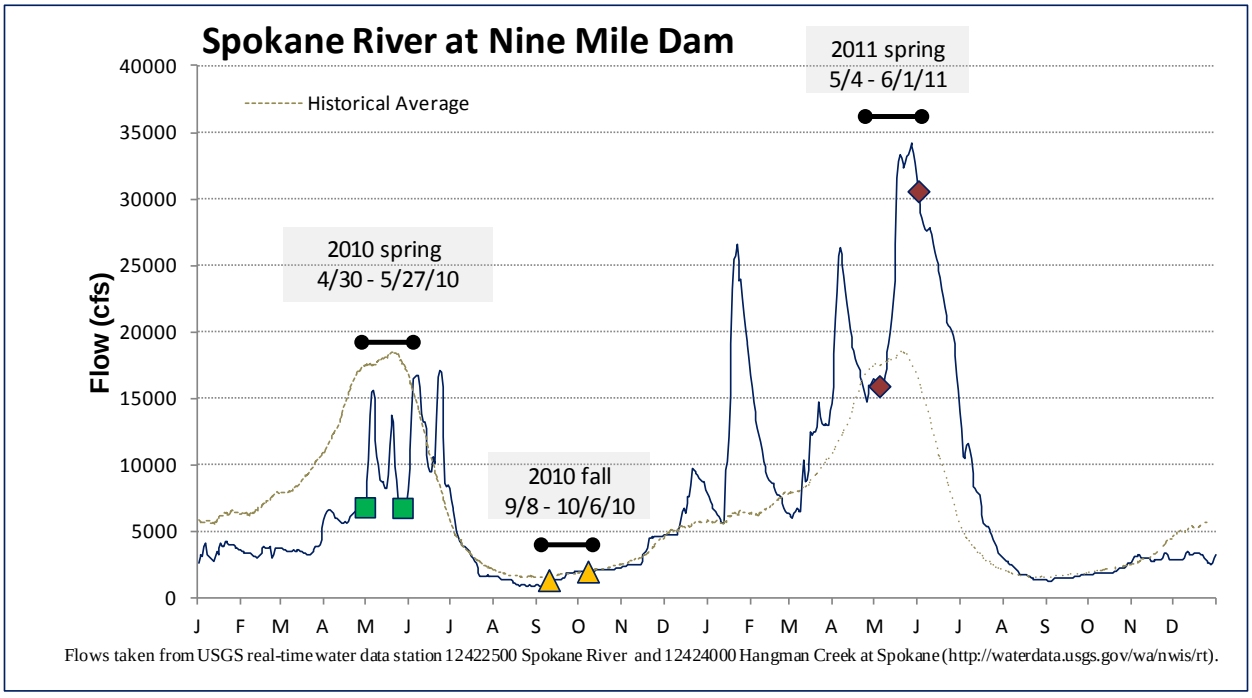
†Some data gaps.
a. Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.
b. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Waste Water Treatment Plant (WWTP). Historical (1995-2011) WWTP monthly mean contribution ranged from .29-8.62%.
RPWRF = Riverside Park Water Reclamation Facility (Spokane, WA).



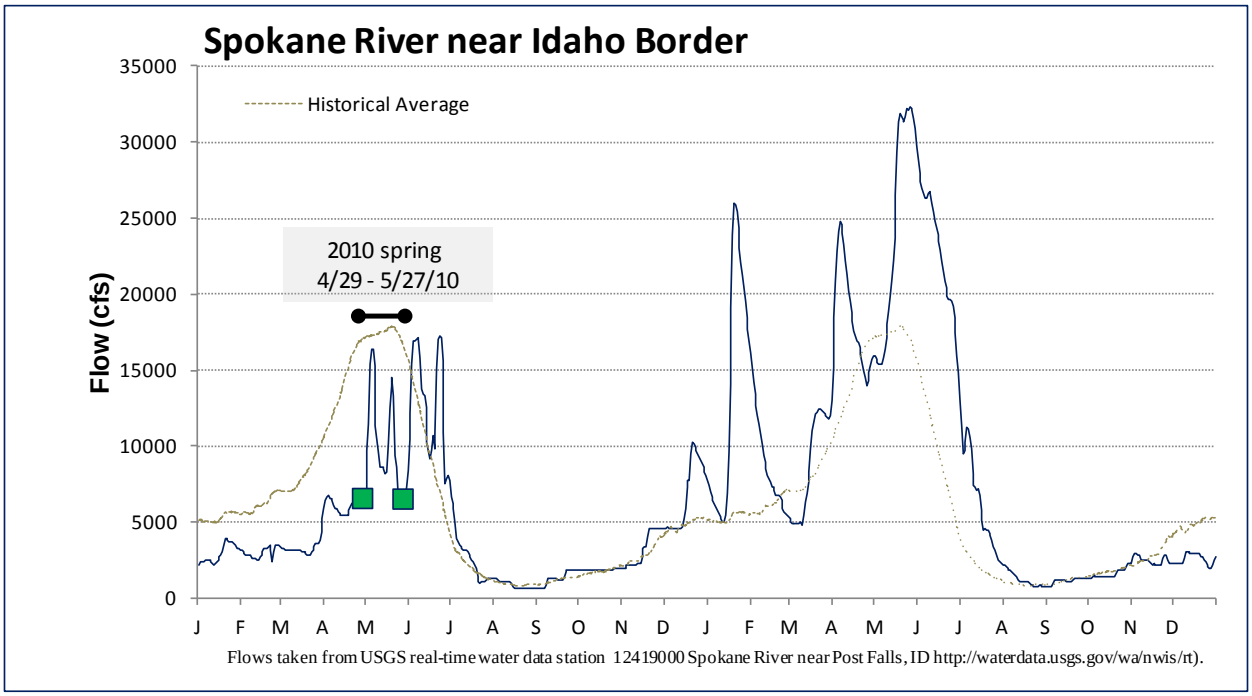
Flows taken from USGS real-time water data station 14246900 Columbia River @ Beaver Army Terminal near Quincy, OR http://waterdata.usgs.gov/wa/nwis/rt).



Flows taken from USGS real-time water data station 12040500 Queets River near Clearwater, WA http://waterdata.usgs.gov/wa/nwis/rt).



Flows taken from USGS real-time water data station 12422500 Spokane River and 12424000 Hangman Creek at Spokane (http://waterdata.usgs.gov/wa/nwis/rt).



Flows taken from USGS real-time water data station 12419000 Spokane River near Post Falls, ID http://waterdata.usgs.gov/wa/nwis/rt).

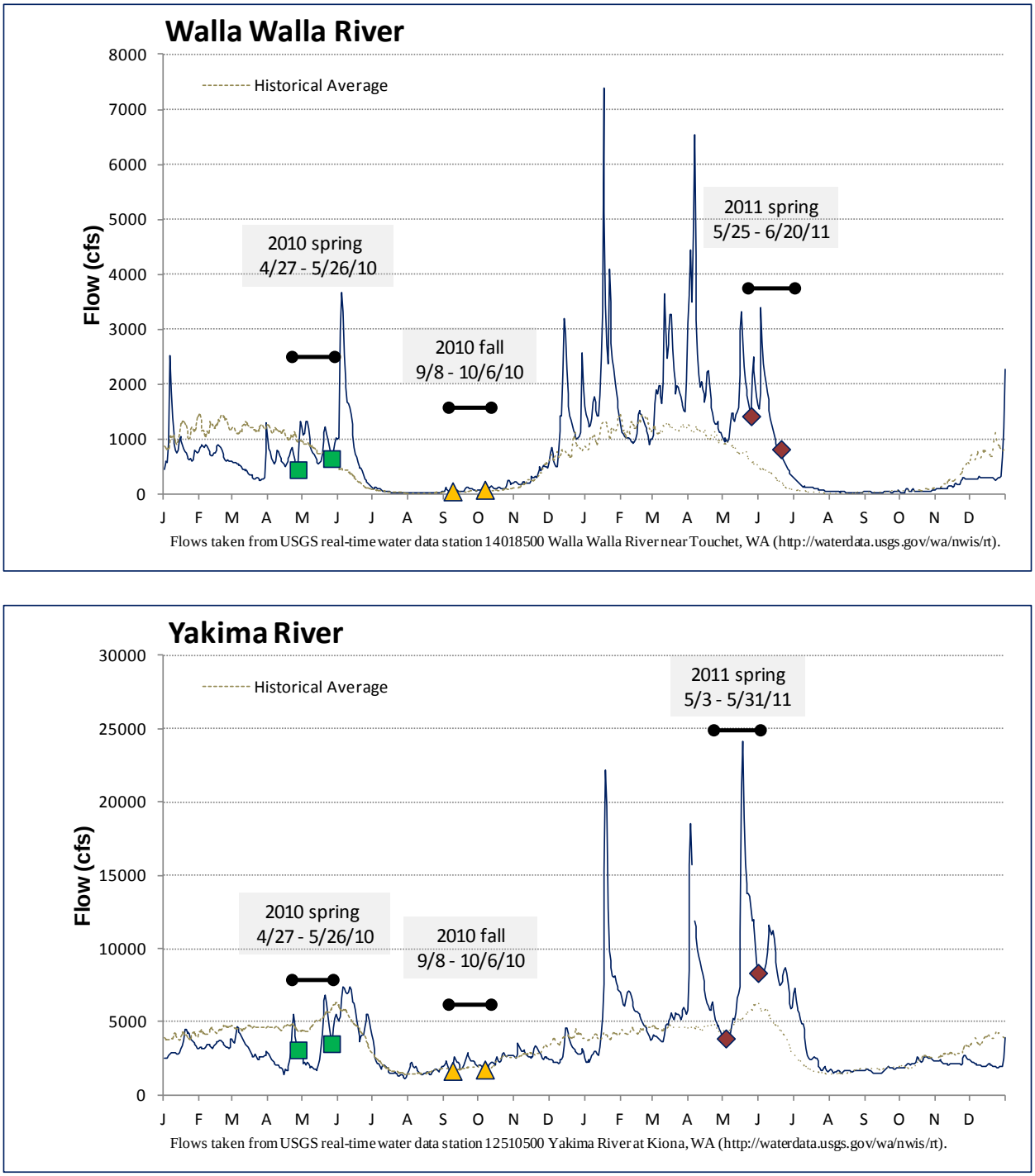


Figure I-1. Flow Charts and Sampling Dates for 2010 and 2011 PBT Monitoring Using SPMDs.

Appendix J. Ancillary Water Quality Data

Table J-1. Ancillary Water Quality Data, Spring 2010.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)		TOC (mg/L)	
Lower Columbia River	LCR	1005025-01	4/30/2010	162	22	J	2.1	
	LCR	1005026-01	5/13/2010	159	18		2.0	
	LCR	1006022-01	5/27/2010	133	19		1.9	
Lake Washington	WASH	1005025-03	4/28/2010	94	1	U	2.3	
	WASH	1005026-03	5/12/2010	96	2		2.4	
	WASH	1006022-03	5/26/2010	98	1		2.5	
Queets River	QUEETS	1005025-05	4/28/2010	*	12		1.0	U
	QUEETS	1005026-05	5/12/2010	62	8		1.0	U
	QUEETS	1006022-05	5/28/2010	56	18		1.0	
Yakima River at Wanawish Dam	YAK	1005025-07	4/27/2010	173	33		2.7	
	YAK	1005026-07	5/10/2010	215	14		2.5	
	YAK	1006022-07	5/26/2010	125	26		2.4	
Walla Walla River	WALLA	1005025-09	4/27/2010	134	19		2.0	
	WALLA	1005026-09	5/10/2010	114	43		2.2	
	WALLA	1006022-09	5/26/2010	131	508	J	2.6	
Spokane River at Nine Mile Dam	SPOK	1005025-11	4/28/2010	92	3		1.5	
	SPOK	1005026-11	5/14/2010	84	4		1.6	
	SPOK	1006022-11	5/27/2010	109	2		1.6	
Spokane River near Idaho Border	SPOKBD	1005025-12	4/29/2010	50	2		1.6	
	SPOKBD	1005026-12	5/14/2010	51	1		1.6	
	SPOKBD	1006022-12	5/27/2010	48	1		1.9	

U = Not detected at or above reported quantitation limit.
* no conductivity meter available.

Table J-2. Ancillary Water Quality Data, Fall 2010.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)		TOC (mg/L)	
Lower Columbia River	LCR	1009052-01	9/8/2010	135	10		1.6	
	LCR	1009053-01	9/22/2010	131	8		1.5	
	LCR	1010015-01	10/6/2010	140	5		1.7	
Lake Washington	WASH	1009052-03	9/9/2010	101	1	U	2.2	
	WASH	1009053-03	9/23/2010	102	1		2.2	
	WASH	1010015-03	10/5/2010	97	1		2.4	
Queets River	QUEETS	1009052-05	9/9/2010	74	2		1.1	
	QUEETS	1009053-05	9/23/2010	66	7.0		1.0	U
	QUEETS	1010015-05	10/7/2010	59	2		1.0	U
Yakima River at Wanawish Dam	YAK	1009052-07	9/8/2010	263	1		2.0	
	YAK	1009053-07	9/22/2010	246	8		1.9	
	YAK	1010015-07	10/6/2010	310	4		1.6	
Walla Walla River	WALLA	1009052-09	9/8/2010	276	2		2.2	
	WALLA	1009053-09	9/22/2010	221	8		2.4	
	WALLA	1010015-09	10/6/2010	353	2		1.9	
Spokane River at Nine Mile Dam	SPOK	1009052-11	9/9/2010	286	3		1.0	
	SPOK	1009053-11	9/23/2010	195	4		1.2	
	SPOK	1010015-11	10/7/2010	189	2		1.0	U

U = Not detected at or above reported quantitation limit.

Table J-3. Ancillary Water Quality Data, Spring 2011.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)		TOC (mg/L)	
Lower Columbia River	LCR	1105028-01	5/4/2011	140	14	J	2.2	
	LCR	1105029-01	5/18/2011	74	36	J	2.2	
	LCR	1106027-01	6/1/2011	65	54	J	2.2	
Queets River	QUEETS	1105028-02	5/5/2011	21	8		1.0	U
	QUEETS	1105029-02	5/19/2011	28	9		1.0	U
	QUEETS	1106027-02	6/2/2011	11	10		1.0	U
Yakima River at Wanawish Dam	YAK	1105028-03	5/3/2011	172	10		2.3	
	YAK	1105029-03	5/25/2011	112	120	J	2.3	
	YAK	1106027-03	5/31/2011	131	86	J	2.0	
Walla Walla River	WALLA	1105028-04	5/25/2011	104	93	J	1.9	
	WALLA	1105029-04	6/12/2011	61	68	J	2.0	
	WALLA	1106027-04	6/20/2011	128	25		2.2	
Spokane River at Nine Mile Dam	SPOKNM	1105028-05	5/3/2011	68	3		2.1	
	SPOKNM	1105029-05	5/17/2011	60	47	J	3.3	
	SPOKNM	1106027-05	5/31/2011	55	6		1.8	

U = Not detected at or above reported quantitation limit.

Appendix K. Estimated Dissolved Concentration in SPMDs, 2010 and 2011

This appendix is available only electronically, as a zip file linked to this report on the internet.

Appendix L. Estimated Total Concentration in SPMDs, 2010 and 2011

This appendix is available only electronically, as a zip file linked to this report on the internet.

Appendix M. Historical Changes in Sampling and Laboratory Procedures, as well as Large-Scale Environmental Changes Potentially Affecting the PBT Monitoring Using SPMDs

The Washington State Department of Ecology (Ecology) began monitoring persistent, bioaccumulative, and toxic (PBT) organic chemicals in surface water in 2007 using semipermeable membrane devices (SPMDs) for the purpose of trend analysis. This was part of a larger effort by Washington State Toxics Monitoring Program (WSTMP) (began in 2000) to investigate the occurrences and concentrations of toxic chemicals in the state's waterbodies.

A brief summary of the initial first year (2007) methods and procedures used to collect and analyze surface water quality data for the PBT monitoring study using SPMDs is presented below. Following the summary, this narrative provides a record of changes that may or may not affect data quality. Each change was carried forward unless otherwise stated. Environmental changes that may potentially affect water quality over a large area are also recorded here.

First Year (2007) Summary

- Initial target chemicals collected included chlorinated pesticides (CP), polychlorinated biphenyls congeners (PCBs), and 13 polybrominated diphenyl ethers (PBDEs). Ancillary data included TOC, TSS, conductivity, water and air temperature, flow, and salinity (two sites).
- Initial 12 sites sampled were Duwamish, Okanogan, Queets, Snohomish, Spokane, Walla Walla, Wenatchee, Yakima, Columbia (three locations) Rivers, and Lake Washington.
- Standard SPMDs were prepared, dialyzed, and extracted by Environmental Sampling Technologies (EST), St. Joseph, MO.
- Field samples consisted of 5 SPMD membranes.
- One field blank (aka field trip blank) was sampled at the Queets River site, assumed to have low risk for air contamination. The field blank consisted of 5 SPMD membranes loose in a quart-sized can and exposed to ambient air for 120 seconds total (deployment plus retrieval) in the spring and for 130 seconds total in the fall.
- One replicate field sample was deployed in the Spokane River each sampling period (spring and fall).
- Laboratory QA: A Day0-dialysis blank contained 5 SPMD membranes and a membrane spike (aka matrix spike) containing one SPMD membrane for each laboratory were analyzed.
- Performance Reference Compounds (PRCs) consisted of PCB-004, -029, and -050 and were spiked by EST into each SPMD membrane before field deployment.
- PRC solution supplied by PACE Analytical Laboratory (PACE). Initial concentration was 200 ng per SPMD membrane (1000 ng/sample).
- Surrogate and membrane spike (aka matrix spike) compounds were spiked by EST into one SPMD membrane for each sample composite after field deployment but before extraction.
- Surrogate and membrane spike solutions for CPs and PBDEs were supplied by Manchester Analytical Laboratory (MEL). CP surrogate concentration was 80 ng/sample. Membrane spike concentration was: PBDEs: 80, 160, and 400 ng/sample (spiked 80 uL at 1, 2, and

5 ug/mL concentration); CPs: 80 ng/sample for each analyte except for toxaphene which was 100 ng/sample.

- Surrogates (PCB-014, -078, 186) and membrane spike solutions for PCBs were supplied by PACE. Surrogate concentration was 50 ng/sample. Membrane spike concentration was 2 ng/sample for each analyte.
- Onset StowAway® TidbiTs™ were used to collect water and air temperature data. These were purchased new for this project.
- Hanna DIST 5 pH/EC/TDS meter or a water thermometer and Beckman conductivity meter was used to measure water temperature and conductivity. Hanna meters were pre-calibrated before each sampling event (spring and fall). Beckman meter was pre-calibrated before each sampling run (each field outing).
- MEL analyzed CP, PBDEs, conductivity, TOC, TSS, and salinity.
- PCB congeners were analyzed by PACE, a contractor.
- Extracted samples were split 50:50 by EST for MEL and the contract laboratory.
- MEL further split the extract samples 50:50 for pesticide and PBDE analysis (totaling a 25% fraction for each analysis).
- Blank correction was achieved by subtracting the detections found in the field blank from the samples and then qualified as estimates (J).
- Estimating water concentration was achieved by using the USGS "Estimated Water Concentration Calculator from SPMD Data Using PRCs" version 5 updated 11/18/2007. Nineteen analytes were added that were not included in the model. These were toxaphene, aldrin, endrin ketone, endrin aldehyde, DDMU, chlordane, and 13 PBDEs. Log K_{ow}s were assigned based on literature search. If multiple log K_{ow} values were found in the literature, a mean value was selected using the t test at 95% confidence for rejection of outliers.
- All analytes were modeled individually for water concentrations except PCBs. PCB congener results were totaled, blank corrected, then used in the water concentration model.

General Changes

- 2008: Researched blank contamination possibilities. Found one possibility for CP contamination at EST: nearby (<.25 mile) company (HPI Chemical Company) was in violation of non-containment and hazardous handling of chemicals. EPA ordered HPI to stop illegal handling of hazardous waste in spring of 2007.
- 2008: Shade devices were employed at all sample locations to protect against photo degradation of light-sensitive PAHs. These are perforated cylinders that fit around the SPMD canisters, which are perforated also. By using different size holes, approximately an additional 40% shade is gained on top of the 50% existing shade of the canister's perforations. This will equal about 80% shade not including the attributes of scattering by the water.
- 2008: Changed replicate SPMD sample location. One replicate sample was deployed in the Walla Walla River each sampling period (spring and fall) instead of the Spokane River as in 2007.
- 2008 fall: Changed PRC supplier. EST supplied PRCs solution. PRCs (PCB-004, 029, 050) concentration was 40 ng per SPMD membrane (200 ng/sample). Note: PRCs in 2008 spring were supplied by PACE at the same concentration as in 2007 (50 ng/sample).

- 2008 spring: Changed location of field blank. One field blank was sampled at the Duwamish River site, assumed to have high risk for air contamination. The field blank designed the same as in 2007 (consisted of 5 SPMD membranes loose in a quart-sized can) was exposed to ambient air for 180 seconds total (deployment plus retrieval).
- 2008 fall: Changed field blank scheme. Three field blanks were sampled at the Duwamish, Spokane, and Queets River sites, assumed to have high risk for air contamination in Duwamish and Spokane Rivers and low risk in Queets River. Field blanks had the same design as in 2007 and spring 2008. Each field blank was exposed to ambient air for 4 minutes (2 minutes during deployment and 2 minutes during retrieval) at each site.
- 2008: An interim change for QA samples was added. Two other blanks were analyzed to help assess contamination during creation and processing of SPMD membranes at EST: a spiked Dialysis and solvent blank. Both contained contamination of individual PCB, PBDE, and PAH compounds, but no CPs.
- 2009: No longer collecting salinity samples. Salinity was not detected in previous results.
- 2009 spring: A one-time change was made to the project plan. An abbreviated QA Project Plan was written to guide development of standard operating procedures (SOPs) for processing, reporting, and better characterizing contamination of, and variability with, SPMD data. Results were also used to update the project plan for this long-term trends monitoring project.
- 2009 spring: Changed sampling site scheme. Eight sites selected for sampling were a subset of the original 12 sites and include: Queets, Spokane, Walla Walla, Yakima, Columbia Rivers (three locations), and Lake Washington. Discontinued sampling at Duwamish, Okanogan, Snohomish, and Wenatchee Rivers because lower levels of contaminants found at these sites make trend detection unlikely.
- 2009 fall: Suspended sampling in the fall except for in the Spokane River. A sampling site was added upstream near the Idaho border in the fall of 2009 and spring of 2010 for a total of two sites in the Spokane River for these sampling events only.
- 2009 spring: Changed replicate SPMD sample location. Replicates were deployed at three locations: the Lower Columbia, Spokane, and Yakima Rivers. No replicates were deployed in 2009 fall.
- 2009: Adopted changed of PRC supplier from 2008 fall. EST supplied PRC solution. PRCs (PCB-004, 029, 050) concentration was 40 ng per SPMD membrane (200 ng/sample)—same as 2008 fall.
- 2009 spring: One-time effort of extra QC samples (blanks) analyzed were included to better understand the sources, magnitude, and variability of contamination of the sampling system. These included: seven field blanks corresponding to each site sampled except Lake Washington; three field-trip extended-air blanks taken at sites most likely (Yakima and Spokane Rivers) and least likely (Queets River) to contaminate the blanks or samples through exposure to air; three Day0-dialysis blanks; three Fresh Day0-dialysis blanks; two Dialysis blanks not spiked; and one Solvent blank. Blanks were created and handled the same as in previous years.
- 2009 fall: One field blank, a Day0-dialysis blank, and a Fresh Day0-dialysis blank were analyzed.
- 2010: Changed sampling site scheme. Six sites were selected for sampling: Queets, Spokane, Walla Walla, Yakima, Lower Columbia Rivers, and Lake Washington. An extra Spokane

River site near the Idaho border was sampled in 2009 fall and 2010 spring only for another study. Suspended sampling at two Columbia River locations upstream of the Lower Columbia River site. The study excluded these sites because the level of contamination was low and the ability to detect trends was unlikely after examining new information gathered in 2009.

- 2010: Changed replicate sample location. Replicates were deployed at three sites: the Lower Columbia, Spokane, and the Queets Rivers.
- 2010: Changed field blank sample location. Three field blanks were exposed to ambient air at each of three sites: the Lower Columbia, Queets, and Spokane Rivers. These sites will remain the field blank exposure sites until further notice.
- 2010: Changed PRC concentration: PCB-004 was 10 ng/SPMD membrane (50 ng/sample); PCB-029 was 5 ng/SPMD membrane (25 ng/sample); and PCB-050 was 5 ng/SPMD membrane (25 ng/sample). PRCs are supplied by EST until further notice.
- 2010: Changes in other QA samples include: the Fresh Day0-dialysis blank contained five SPMD membranes (instead of one) and was held frozen at MEL (not analyzed unless needed).
- 2011: Changed sampling site scheme. Five sites were selected for sampling: Queets, Spokane, Walla Walla, Yakima, and Lower Columbia Rivers. Discontinued sampling at Lake Washington.
- 2011: Fall sampling was suspended to allow time to assess results and data.
- 2011: Changed replicate sampling scheme. Replicates were deployed at two sites (instead of three sites): the Lower Columbia and Spokane Rivers.
- 2011: Changed contract laboratory for analyzing PCB congeners because the lowest bid was awarded the work. AXYS Analytical Services, LTD analyzed the PCB congeners following the most recent changes listed to date.
- 2011: A onetime change for additional QA samples included: (1) three additional field blanks were used. The SPMD membranes were mounted on spider rays like the field samples versus loose in a can like the regular field blanks. These were added to sample ambient air at the same three sites as the field blanks (Lower Columbia, Queets, and Spokane Rivers) for comparing differences in sampling procedures in field blanks; (2) three additional Day0-dialysis blanks were analyzed. Three Day0-dialysis were spiked with extraction internal standards (EIS) at EST before extraction, and one was spiked EIS at the contract lab (AXYS). One of the Day0-dialysis blanks (#2) was considered the PCB method blank; (3) A spiked blank consisting of two SPMD membranes was prepared like the other samples and went through extraction and dialysis. The extract was then split 50:50 with half going through GPC and the other half not going through GPC. Both halves were analyzed for PCB congeners only.

Chlorinated Pesticides

- 2008 fall: CP surrogate concentration was 640 ng/sample.
- 2009 spring: CPs were analyzed in the spring only. Changed CP surrogate concentration to 400 ng/sample (spiked 50 uL at 8 ng/uL).
- 2010: Changed CP sampling method. A separate sample of five SPMD membranes was used to collect and analyze for CPs at each site except one. It was advised that the PCB EIS be

spiked into samples after field deployment but before extract may interfere with CP analysis. Therefore, these were separate samples that were not spiked with EIS. Exception: since CPs were not analyzed in the Spokane River, there was no need for a separate sample for CPs.

- 2010: Adjusted CP membrane spike concentration: 80 ng/sample (spiked 100 uL at 0.8 ug/mL (ng/uL) for various compounds) and 500 ng/sample (spiked 100 uL at 5.0 ug/mL for toxaphene).
- 2011: Discontinued separate samples for CPs because levels of PCB EIS was found to be too low to interfere with CP analysis.
- 2011: Adjusted for CP membrane spike concentration: 80 ng/sample (spiked 50 uL at 1.6 ug/mL (ng/uL) for various compounds) and 500 ng/sample (spiked 50 uL at 10 ug/mL for toxaphene).

PBDEs

- 2008 fall: PBDE surrogate concentration was 640 ng/sample.
- 2009: Changed PBDE surrogate concentration to 400 ng/sample (spiked 50 uL at 8 ng/uL).
- 2010: Adjusted PBDE membrane spike concentration: 80 ng/sample (spiked 80 uL at 1.00 ug/mL (ng/uL) for PBDE-047, -049, -066, -071, -099, -100); 160 ng/sample (spiked 80 uL at 2.00 ug/mL for PBDE-138, -153, -154, -183, -184, -191); 400 ng/sample (spiked 80 uL at 5.00 ug/mL for PBDE-209). Note: EST was instructed to spike 50 uL but spiked 80 uL, hence the values presented here.
- 2011: Adjusted PBDE membrane spike concentration: 25 ng/sample (spiked 25 uL at 1.00 ug/mL (ng/uL) for PBDE-047, -049, -066, -071, -099, -100); 50 ng/sample (spiked 25 uL at 2.00 ug/mL for PBDE-138, -153, -154, -183, -184, -191); 125 ng/sample (spiked 25 uL at 5.00 ug/mL for PBDE-209).

PCBs

- 2008 spring: PCB membrane spike solution supplied by PACE adjusted concentration of 1 ng/sample (instead of 2 ng/sample in 2007) for each analyte.
- 2008 fall: Changed PCB membrane spike supplier. Analytical Perspectives Laboratory (AP) supplied a PCB membrane spike solution for EST to spike after field deployment but before extraction. The membrane spike concentration was 2 ng of various labeled PCB congeners, 1 ng of unlabeled analyte solution, and 1 ng of NOAA standards #170, #180, #153/sample for each analyte.
- 2008 fall: Changed PCB surrogate solution to be supplied by EST. The PCB surrogate (PCB-014, 078, 186) concentration was 50 ng/sample.
- 2008 fall: PCB congeners analyzed by AP, a contractor.
- 2008 fall: EIS were added to sample extracts at the contract lab, Analytical Perspectives (AP). The extraction standard solution contained various labeled PCB congeners at a concentration of approximately 2 ng each.
- 2009: PCB surrogate solution was supplied by EST. The PCB surrogate (PCB-014, 078, 186) concentration was 100 ng/sample. EST claims the concentration 50 ng/sample was as in 2008 fall, but analysis of the spiking solution shows it to be twice as high.
- 2010: Changed procedure for spiking EIS in samples to follow EPA's Method 1668A for PCB analysis more closely. The contract laboratory (AP) supplied EIS to EST for spiking

into samples after field deployment but before extraction. Exceptions included the Day0-dialysis blank where AP would add the EIS upon arrival at their laboratory.

- 2010: Changed membrane spike to Ongoing Precision and Recovery (OPR) to more accurately follow EPA's Method 1668A. AP prepared a vial of OPR standard solution instead of the membrane spike for PCBs. The OPR standard solution contained 2 ng of labeled PCB congeners and 1 ng of corresponding unlabelled PCBs. This solution was spiked in a fresh sample with 5 SPMD membranes after field deployment but before extraction of field samples.
- 2010: Changed procedure for EPA's Method 1668A by adding a PCB method blank prepared at EST with five SPMD membranes. This blank was spiked the same as the field samples.
- 2010: Changed PCB surrogate concentration to 5.0 ng/sample (spiked 50 uL at 0.10 ng/uL) but EST inadvertently produced a higher concentration, which ended up to be 50 ng/sample (spiked 50 uL at 1.0 ng/uL) for both spring and fall.
- 2011: Discontinued PCB surrogates because they are not necessary when using EIS.

PAHs

- 2008: Included polycyclic aromatic hydrocarbons (PAHs) for analysis. Surrogate and membrane spike solutions for PAHs were supplied by MEL. PAH surrogate and membrane spike concentration was 2000 ng/sample. Analysis performed by MEL using the same 25% fraction as for PBDE analysis.
- 2010: Adjusted PAH surrogate concentration: 2000 ng/sample (spiked 50 uL at 40 ng/uL).
- 2010: Adjusted PAH membrane spike concentration: 1000 ng/sample (spiked 25 uL at 40 ng/uL).
- 2011: Discontinued PAH analysis because only low levels were found in relation to environmental risk.

Temperature and Conductivity

- 2009 fall: Began pre- and post-calibration checks on TidbiTs™ according to Ecology's Standard Operating Procedures (SOPs) for continuous temperature monitoring of fresh water rivers and streams conducted in a Total Maximum Daily Load (TMDL) project for stream temperature written by D. Bilhimer and A. Stohr in fall of 2009.
- 2010: Added shade device for TidbiTs™ monitoring air temperature at each site.

Streamflow

- 2010: Changes to the Spokane River site at Nine Mile Dam. In 2010 Avista completed installation of new, computerized spillway gates at the Nine Mile Dam. The new system consists of metal gates supported by air-filled rubber bladders, and replaces their old wooden flashboard process, which had been in use since 1928. The upgraded system gives Avista operators the ability to raise and lower the height of the spillway gate at any time in order to maintain the reservoir pool at a more constant level throughout the entire year.
- 2012: Recalculated historical monthly mean contribution of the Spokane Waste Water Treatment Plant flow to the Spokane River flow at Nine Mile Dam (1995-2011). Updated range to .29-8.62%.

Data Reduction

- 2008: Blank correction was achieved by first screening results that were greater than the mean plus two standard deviations of the field blanks then subtracting the field blank mean from the samples. Corrected results were qualified as estimates with an unknown bias (JK). For non-correctable results, the original result was used as an estimated reporting limit and qualified as below the detection limit (UJK). The detection limit was used where a compound was not detected. The mean of the three field blanks in the fall were assumed to represent the mean SPMD background contamination for the spring, which only had one field blank. The assumption was made that the proportion of standard deviation to mean for one sampling period is similar to another sampling period.
- 2008: Estimating water concentration was achieved by using the USGS "Estimated Water Concentration Calculator from SPMD Data Using Multiple PRCs" version 5 updated 11/15/2006. This version was sent via email from USGS as the only version available at the time (during 2008) because the USGS website was under revision and the passive sampler pages were taken off-line. USGS verified that version 5 was the latest version.
- 2008: Individual PCB congener results were blank-corrected then run through the water concentration model as individual congeners.
- 2009: Blank-correction followed the same procedure as in 2008, except the mean of seven field blanks corresponding to seven of the eight sites sampled in the spring was used to determine the mean of the one field blank used in the fall.
- 2011: Eliminated blank-correction and changed the way the results were censored. Results above the limit of quantitation (LOQ) (field blank mean plus ten standard deviations) were used as reported (no correction). For results below the limit of detection (LOD) (field blank mean plus three standard deviations), results were censored as nondetects (U) at the associated LOD value. If the result is greater than the LOD but less than the LOQ, the reported result is used as the associated value for "U".

Appendix N. Glossary, Acronyms, and Abbreviations

Glossary

Ampoule: a small sealed vial used to contain and preserve a sample.

Analyte: Water quality constituent being measured (parameter).

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

Blank: A clean sample or sample of matrix prepared to contain none of the analyte of interest so as to measure artifacts in the measurement (sampling and analysis) process. 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.

Blanks in this study

- Day0-dialysis: SPMD fabrication blank. Represents contamination from pre-field processing, storage, and post-field processing. This blank also can serve as a reference for PRC loss.
- Day0-method: Method blank for HRGC/MS PCBs only. Represents contamination from pre-field processing, storage, and post-field processing. This blank also can serve as a reference for PRC loss. The Day0-dialysis blank could be used for the PCB method blank.
- Field: field blank. Represents contamination from all processes, storage, and handling of samples including contaminants from air exposure during deployment and retrieval.
- Fresh Day0: SPMD process blank. Represents contaminants from post-field processing.
- OPR/recovery: Membrane spiked with native congeners. Evaluates matrix effects; for PCBs only. Represents contaminants from post-field processing.
- Solvent: Reagent blank (no SPMD). Represents contaminants from post-field processing within the solvent only (no membrane influences).
- Spiking: SPMD process and procedural blank. Represents post-field processing with extended exposure to processing laboratory (EST) air during spiking.

Blank-correction: Correcting the observed value (results from sample) using values of a blank as a specified part of a method procedure.

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.

Congener: In chemistry, congeners are related chemicals. For example, polychlorinated biphenyls (PCBs) are a group of 209 related chemicals that are called congeners.

Dissolved water concentration: The abundance (e.g. mass) of the dissolved form of a constituent (e.g. chemical) in a volume of water (e.g. pg/L picograms per liter).

Extract: The substance separated from a matrix.

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Matrix: The non-analyte components of a sample (e.g. SPMD membranes).

Noise: The sum of all interference in a measurement which is independent of the data signal or true analyte result found in the sample.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Residue: Analyte found in the extract from the sample.

Sample: A small quantity of something or subset of a population.

Signal: The amount of analyte found in the sample. In this report, the true signal is the level of contaminant in the environment only versus the response (signal) from the environment and the measuring system.

Spatial trend: In this report, spatial refers to how concentrations differ among various waterbodies or parts of the same waterbody over time.

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.

Surrogate: A pure compound different from, but similar enough to, the analyte that, when added at a known concentration to the sample prior to processing, provides a measure of the overall efficiency of the method (recovery). Surrogates have chemical characteristics that are similar to that of the analyte and must provide an analytical response that is distinct from that of the analyte.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from not meeting (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): The suspended particulate matter in a water sample as 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.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Whole water concentration: The abundance of the dissolved + particulate fraction of a constituent (e.g. chemical) in a volume of water = total water concentration (e.g. pg/L picograms per liter).

Acronyms and Abbreviations

AKA	also known as
AP	Analytical Perspectives Laboratory
AXYS	AXYS Analytical Services Ltd.
BHC	benzene hexachloride (alpha-, beta-, gamma (gamma- also known as Lindane)
CP	chlorinated pesticides
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) ethylene (a breakdown product of DDE)
DDT	dichlorodiphenyltrichloroethane (o,p' and p,p'; 2,4' and 4,4')
DL	detection limit (DL = LOD in this study)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EST	Environmental Sampling Technologies, Inc.
GIS	Geographic Information System software
GC-ECD	gas chromatography – electron capture detection
GC-MS	gas chromatography – mass spectrometry
GPC	gel permeation chromatography
HPAH	high molecular PAH
HRGC/MS	high resolution gas chromatography/mass spectrometry
K_{oc}	carbon-water partition coefficient
K_{ow}	octanol-water partition coefficient
LOD	limit of detection
LOQ	limit of quantitation
LPAH	low molecular weight PAH
MEL	Manchester Environmental Laboratory
n	number

NOAA	National Oceanic Atmospheric Administration
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyl
PRC	permeability/performance reference compound
QA	quality assurance
QC	quality control
Rep	replicate
RL	reporting limit (RL = LOQ in this study)
RM	river mile
RPD	relative percent difference
RSD	relative standard deviation
SOP	standard operating procedures
SPMD	semipermeable membrane device
T-DDT	total DDT (sum of detected metabolites)
TMDL	(See Glossary above)
T-PAH	total PAH
T-PCB	total PCBs (sum of detected congeners)
TOC	total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WRIA	Water Resource Inventory Area
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
cm	centimeter
ft	feet
m	meter
mg	milligrams
mg/L	milligrams per liter (parts per million)
mL	milliliters
ng	nanograms
pg/L	picograms per liter (parts per quadrillion)
ug/L	micrograms per liter (parts per billion)
uL	microliters
um	micrometer
uS/cm	microsiemen per centimeter, a unit of conductivity