Quality Assurance Project Plan

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

by
Art Johnson

Washington State Department of Ecology
Environmental Assessment Program
Olympia, Washington 98504-7710

June 2007

Publication Number 07-03-104

This plan is available on the Department of Ecology's website at
www.ecy.wa.gov/biblio/0703104.html.

Quality Assurance Project Plan

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

June 2007

303(d) Listings Addressed in this Study: None

Waterbody Number: Statewide

Project Code: 07-501

Approvals

Approved by:	May 2007
Mike Gallagher, Client, Industrial Section, Solid Waste & Financial Assistance Program	Date
Approved by:	May 2007
Carol Kraege, Section Manager, Industrial Section, Solid Waste & Financial Assistance Program	Date
Approved by:	May 2007
Maria Peeler, Client, Hazardous Waste & Toxics Reduction Program	Date
Approved by:	June 2007
Ken Zarker, Section Manager, Hazardous Waste & Toxics Reduction Program	Date
Approved by:	May 2007
Art Johnson, Author (Quality Assurance Project Plan), Watershed Ecology Section	Date
Approved by:	May 2007
Patti Sandvik, Project Manager and Environmental Information and Management System Data Engineer, Watershed Ecology Section	Date
Approved by:	May 2007
Dale Norton, Unit Supervisor, Toxics Studies Unit	Date
Approved by:	May 2007
Will Kendra, Section Manager, Watershed Ecology Section	Date
Approved by:	May 2007
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	May 2007
Bill Kammin, Ecology Quality Assurance Officer	Date

Table of Contents

Page

Abstract 4

Background 5

Project Description 6

Organization and Schedule 7
- Organization 7
- Schedule 7

Sampling Design 8
- Monitoring for Trends 8
- Monitoring Stations 14
- Sample Timing and Frequency 21
- Chemical Analyses 23

Quality Objectives 24

Sampling Procedures 26

Measurement Procedures 28

Quality Control Procedures 30
- Field 30
- Laboratory 31

Data Management Procedures 33

Audits and Reports 34
- Audits 34
- Reports 34

Data Verification 35

Data Quality (Usability) Assessment 36

References 37

Appendices 41

Appendix A. Chemicals and Chemical Groups on the PBT List

Appendix B. Chemicals to be Analyzed in SPMDs Starting in 2007

Abstract

A trend monitoring design is proposed for chlorinated pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in nine major Washington rivers and lakes. These compounds are among the primary contaminants of human health concern in local freshwater fish and include chemicals classed as Persistent Bioaccumulative Toxins targeted for cleanup, reduction, and, where possible, elimination. Monitoring will be done with a passive sampling technique that employs a Semipermeable Membrane Devices (SPMDs). SPMDS will be deployed at eleven stations, twice a year (spring and fall) as follows: Spokane, Okanogan, Wenatchee, Yakima, Walla Walla, Snohomish, Columbia (three stations), and the Green/Duwamish rivers and Lake Washington.

Background

The Washington State Toxics Monitoring Program (WSTMP) was initiated by the Washington State Department of Ecology (Ecology) in 2001. WSTMP investigates the occurrence and concentrations of toxic chemicals in rivers, lakes, and streams (www.ecy.wa.gov/programs/eap/toxics/index.html). The focus has been primarily on exploratory sampling to identify new instances of fish tissue contamination (Seiders et al., 2006).

One of WSTMP's long-term objectives is to monitor contaminant trends over time. Quality Assurance (QA) Project Plans for assessing mercury trends in fish and sediment cores were recently completed (Seiders, 2006; Coots, 2006). Sample collections for these efforts began in 2005 and 2006, respectively.

This QA Project Plan describes a trend monitoring component in WSTMP for organic compounds in major Washington rivers and lakes. The initial compounds of interest are chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Ecology has identified these and other chemicals with similar properties as Persistent Bioaccumulative Toxins (PBTs) targeted for cleanup, reduction, and, where possible, elimination. Appendix A shows the chemicals on the PBT list

There are several reasons for focusing a trend monitoring effort on these compounds. PCBs and CPs are the contaminants most frequently detected in fish samples from local rivers, lakes, and streams and occur at the highest concentrations. The majority of Washington's 303(d) listings and Total Maximum Daily Loads (TMDLs) for toxics are directed at PCBs or CPs. The Washington State Department of Health (WDOH) issues multiple fish consumption advisories which are driven by PCBs, CPs, and mercury. The Environmental Protection Agency (EPA) concluded that the organic chemicals contributing the greatest health hazard and cancer risk through fish consumption in the Columbia River basin were PCBs, followed by certain CPs and dioxins (EPA, 2002).

PBDE flame retardants have recently emerged as a new class of environmental contaminants that may have significant adverse effects on human health. PBDE levels have been increasing in many types of environmental samples (e.g., Norén and Mieronyté, 2000; She et al., 2002; Luross et al., 2000). PBDEs are the subject of Ecology's second and most recent Chemical Action Plan (CAP) www.ecy.wa.gov/biblio/0507048.html. The first CAP was for mercury.

WSTMP plans to add other PBTs for trend monitoring over the next few years. The next candidates are lead, polycyclic aromatic hydrocarbons (PAHs), and perfluorooctane sulfonates (PFOS). These are the three chemicals scheduled for CAPs between now and 2010. Analyzing PBTs in bottom sediments at SPMD sites is also being considered to evaluate the linkage between sediments and the water column.

Project Description

Beginning in spring 2007, WSTMP will monitor nine major Washington rivers and lakes twice a year to identify time-trends in the levels of CPs, PCBs, and PBDEs. A passive sampling technique using a standardized Semipermeable Membrane Device (SPMD) will be employed to reduce variability in the data and improve the ability to detect trends. The SPMDs will be deployed to provide time-weighted average concentrations for the chemicals of interest—spanning one month in the spring and one month in the fall. Studies in Washington have shown that peak levels of these chemicals tend to occur during these periods.

The rivers and lakes selected for trend monitoring are among the most contaminated in Washington. Six waterbodies will be monitored in the Columbia River system: Spokane River; Okanogan River; Wenatchee River; Yakima River; Walla Walla River; and (6) one station each on the upper, middle, and lower Columbia mainstem. Three waterbodies will be monitored in the Puget Sound basin—Lake Washington, Green/Duwamish River, and Snohomish River.

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

Organization and Schedule

Organization

Name	Organization	Phone No.	Role
Art Johnson	EAP-WES-TSU	360-407-6766	QAPP Development
Patti Sandvik	EAP-WES-TSU	360-407-7198	Project Manager
Casey Deligeannis	EAP-WES-TSU	360-407-7395	Field Assistance
Dale Norton	EAP-WES-TSU	360-407-6765	Unit Supervisor
Terri Spencer	Environmental Sampling Technologies	816-232-8860	SPMD Preparation and Extraction
John Weakland	Manchester Laboratory	360-871-8820	Organics Supervisor
Dean Momohara	Manchester Laboratory	360 871-8808	Chemistry Units' Supervisor
Stuart Magoon	Manchester Laboratory	360-871-8801	Lab Director
Karin Feddersen	Manchester Laboratory	360-871-8829	Contract Lab Services
Chuck Sueper	Pace Analytical	1-888-PACE	PCB Contract Laboratory
Bill Kammin	EAP	360-407-6964	Quality Assurance Officer
Patti Sandvik	EAP-WES-TSU	360-407-7198	EIM Data Management

Schedule

Environmental Information System (EIM) Data Set	
EIM Data Engineer	Patti Sandvik
EIM User Study ID	SPMDTR07
EIM Study Name	WSTMP SPMD Trend Monitoring
EIM Completion Due	May 08; annually thereafter
Progress Report	
Report Author Lead	Patti Sandvik
Schedule	
Report Supervisor Draft Due	March 08; annually thereafter
Report Client/Peer Draft Due	April 08; annually thereafter
Report External Draft Due	NA
Report Final Due	May 08; annually thereafter

Sampling Design

Monitoring for Trends

Most time series patterns can be described in terms of three basic components: trend, seasonality, and random fluctuations. Seasonality and random fluctuations complicate trend detection. A water quality program that monitors for trends must take seasonal cycles into account; for example, duration of the irrigation season and timing of the spring snowmelt. The sampling design must consider the impact of random fluctuations and other short-term changes, such as those caused by storm events or hydropower.

The monitoring data need to be representative of the waterbody in question and have a high degree of precision. Biased data can be tolerated if magnitude and direction are consistent. Bias, needs to be low, however, when the objective is to assess progress toward numerical water quality targets.

For ultra-trace contaminants like PBTs, there are additional constraints. Results of low-level organics analyses are typically heavily qualified, with many non-detects. Therefore, the samples must contain enough chemical residue to reliably quantify. The level of contamination in the waterbody under investigation should be substantial so there is room to document changes and determine if they are significant. Finally, the cost of analyzing organic compounds is substantial—$200 or more per sample for most analyses.

Statistical methods have been developed to deal with season cycles (Kendall Test, Sen Test). Alternately, the monitoring effort can be focused on specific times of the year (low flow for example) thereby largely avoiding the seasonality issue.

Random and other short-term changes in water quality pose difficulties for conventional sampling techniques. Large variances are often associated with water samples and many samples are needed to detect a trend. Hallock and Ehinger (2003) concluded that up to 10 years of monthly samples could be required to detect trends in general water quality parameters for Ecology's Ambient Monitoring Program. For organic PBTs, the cost of such an effort becomes prohibitive for a statewide program.

Fish and other aquatic organisms integrate water column concentrations over time and concentrate many PBTs, but the variability associated with biological samples is high. Table 1 shows results from replicate fish samples analyzed for PBTs by WSTMP during 2004-2005. Each sample is a separate composite of five-to-ten individual fish. In more than half the cases, the relative percent difference (RPD*) between replicates is greater than 50%.

Variability in fish tissue data stems from movements of fish and the difficulty of consistently obtaining individuals of the same species, sex, and year class. These are less of a drawback with invertebrates, but their bioaccumulation potential is relatively low for organic compounds and useful indicator species are limited in local freshwaters.

_____

*RPD = range of replicates as a percent of mean value

Table 1. Relative Percent Difference Between Replicate Composite Fish Fillet Samples Analyzed for Selected CPs, PCBs, and PBDEs in the 2004-05 WSTMP (ug/Kg; analyzed by Manchester Laboratory)

Chemical	Rep. 1	Rep. 2	RPD	Species (No. fish in each replicate)	Waterbody
4,4'-DDE	300	370	21%	Channel Catfish (5)	Snake River
Dieldrin	1.2	3.6	100%	"	(bw Lower Monumental Dam)
Total PCBs*	57 J	164 J	97%	"	"
PBDE-47	9.3	18	64%	"	"
PBDE-99	3.8	10.6	94%	"	"
PBDE-100	2.0	4.9	84%	"	"
4,4'-DDE	5.0	9.5 J	62%	Cutthroat Trout (7)	Chehalis River
Dieldrin	0.50 U	0.50 U	ND	"	(near Satsop)
Total PCBs*	7.1 J	12 J	51%	"	"
PBDE-47	0.64	0.98	42%	"	"
PBDE-99	0.50 U	14 J	>190%	"	"
PBDE-100	0.50 U	0.50 U	ND	"	"
4,4'-DDE	280	440	44%	Mountain Whitefish (10)	Columbia River
Dieldrin	0.48 U	0.48 U	ND	"	(bw Wells Dam)
Total PCBs*	22	33 J	40%	"	"
PBDE-47	0.48 U	56	>200%	"	"
PBDE-99	0.48 U	16	>190%	"	"
PBDE-100	0.48 U	5.4	>170%	"	"
4,4'-DDE	20	23	14%	Cutthroat Trout (5)	Cowlitz River
Dieldrin	2.4 U	2.4 U	ND	"	(RM 24-27)
Total PCBs*	49	49	0%	"	"
PBDE-47	2.2	2.8	24%	"	"
PBDE-99	1.0	1.6 J	46%	"	"
PBDE-100	0.72	0.9 J	22%	"	"
4,4'-DDE	15 J	23 J	42%	Smallmouth Bass (5)	Liberty Lake
Dieldrin	0.50 U	0.50 U	ND	"	"
Total PCBs*	12	25	70%	"	"
PBDE-47	1.2	2.0	50%	"	"
PBDE-99	0.10 J	0.57	140%	"	"
PBDE-100	0.26 J	0.44 J	51%	"	"
4,4'-DDE	2.0 J	2.1 J	5%	Mountain Whitefish (5)	Snohomish River
Dieldrin	2.0 U	2.0 U	ND	"	(RM 15-18)
Total PCBs*	20	21	5%	"	"
PBDE-47	12	13	8%	"	"
PBDE-99	12	15	22%	"	"
PBDE-100	3.1	3.7	18%	"	"
					"

Source: EIM *Aroclor analysis U = not detected J = estimated value

Bottom sediment samples can meet the requirements of low variance and representativeness. However, sedimentation rates in most aquatic environments are too low for the surface layers to reflect recent changes in the rate of chemical inputs. In the absence of resuspension, sediment traps sequester recent material, but the small size of the sample limits the number of analyses that can be conducted. Non-detects can be an issue for both suspended and deposited particulates, depending on the chemicals being analyzed.

In view of the shortcomings associated with traditional approaches, a passive sampling technique using a Semipermeable Membrane Device (SPMD) is proposed for monitoring trends of organic PBTs in the WSTMP. A SPMD is composed of a thin-walled, layflat polyethylene tube filled with triolein, a neutral lipid (Figure 1). When placed in water, dissolved lipophilic organic compounds diffuse through the membrane and are concentrated over time. A SPMD will effectively sample up to 10 liters of water per day, depending on the compound in question. The typical deployment period is 28 days, after which the membranes are retrieved, extracted, and analyzed for the chemicals of interest.

Figure 1. Standard SPMD Membrane Mounted on a Spider Carrier.

SPMDs were developed by the U.S. Geological Survey (USGS) and are now of standardized design, patented, and commercially available through Environmental Sampling Technologies (EST), St. Joseph, MO (www.est-lab.com/index.php). 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).

SPMDs take up a wide range of organic compounds including most PBTs. Table 2 shows some of the chemicals they are known to concentrate. Nearly all hydrophobic compounds with log K_{ow}* ≥ 3 are amendable to monitoring with SPMDs. The use and practicality of SPMDs for environmental monitoring is now well established. There are more than 180 peer reviewed publications in the open scientific literature where SPMDs have used for detecting chemical contaminants in the environment (Huckins et al., 2006).

Table 2. Chemicals Known to Concentrate in SPMDs
[modified from Huckins et al., 2006]

CPs*	PCDFs*
Other pesticides: including diazinon, pryethroids, trifluralin, chlorpyrifos, dacthal, fenvalerate, allethrin	PFOs*
	Nonyl phenols
	Triclosan
PCBs*	Tributyltin
PBDEs*	Chlorinated anisoles
Priority pollutant PAHs*	Chlorinated veratroles
Alkylated PAHs	Alkylated selenides
Chlorinated napthalenes	Sulfur
PCDDs*	

*PBTs or includes PBTs

The amount of chemical absorbed by a SPMD is proportional to the local water column concentration. Therefore, trends in contaminant levels at a particular site can be assessed by directly comparing absorbed amounts over the monitoring period.

SPMDs also provide a time-weighted average concentration for the chemicals of interest. Estimates of average water column concentrations are obtained using Permeability/Performance Reference Compounds (PRCs) spiked into deployed SPMDs. PRC loss rates are used to derive an exposure adjustment factor (EAF) to calibrate for the effects of temperature, water velocity, and biofouling. PRCs can be used to predict the EAFs of chemicals over a wide range of K_{ow}s. Studies have shown that chemical concentrations derived from SPMDs are comparable to other low-level sampling methods such as solid-phase and liquid-liquid extraction, generally agreeing within a factor of two (Ellis et al., 1995; Rantalainen et al., 1998; Hyne et al., 2004).

*Octanol-water partition coefficient; a measure of bioaccumulation potential.

SPMDs have a number of advantages over traditional sampling techniques in a trend monitoring program for PBTs:

- Random fluctuations are smoothed and representative of the improved data because SPMDs measure the long-term average concentration of a chemical.

- Standardized design has good reproducibility which improves comparisons within and between sampling stations. Table 3 shows results from SPMDs deployed side by side in the Columbia River basin and analyzed for CPs, PCBs, and PBDEs. RPDs in these samples were 10% or less for DDE, 22% or less for dieldrin, 12% for total PCBs, and 7% or less for PBDEs. The higher RPDs for dieldrin are from waterbodies where dieldrin was near the detection limit. RPDs less than 10% are anticipated where concentrations are higher.

- Large chemical residues accumulated in an SPMD give a stronger analyte signal, which translates into parts per trillion detection limits or lower.

- Cost is less because fewer samples are needed.

- SPMDs are easier and less labor intensive to use than most other low-level sampling techniques.

Potential disadvantages of relying on SPMDs for a trend monitoring program include:

- Compared to other types of samples, there is an increased chance of having data gaps in the time series: either due to vandalism or the array being swept away and otherwise lost in the waterbody. There is no means of re-deploying to obtain an equivalent sample for the targeted time period.

- SPMDs are potent air samplers. Contamination must be controlled for while the membranes are being prepared, deployed, retrieved, and transported to the laboratory.

- The sampling design for the present program relies on obtaining one set of long-term average values per year for each of two time periods of interest. Estimates of the uncertainty associated with each data point will be limited to results from a small number of replicate samples and field blanks.

- Total chemical concentrations determined from SPMDs are estimates based on organic carbon-water equilibrium partitioning. Because the dissolved component is the bioavailable fraction, this is not a significant drawback in the present study which is driven by human health concerns for fish consumption.

Table 3. Relative Percent Difference Between Replicate SPMDs Deployed in the Columbia River Basin and Analyzed for Selected CPs, PCBs, and PBDEs. (ng/SPMD; analyzed by Manchester Laboratory except PCBs by STL, Sacramento CA)

Chemical	Rep. 1	Rep. 2	RPD	Waterbody	Ref.
4,4'-DDE	459	459	0%	Yellowhawk Creek	1
Dieldrin	127	127	0%	"	
4,4'-DDE	77	86	11%	Willamette River	2
Dieldrin	16	20	22%	"	
4,4'-DDE	88	80	10%	Columbia R. near Beaver OR	2
Dieldrin	18 U	15 J	<18%	"	
4,4'-DDE	83	89	7%	Columbia R. bw Bonneville Dam	2
Dieldrin	7.0	7.8	11%	"	
4,4'-DDE	61	55	10%	Multnomah Channel	2
Dieldrin	34	29	16%	"	
Tot. PCBs*	168	190	12%	"	
PBDE-47	532	572	7%	Spokane R. at Nine-Mile Dam	3
PBDE-99	213	225	5%	"	
PBDE-100	52	55	6%	"	

1 = Johnson et al. (2004) 2= Johnson and Norton (2005) 3 = Johnson et al. (2006)
U = not detected
J = estimated value
*Congener analysis

Monitoring Stations

Beginning in 2007, WSTMP will initiate trend monitoring with SPMDs at eleven stations located on nine major Washington rivers and lakes (Figure 2). These waterbodies were selected based on the following considerations:

- Levels and types of contaminants reported in fish.
- 303(d) listings and TMDL status.
- Fish consumption advisories.
- Availability of a secure sampling site.

The final list was paired down by selecting sites that give a statewide distribution of sampling effort. Extra weight was given to waterbodies where water quality improvements were deemed likely to occur in the foreseeable future.

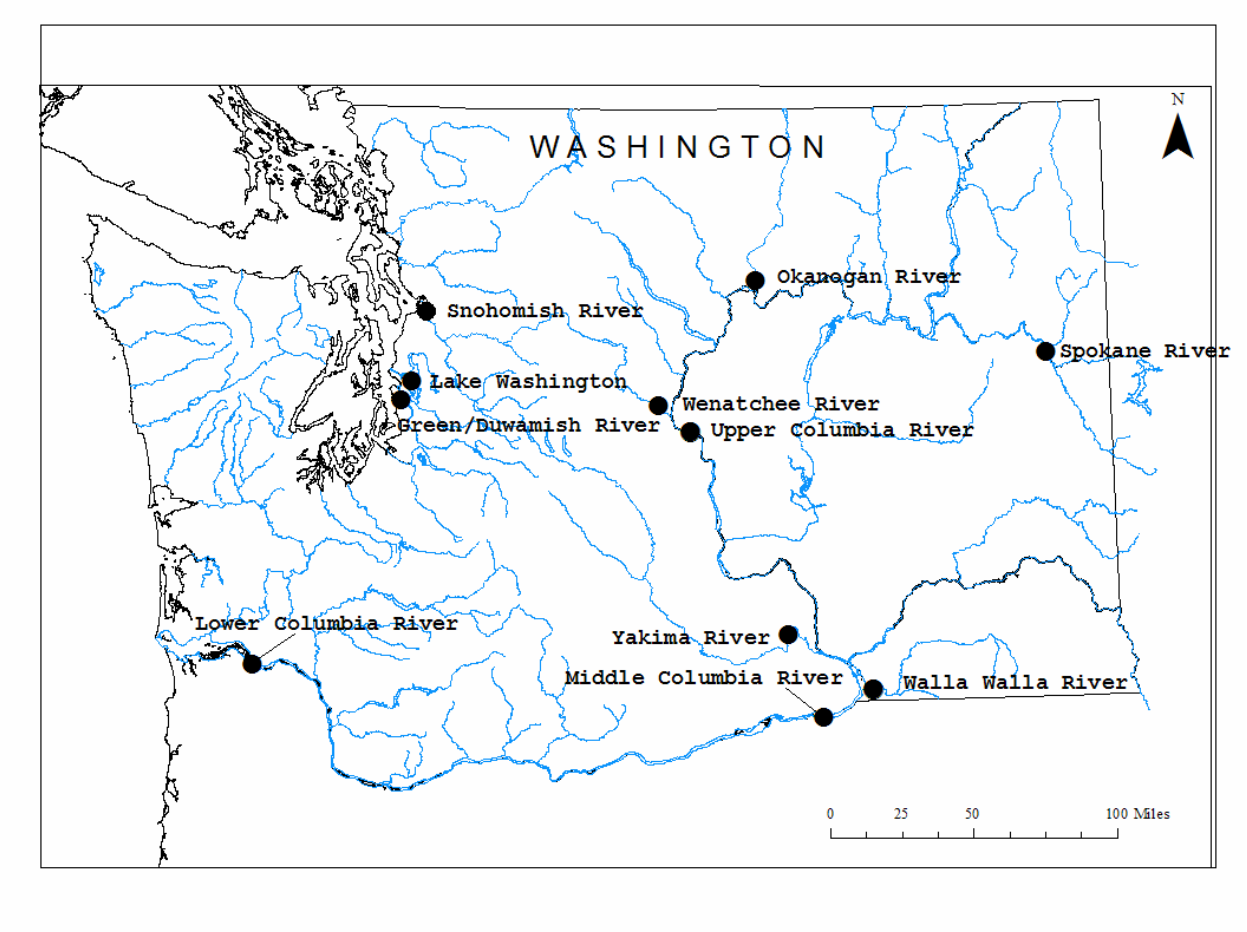


Figure 2. Proposed Trend Monitoring Stations for Organic PBTs.

A brief summary of the contaminant status of each waterbody proposed for trend monitoring is provided below. The chemical data referred to were obtained from WSTMP reports, Ecology's Environmental Information Management system (EIM), or the published studies cited.

1. Spokane River at Nine-Mile Dam

Historically, the Spokane River has had the highest PCB levels recorded in Washington State freshwater fish. Maximum concentrations exceeding 1,000 ug/Kg total PCBs (parts per billion) were reported in fish fillets in the early 1990s. Levels have decreased since then, but remain at approximately 200-300 ug/Kg total PCBs in fillets from some areas and up to 3,000 ug/Kg in whole fish samples.

The Spokane River also had the highest PBDE levels measured in fish and water samples during a recent Ecology survey (Johnson et al., 2006). Total PBDE concentrations in rainbow trout and mountain whitefish fillets from the Nine-Mile reach averaged 420 and 1,100 ug/Kg, respectively. Whole trout and whitefish from this part of the river had 1,770 and 4,100 ug/Kg total PBDEs, concentrations that appear elevated in a national perspective.

CP levels are relatively low in the Spokane. Whole fish samples analyzed from Nine-Mile in 2005 had DDE concentrations of 50 ug/Kg or less. Other CPs were less than 10 ug/Kg and most were not detected. The Spokane is currently 303(d) listed for total PCBs and 2,3,7,8-TCDD (dioxin) in edible fish tissue. A TMDL evaluation was recently conducted for PCBs (Serdar et al., 2006 draft).

WDOH has issued a fish consumption advisory on the Spokane River that is primarily driven by PCBs (www.doh.wa.gov/ehp/oehas/EHA_fish_adv.htm). The current advisory recommends no consumption of any fish species from Upriver Dam to the Idaho border. WDOH is currently reviewing this advisory to include data collected by Ecology in 2005, which evaluated PCBs, PBDEs, and select metals in a variety of fish species.

Nine-Mile Dam is located below the city of Spokane at river mile (r.m.) 58 and downstream of most of the known or suspected sources of contamination. SPMDs were successfully deployed here in 2005-2006 for the above-mentioned PBDE survey. The SPMD site is on the upstream side of the dam at center channel.

2. Okanogan River at Monse

The Okanogan has consistently placed alongside the Yakima as the two Washington rivers with the highest levels of dichlorodiphenyltrichloroethane (DDT) compounds in fish tissue. Edible fish tissue samples collected by Ecology between 1984 and 1995 had 1,700 - 3,000 ug/Kg total DDT (DDT+DDE+DDD). Serdar (2003) reported maximum total DDT concentration of 600 ug/Kg in fish fillets collected in 2001. PCB concentrations were much lower, 40 ug/Kg or less. PBDEs have not been analyzed in the Okanogan system.

Serdar (2003) conducted a TMDL evaluation for DDT compounds and PCBs in the Okanogan River and a cleanup plan is in place (Peterschmidt, 2004). WDOH has evaluated fish tissue data from the Okanogan River and determined that no fish consumption advisory is warranted.

Monse is located on the lower Okanogan River at r.m. 5.0. A specific sampling site in the Monse area has not yet been identified.

3. Wenatchee River near Mouth
Elevated concentrations of PCBs have been reported in Wenatchee River fish and water (Davis et al., 1995; McCarthy and Gale, 1999). Era-Miller (2004) followed up on these findings in 2003 and found up to 1,300 ug/Kg total PCBs in mountain whitefish fillets from the upper river. A federal fish hatchery that used PCB-containing, antifouling paint has been implicated as a major source. Total DDT concentrations ranged from 39–273 ug/Kg in Wenatchee River whitefish and sucker fillets. Mission Creek drainage is a significant source of DDT to the Wenatchee River and has been addressed in a TMDL (Serdar and Era-Miller, 2004).

WSTMP analyzed PBDEs in two of the Era-Miller (2004) fish samples from the Wenatchee. Total PBDE concentrations in mountain whitefish fillets were 7.2 ug/Kg in the upper river and 40 ug/Kg in the lower river. The lower river result is among the higher concentrations so far recorded in Washington.

WDOH is currently evaluating the available fish tissue data.

A specific sampling site on the Wenatchee River has not yet been identified. The site should be close to the mouth and downstream of fruit orchards, which line the river and are potential sources of CPs.

4. Upper Columbia River at Rock Island Dam
In view of the size of the Columbia River and the many PBT sources discharging to it, three trend monitoring stations are proposed: Upper Columbia River at Rock Island Dam, Mid-Columbia River at McNary Dam, and Lower Columbia River near Clatskanie, Oregon. Each station is intended to integrate the effects of upstream sources.

Fish tissue data are limited for the Columbia mainstem near Rock Island Dam. WSTMP analyzed one sample each of fillets from three resident fish species collected immediately above the dam in 2004. Concentration ranges were 144–400 ug/Kg total DDT, 15–52 ug/Kg total PCBs, and 6–22 ug/Kg total PBDEs. Similar results were obtained in WSTMP fish samples collected further upstream near Rocky Reach Dam and up to 80 ug/Kg total PBDEs below Wells Dam.

Several tributaries that discharge to the Columbia River above Rock Island are known sources of CPs, PCBs, or PBDEs. As previously mentioned, these include the Spokane River (PCBs and PBDEs), Okanogan River (DDT compounds), and the Wenatchee River (PCBs, DDT compounds, and PBDEs). Lake Chelan, which drains into the Columbia River above Wenatchee, had the highest total DDT concentrations in EPA's recent National Lake Fish Tissue Survey (www.epa.gov/waterscience/fishstudy/). Coots and Era-Miller (2005) reported average total DDT concentrations of 943 ug/Kg in lake trout fillets and 315 ug/Kg in burbot fillets collected from Lake Chelan in 2003. Coots and Era-Miller proposed a TMDL for DDT and PCBs. PCB levels, however, are low—15 ug/Kg or less.

Rapidly increasing PBDE levels have been reported further upstream in mountain whitefish collected in the Columbia River above the Canadian border (Rayne et al., 2003). The doubling period for PBDEs was 1.6 years between 1995 and 2000.

Although there are currently no 303(d) listings for the Columbia mainstem in the vicinity of Rock Island, the 2004 WSTMP findings will result in DDE and PCB listings. Further upstream, Lake Roosevelt has been 303(d) listed for DDD, DDE, alpha-BHC, PCBs, and mercury in edible fish tissue. The CP levels here are relatively low, indicating the major sources are downstream. There are no fish consumption advisories on the upper Columbia mainstem, except for a mercury advisory in Lake Roosevelt.

Rock Island Dam is located ten miles below the city of Wenatchee. SPMDs will tentatively be deployed for trend monitoring on the upstream side of the dam (r.m. 453).

5. Yakima River at Horn Rapids Dam

The Yakima is the most intensively sampled river in Washington and has been the subject of toxics studies by USGS, U.S. Fish and Wildlife Service (USFWS), EPA, and Ecology dating back to the 1970s. Total DDT levels of approximately 1,000–3,000 ug/Kg were documented in fish fillets as recently as the early 1990s. A majority of fish samples analyzed by EPA in the late 1990s were in the 500–1,500 ug/Kg range for total DDT. Total PCB levels in EPA's samples exceeded 200 ug/Kg in mountain whitefish fillets.

The Lower Yakima River ranked among the ten waterbodies with the highest PBDE levels in Ecology's 2005–2006 survey. Total PBDE concentrations in fish fillets collected near Horn Rapids reached 29 ug/Kg. Preliminary data from samples collected further upstream in 2006 show total PBDE levels exceed 100 ug/Kg in some species (WSTMP Unpublished Data).

TMDLs have been established for suspended sediment and chlorinated pesticides in the Yakima River (Joy and Patterson, 1997; Joy, 2002). BMPs have been implemented to reduce soil erosion and associated pesticide inputs. Effectiveness monitoring shows there have already been substantial reductions in total suspended solids and turbidity in the lower river (Coffin et al., 2006).

Data that became available after the TMDLs have resulted in additional Yakima River 303(d) listings for edible fish tissue that now include chlordane, alpha-BHC, PCBs, and TCDD. WDOH issued a fish consumption advisory for DDT compounds in 1993 and will be re-evaluating the advisory in 2007, based on new data being collected by Ecology (Johnson, 2006).

Horn Rapids Dam is on the Lower Yakima River (r.m. 18.0) below all major irrigation returns and urban centers. SPMDs were successfully deployed here in 2005–2006 for the Ecology PBDE survey. The SPMD site is on the outside edge of the diversion channel to the Columbia and Richland irrigation canals.

6. Lower Walla Walla River

Water and fish samples collected for a recent TMDL evaluation showed the Walla Walla River and a number of its tributaries exceed human health criteria for DDT compounds, dieldrin, toxaphene, chlordane**,** hexachlorobenzene, heptachlor epoxide, and PCBs (Johnson et al., 2004). Average total DDT and total PCB concentrations in lower river fish ranged from 30–650 ug/Kg and 9–240 ug/Kg, respectively. PBDEs have not been analyzed.

The TMDL has been completed and a cleanup plan is in place (Gray et al., 2006). There is a WDOH fish consumption advisory for PCBs in carp and pike minnow.

The trend monitoring station will be located in the lower river, upstream of the backwater formed by the Columbia River McNary pool. A sampling site has tentatively been identified on private property at approximately r.m. 9.

7. Middle Columbia River at McNary Dam

McNary Dam is downstream of the Hanford/Tri-Cities area and confluence of the Yakima, Snake, and Walla Walla Rivers. EPA (2002) analyzed fish tissue samples from the Hanford Reach in the late 1990's and reported DDE concentrations of 260–710 ug/Kg in sucker and mountain whitefish fillets, with up to 1,400 ug/Kg in sturgeon fillets. Total PCB levels in the same samples ranged from 47–400 ug/Kg. These concentrations are high when compared to freshwater fish statewide.

PBDEs were analyzed in fillets from yellow perch, channel catfish, and suckers collected above McNary Dam for the 2005 WSTMP. Total PBDEs ranged from <1–21 ug/Kg (Johnson et al., 2006).

There are numerous fish tissue-based 303(d) listings between Rock Island Dam and McNary Dam. These include: Lower Crab Creek drainage (DDE, dieldrin, PCBs, and TCDD), Hanford Reach (DDE, dieldrin, aldrin, chlordane, and PCBs), and Snake River (DDE, chlordane, dieldrin, and PCBs). The Yakima and Walla Walla 303(d) listings and TMDLs were previously mentioned.

WDOH has not issued a fish consumption advisory for this reach of the Columbia. To address tribal concerns, EPA has evaluated fish tissue data and has provided consumption guidance to the Columbia River Intertribal Fish Commission (CRITFC).

SPMDs will be deployed from the upstream side of McNary Dam (r.m. 292) near the navigation lock. This site was used for Ecology's PBDE survey in 2005-2006.

8. Lower Columbia River near Clatskanie, Oregon

The Bi-State Program was among the first to report elevated levels of CPs and PCBs in Lower Columbia River fish (e.g., Tetra Tech, 1996). EPA (2006) followed with the Columbia River Basin Fish Contaminant Survey in 1996–1999, but almost all of these samples were upstream of the Longview/Portland area.

The most recent fish samples from the river downstream of Longview come from the WSTMP. WSTMP analyzed fillets from one composite each of suckers, pike minnow, and peamouth chub collected near Cathlamet in 2005. The following concentrations were detected: 28–32 ug/Kg total DDT, 47–76 ug/Kg total PCBs, and 8–31 ug/Kg total PBDEs.

Ecology and USGS have used SPMDs to monitor organochlorines in the Lower Columbia River (Johnson and Norton, 2005; McCarthy and Gale, 1999). Results from these studies may be more representative of river conditions. Ecology observed that water column concentrations of PCBs increased going from Bonneville Dam to below Longview. DDT compounds and dieldrin

concentration, however, decreased over this same reach, suggesting the major sources are upstream of Bonneville. Similar results were obtained by the USGS. The concentrations estimated for Ecology's SPMD site below Longview (Clatskanie, Oregon) were 14–130 pg/L dieldrin, 570–840 pg/L total DDT, and 650–1,800 pg/L total PCBs parts per quadrillion. The corresponding human health criteria are 140, 590, and 170 pg/L, respectively.

SPMDs deployed in the Columbia River during 2005–2006 showed PBDE levels were higher in the middle and lower reaches, compared to the upper river (Johnson et al., 2006). Total PBDE concentrations at the Clatskanie, Oregon, site were estimated at 20–60 pg/L.

For the trend monitoring project, SPMDs will be deployed off the upstream end of the Portland General Electric dock (former Beaver Army Terminal), approximately r.m. 53. This is the same site used for the 2005–2006 PBDE survey. The previous SPMD studies in the Lower Columbia monitored in the same general vicinity.

WDOH conducted a health risk assessment for DDT, dieldrin, and PCBs in Lower Columbia River fish, based on data from the Bi-State study (LaFlamme and Gilroy, 1996). WDOH ultimately concluded that the sample size was not large enough to be representative and did not issue an advisory.

9. Lake Washington

The Lake Washington watershed is one of the most densely populated urban areas in Washington. WDOH and the University of Washington (UW) conducted a study of chemical contaminants in Lake Washington fish in 2001–2003. Only whole fish were analyzed. The highest mean concentrations of total PCBs were observed in the largest size classes of northern pike minnow (1,070 ug/Kg), cutthroat trout (377ug/Kg), and yellow perch (191 ug/Kg). WDOH issued a fish consumption advisory for these species.

Preliminary data from more recent fish sampling by WDOH and UW in 2005 suggest that CP levels in Lake Washington are relatively high for western Washington. DDE concentrations in the 100–200 ug/Kg range and dieldrin concentrations approaching 5 ug/Kg were observed in fillets from some species (WDOH Unpublished).

Fish fillets analyzed for Ecology's PBDE survey showed total concentrations up to 55 ug/Kg in Lake Washington. The lake was ranked fourth most contaminated among the waterbodies surveyed.

For trend monitoring, SPMDs will be suspended on a subsurface buoy near the entrance to Union Bay, which is Lake Washington's outlet to Lake Union and the Lake Washington Ship Canal.

10. Lower Green/Duwamish River

The Green/Duwamish watershed has a population of almost half a million people. The lower portion—Duwamish Waterway—is heavily industrialized.

Sediment contamination in the Lower Duwamish Waterway (LDW) has been the focus of most of the previous investigations. Gries (2006) describes the regulatory history as follows:

"Ecology first identified certain areas within the LDW as being of potential concern in its 1996 Contaminated Sediment Site List. Parts of the river that showed signs of impairment have appeared on subsequent federal Clean Water Act 303(d) lists for various contaminants in water, fish, and sediment. The U.S. Environmental Protection Agency (EPA) Superfund Program placed a substantial portion of the LDW—from approximately river mile 0.0 at the south end of Harbor Island to approximately river mile 5.0 south of the turning basin—on the National Priority List in 2000. Ecology signed an Agreement On Consent that made the LDW a Model Toxics Control Act (MTCA – Ecology, 2001 and 2005a) and Sediment Management Standards (SMS - Ecology, 1995) cleanup site that same year."

"This stretch of waterway has been under remedial investigation ever since. The major contaminants of concern found in surface sediments throughout much of the LDW are polychlorinated biphenyls (PCBs) and phthalates."

As part of the remedial investigation, numerous fish tissue samples were taken in 2004 and 2005, revealing some of the highest PCB levels in the state and other PBTs were detected. This information prompted WDOH to update the existing advisory to no consumption of fish, shellfish, and crab. Salmon that utilize the Duwamish River were evaluated as part of the Puget Sound health assessment.

The Duwamish Waterway and River is currently 303(d) listed for DDT compounds, alpha-BHC, PCBs, and PAHs in edible fish tissue, based on data collected between 1985 and 1997 by Ecology and WDFW. The Green River is not listed for toxics.

The Lower Duwamish River is tidally influenced. During low tide, access to the freshwater portion is poor due to soft mudflats and the river being shallow. Therefore, the trend monitoring station will be located in the more highly contaminated Duwamish Waterway, tentatively in the vicinity of the south end of Harbor Island. (~ r.m. 0.5). This is the one-of-two estuarine stations initially proposed for trend monitoring. A specific monitoring site has not been selected.

11. Lower Snohomish River

Limited data suggest the Snohomish River has somewhat elevated levels of PCBs and PBDEs compared to other western Washington rivers. WSTMP analyzed fillets from four species of fish collected from river mile 15–18 in 2004. Total PCBs ranged from 20–48 ug/Kg and total PBDEs ranged from 11–32 ug/Kg. These PBDE concentrations ranked in the top five in Ecology's PBDE survey. CP levels were less than 5 ug/Kg in the WSTMP samples.

A monitoring site for the Lower Snohomish River remains to be selected. Potentially higher PCB and PBDE concentrations than those observed in the WSTMP samples exist farther downstream where the river flows through the urban/industrial area of Everett. Saltwater influence can extend upstream for a distance of up-to-six miles during spring flood tides.

The chemicals of primary interest for trend monitoring at each of the above eleven stations are summarized in Table 4.

Table 4. Trend Monitoring Stations and Chemicals of Primary Interest

Monitoring Station	Chemicals of Primary Interest		
	CPs	PCBs	PBDEs
1. Spokane River @ Nine Mile Dam		x	x
2. Okanogan River @ Monse	x		no data
3. Wenatchee River near Mouth	x	x	x
4. Upper Columbia River @ Rock Island Dam	x	x	x
5. Yakima River @ Horn Rapids Dam	x	x	x
6. Lower Walla Walla River	x	x	no data
7. Midddle Columbia River @ McNary Dam	x	x	x
8. Lower Columbia River near Beaver OR	x	x	x
9. Lake Washington near Outlet	x	x	x
10. Lower Green/Duwamish River		x	x
11. Lower Snohomish River		x	x

Sample Timing and Frequency

SPMDs will be deployed at each monitoring station for approximately one month in the spring (May) and one month in the fall (September). Deployments during these time periods will capture spring runoff and summer low-flow conditions (Figure 3).

Studies in Washington have shown that peak concentrations of CPs, PCBs, and PBDEs tend to occur during these periods. For example, the highest total DDT concentrations in Lake Chelan occur in May and June due to a combination of the start of irrigation, wet season precipitation, and snowmelt (Coots and Era-Miller, 2005). Peak concentrations of DDT compounds and dieldrin in the Yakima River occur during the irrigation season, April to October (Joy and Patterson, 1997; Joy, 2002). The Walla Walla River toxics TMDL identified late winter and spring as the critical period for CPs and PCBs, likely due to erosion of agricultural soils and urban runoff (Johnson et al., 2004).

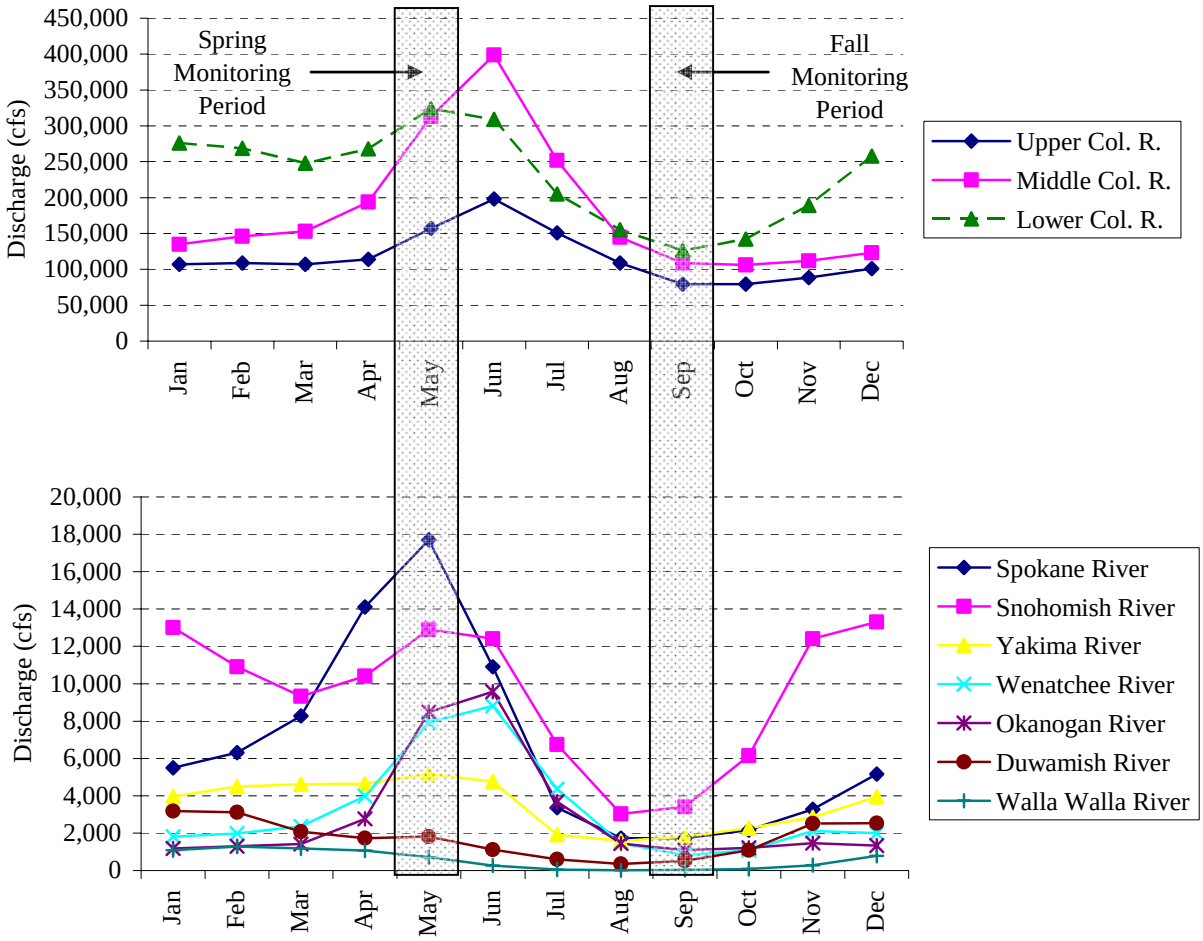


Figure 3. Annual Flow Pattern for Selected Monitoring Stations Showing Approximate Time When SPMDs Will be Deployed (USGS flow data)

USGS reviewed data on the occurrence of pesticides in Pacific Northwest surface waters and concluded that the type of runoff was the major controlling factor. Pesticide detections in the west and in urban areas were dominated by rainfall runoff in the winter and spring, and on the eastside were dominated by the irrigation season in the spring and summer (Anderson et al., 2005).

SPMDs analyzed for the Spokane River PCB TMDL showed concentrations were highest in October and April, with much lower concentrations in February (Serdar et al., 2006-draft). Two SPMD studies in the Lower Columbia River found the highest PCB concentrations in the spring (Johnson and Norton, 2005) or fall (McCarthy and Gale, 1999).

Water column concentrations of PBDEs showed substantial seasonal variation in Ecology's recent PBDE survey (Johnson et al., 2006). Much higher concentrations were found in Lake Washington and the Lower Columbia and Yakima Rivers in the spring vs. the fall. This probably reflects the greater amount of urban runoff during this period, or, for the Yakima, an effect

related to the beginning of the irrigation season. The opposite phenomenon was seen in the Spokane River where total PBDE concentrations were about five-times lower in the spring, likely due to dilution of local sources by snowmelt upstream.

Chemical Analyses

All SPMD samples from this project will be analyzed for CPs, PCBs, and PBDEs. Appendix B lists the target compounds.

The SPMDs will be prepared and extracted at EST. The extracts will be analyzed for CPs and PBDEs at the Ecology Manchester Environmental Laboratory (MEL) using Gas Chromatography/Electron Capture Detection (GC/ECD) and Gas Chromatography/Mass Spectrometry (GC/MS) methods, respectively. A high resolution GC/MS analysis will be employed for individual PCB congeners to obtain low detection limits and ensure that PCBs are quantified in all samples. MEL has contracted with Pace Analytical to analyze PCB congeners for the first three years of this project.

Ancillary data will be collected to characterize water quality at each monitoring station to include temperature, conductivity, total suspended solids (TSS), and total organic carbon (TOC). Salinity will be analyzed for the Lower Duwamish and Lower Snohomish (if an estuarine location is selected). Flow data are available for most of these stations through USGS, Ecology, or local entities.

Quality Objectives

MEL and Pace Analytical are expected to meet all Quality Control (QC) requirements of the analytical methods being used for this project. Measurement quality objectives (MQOs) are shown in Table 5.

Table 5. Measurement Quality Objectives for Trend Monitoring with SPMDs

Analysis	Check Stds./ Lab Control Samples (% recov.)	Laboratory Duplicates (RPD)	Surrogates (% recov.)	Matrix Spike (% recov.)	Labeled Congeners (% recov.)	Lowest Concentration of Interest
Chlorinated pesticides	50-150%	NA*	50-150%	50-150%	NA	10 ng/SPMD
PBDEs	50-150%	NA*	50-150%	50-150%	NA	2 ng/SPMD
PCB congeners	50-150%	NA*	50-150%*	50-150%*	25-150%	0.1 ng/SPMD
TSS	80-120%	±20%	NA	NA	NA	1 mg/L
TOC	80-120%	±20%	NA	75-125%	NA	1 mg/L
Salinity	80-120%	±20%	NA	75-125%	NA	1 g/Kg

NA = not analzyed
*see text

The MQOs for precision and bias correspond to MEL's Action Limits. The MQO for recovery of labeled congeners in the PCB analysis is the QC limit specified in the method. Data outside these limits will be evaluated for appropriate corrective action.

Check standards and laboratory control samples contain known amounts of analyte and indicate bias due to sample preparation and calibration. These QC samples apply to the analyzing laboratories only.

Results on duplicate (split) samples provide estimates of analytical precision. Precision of the SPMD data for the present study will be assessed with field replicates rather than laboratory duplicates (see Quality Control Procedures)

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

EST will do a matrix spike of field quality SPMD membranes. Matrix spikes may provide an indication of bias due to interferences from components in the sample. To reduce cost, there will be no duplicate matrix spike and MEL will be requested not to run a separate MS/MSD for their procedure, except for TOC as is routinely done.

The PCB analysis for this study is by an isotopic dilution method using labeled congeners. The 12 PCBs designated as toxic by the World Health Organization (also known as dioxin-like PCBs) and the earliest and latest eluted congener at each level of chlorination are determined by isotope dilution quantitation. The remaining congeners are determined by an internal standard quantitation technique. Surrogates and matrix spikes are not part of the method and it is not practical to add the labeled compounds at EST Laboratory prior to extracting the SPMDs. Therefore, recovery of PCBs through the entire procedure (dialysis, cleanup, and analysis) will be assessed using selected PCB congeners as surrogates. Bias will similarly be assessed with a matrix spike of selected congeners (see Quality Control).

The lowest concentrations of interest shown for SPMDs in Table 5 are based on reporting limits MEL or their contractors have achieved in analyzing SPMD extracts in the recent past. These have been adequate to quantify the target compounds in waterbodies with moderate to low levels of contamination.

Sampling Procedures

Deployment and retrieval procedures for SPMDs will follow the guidance in Huckins et al. (in press) and the Environment Assessment (EA) Program's Standard Operating Procedures for SPMDs (Johnson, 2007). Standard SPMDs (91 x 2.5 cm membrane containing 1 mL of 99% pure triolein) and the stainless steel canisters (16.5 x 29 cm) and spider carrier devices that hold the membranes during deployment will be obtained from EST. The SPMDs are preloaded onto the carriers by EST in a clean room and shipped in solvent-rinsed metal cans under argon atmosphere.

Five SPMD membranes will be used for each sample to ensure that sufficient residues are obtained for chemical analysis. The membranes will be deployed in a single canister (Figure 4). For sampling sites where security is a concern, the membranes will be split among two canisters. The SPMDs will be kept frozen until deployed.

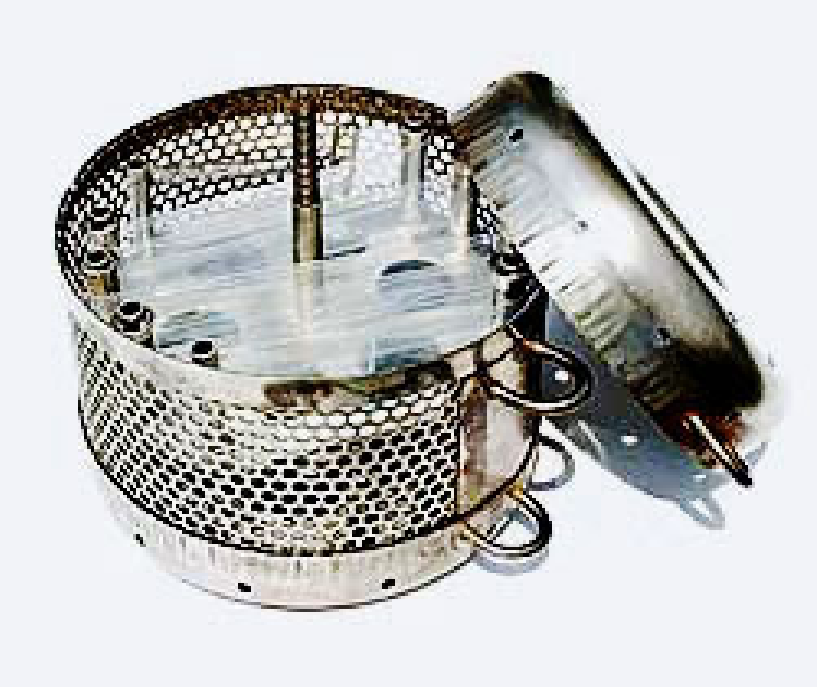


Figure 4. SPMD Array in Stainless Steel Deployment Canister
(Two-Membrane Canister Shown; Five-Membrane Canister to be Used for PBT Monitoring.)

On arrival at the monitoring station, the cans will be pried open, spindles slid into the canisters, and the device suspended from a surface structure or anchored to the bottom. Field personnel will wear nitrile gloves and not touch the membranes. The SPMDs will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for anticipated fluctuations in water level. Because SPMDs are potent air samplers, this procedure should be done as quickly as possible. For deepwater sites, the SPMDs will be positioned in the top 20 feet of the water column, above the summer thermocline.

The SPMDs will be deployed for approximately 28 days as recommended by USGS and EST. During a 28-day deployment, chemical uptake by an SPMD is linear and there are no significant losses of accumulated residues. A 28-day deployment has provided useful results in past Ecology studies. The retrieval procedure is essentially the opposite of deployment. The cans holding the SPMDs must be carefully sealed and the SPMDs must be maintained at or near freezing until they arrive at EST for extraction.

At the beginning, middle, and end of each deployment period, TOC and TSS samples and conductivity and temperature measurements will be taken at each station. TOC can be used to estimate total concentrations from the dissolved data. Salinity will be determined for the Lower Duwamish and Lower Snohomish stations. TOC, TSS, and salinity samples will be collected in appropriate containers (Table 6).

Table 6. Field Procedures for Conventional Water Quality Parameters

Parameter	Min. Sample Size	Container	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4^oC	7 days
TOC	20 mL	60 mL poly bottle	HCl to pH<2, 4^oC	28 days
Salinity	300 mL	500 mL	Cool to 4^oC	28 days

The latitude and longitude of each monitoring station will be recorded.

Measurement Procedures

Table 7 shows the types and numbers of samples to be analyzed, expected range of results, required reporting limits, and sample preparation and analysis methods. To the extent possible, methods were chosen to give reporting limits equal to or less than the lowest concentrations of interest.

Table 7. Laboratory Procedures for Trend Monitoring with SPMDs

Analysis	Number of Field Samples*	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical Method
Chlor. Pesticides	13	1-1,000 ng	10 ng/SPMD	dialysis/GPC**	EPA 8081
PBDEs	13	1-1,000 ng	2 ng/SPMD	dialysis/GPC**	EPA 8270
PCB congeners	13	1-500 ng	0.1 ng/SPMD	dialysis/GPC**	EPA 1668A
TSS	33	1 - 1,000 mg/L	1 mg/L	N/A	EPA 160.2
TOC	33	1-10 mg/L	1 mg/L	N/A	EPA 415.1
Salinity	6	1-15 g/Kg	2 g/Kg	N/A	SM2520

*per monitoring period, i.e. twice a year (includes one SPMD field blank and one replicate SPMD)
**EST SOPs E14, E15, E19, E21, E33, E44, E48
N/A = not applicable

The success of this trend monitoring project hinges on consistent application of field and laboratory procedures. The analyzing laboratories will adhere closely to the methods and procedures described in this QA Project Plan. They will notify the project lead in advance of any proposed changes in how the samples are to be analyzed.

EST will extract the SPMDs (referred to as dialysis), perform gel permeation chromatography (GPC) cleanup on the extracts, split the extracts 50:50 (except for matrix spikes), and ship the ampulated extracts to MEL. MEL will send the PCB extracts to the congener laboratory.

The dialysis method used by EST Laboratory is a patented procedure, described in Huckins et al. (in press). EST Laboratory dialysis and GPC methods are documented in SOPs which are on file at Ecology.

The SPMD results will be reported as total ng in the entire extract (i.e., multiply by 2 due to the 50:50 split, except for the matrix spikes which are specific to each laboratory and not split by EST Laboratory). The PRCs PCB-4, -29, and -50 will be quantified in the congener analysis. The congener laboratory will not include the PRCs or PCB surrogates when calculating homologue totals or total PCBs.

The total cost of analyzing samples for this project is estimated at $22,955 per monitoring period or $45,910 per year (Table 8). This cost estimate is based on the MEL 50% discounted price; true cost is two times for analyses conducted at MEL. The cost for contract lab analyses includes MEL's surcharge of 25%. Results from the first year of monitoring may indicate that some of these analytes could be dropped at certain stations to reduce costs.

Table 8. Estimate of Laboratory Costs for Trend Monitoring with SPMDs

SPMD Preparation and Extraction (per monitoring period)

	Number of Stations	Membranes per Station	Total Membranes	Unit Cost	Cost Subtotals
Monitoring Stations *	12	5	60	45	2700
Field Blank	1	5	5	45	225
Dialysis +GPC	13			240	3120
PRC & Surrogate Spikes	13	5	65	2	130
Matrix Spike	no charge				0
EST lab blanks	no charge				0
					$6,175

Chemical Analyses (per monitoring period)

	Field Samples†	Matrix Spike	Total Samples	Unit Cost	Cost Subtotals
Chlorinated pesticides	13	1	14	225	3150
PBDEs	13	1	14	125	1750
PCB congeners	13	1	14	750	10500
TOC**	33	2††	33	30	990
TSS**	33	NA	33	10	330
Salinity**	6	NA	6	10	60
					$16,780

Estimated Lab Cost per Monitoring Period = $22,955

Estimated Annual Lab Cost = $45,910

*includes one replicate SPMD sample

†includes one replicate SPMD sample and one field blank SPMD

**three samples per station (up to two salinity stations only)

††MS/MSD, no charge

NA = not analyzed

Quality Control Procedures

Field

The field QC samples to be analyzed for this project are shown in Table 9.

Table 9. Field Quality Control Samples for Trend Monitoring with SPMDs
[per monitoring period]

Sample Type	Analysis	Replicates	Trip Blanks
SPMDs	Chlorinated Pesticides	1	1
"	PBDEs	1	1
"	PCB congeners	1	1
Water	TSS	NA	NA
"	TOC	NA	NA
	Salinity	NA	NA

NA = not analyzed

EST will spike each SPMD membrane with PRCs prior to their being deployed in the field, including the field trip blank and day-zero blank (see Laboratory QC). PCB-4, -29, and -50 will serve as PRCs for this project. These congeners are not present in significant amounts in the environment and have shown appropriate rates of loss in past Ecology studies. [Loss rates should be 20-80%.] The spiking level will be 0.2 ug of each congener per SPMD membrane (1.0 ug per sample). Pace will supply the PCB spiking solution.

Field replicates will provide estimates of the total variability in the SPMD data (field + laboratory). Replicate SPMDs will be deployed at one station for each deployment period. Stations targeted for replication will be rotated. For 2007, replicate SPMDs will be set out for the Spokane and Yakima Rivers as these two stations are likely to have the widest variety and highest concentrations of target compounds.

Because SPMDs sample vapors while exposed to air, a field trip blank is needed to record potential chemical accumulation during deployment, retrieval, and transport. The field blank SPMD is opened to the air for the same amount of time it takes to open and place the SPMD array in the water, then the blank is resealed and refrigerated. The blank is stored frozen and taken back into the field and opened and closed again to mimic the retrieval process. Total exposure time is typically two minutes or less. The blank is processed and analyzed the same as deployed SPMDs. There will be one SPMD field blank consisting of five membranes for each deployment period. The blank will be rotated among the eleven stations.

Laboratory

The laboratory QC samples to be analyzed for this project are shown in Table 10.

Table 10. Laboratory Quality Control Samples for Trend Monitoring with SPMDs
[analyzing laboratory, except as noted]

Analysis	Method Blanks*	Check Std./ LCS	Surrogate Spikes	Matrix Spike	OPR Stds./ Labelled Cmpds.	Duplicates
Chlor. Pesticides	2/batch	1/batch	all samples†	1/batch†	NA	NA
PBDEs	2/batch	1/batch	all samples†	1/batch†	NA	NA
PCB congeners	1/batch	1/batch	all samples†	1/batch†	all samples	NA
TSS	1/batch	1/batch	NA	NA	NA	1/batch
TOC	1/batch	1/batch	NA	1/batch	NA	1/batch
Salinity	1/batch	1/batch	NA	NA	NA	1/batch

*see text for additional method blanks prepared by EST

†to be spiked at EST
LCS = laboratory control sample
OPR = ongoing precision and recovery
NA = not analyzed

EST Laboratory will prepare the following method blanks for each SPMD deployment:

- Spiking-blank SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST Laboratory and later dialyzed with project samples.
- Day-zero SPMD blank to serve as a reference point for PRC loss.
- Dialysis-blank SPMDs from the same lot as the project batch, to represent background during dialysis and cleanup.
- Day-zero blank SPMD, prepared just prior to dialysis, to serve as a control.
- Reagent blank to assess contamination independent of the SPMDs.

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

EST Laboratory will add surrogate compounds to each SPMD sample prior to dialysis. The surrogates for the chlorinated pesticide analysis will be tetrachloro-m-xylene, 4,4-

dibromooctafluorobiphenyl, and dibutylchlorendate. The surrogate for the PBDE analysis will be hexabromobiphenyl. The surrogates for the PCB analysis will be -14 or -36 on the low end, -78 for the middle, and -186 on the high end. The pesticide and PBDE surrogates will be spiked at 80 ng each. The PCB surrogates will be spiked at 10-40 ng each. The analyzing laboratories will supply the spiking solution for their respective surrogates.

For each dialysis batch, EST Laboratory will do a matrix spike of field quality SPMD membranes using target compounds. The spiking level will be 80 ng for each of the pesticides and PBDEs, using MEL's standard matrix spike mix. Pace's standard matrix spike mix for PCB congeners will be used; the spiking level has not been determined at this time. The pesticide/PBDE matrix spikes and PCB matrix spikes will be done on two separate membranes to avoid interferences. MEL and Pace Analytical will supply the matrix spike solutions for their respective analyses.

Data Management Procedures

Field data and observations will be recorded in a bound notebook of waterproof paper.

The data package from MEL will include a case narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. This should include results for all method blanks, check standards/laboratory control samples (LCS) blanks, surrogate compounds, matrix spikes, and ongoing precision and accuracy (ORP) standards/labeled compounds included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual on the project team.

All project data will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal data review procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

Audits

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

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

Reports

A draft progress report will be prepared for review by the client and other interested parties on or before March 2008 and annually thereafter. The progress report will be finalized within one-to-two months, depending on when review comments are received. Responsible staff member: Patti Sandvik.

The annual progress report will include:

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

The project data will be entered into EIM on or before the date of the final progress report. Responsible staff member: Patti Sandvik.

Data Verification

MEL will conduct a review of all laboratory data and case narratives. MEL will verify that: (1) methods and protocols specified in the QA Project Plan were followed, (2) all calibrations, checks on quality control, and intermediate calculations were performed for all samples, and (3) the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

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

The project lead will review the laboratory data packages and MEL's data verification report. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered. Data validation will be documented in the annual progress reports.

Data Quality (Usability) Assessment

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

Water column concentrations of dissolved CPs and PCBs will be calculated using the most recent version of the SPMD Water Calculator spreadsheet developed by USGS. Currently this is v5_10Jan07.xls, David Alvarez, Columbia Environmental Research Center. The spreadsheet calculates SPMD sampling rates from PRC-derived sampling rates, using an empirical uptake model described in Huckins et al. (2006). The spreadsheet can be found at Y: \Shared\SPMDs\SPMD Water Calculator v5_10Jan07 (Ecology access only). The same equations will be used to calculate PBDE concentrations (PBDEs are not included in the spreadsheet). Total concentrations for these compounds will be estimated using the relationship with TOC developed by Meadows et al. (1998).

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

Data analysis for this project will be straightforward. For the first several years, the analysis will be limited to examining simple time-series plots of both the residue (ng/SPMD) and concentration data (ng/L) for qualitative evidence of increasing or decreasing trends over time. Box-and-whisker plots will be used to identify seasonal differences at each station. As more data accumulate, the Mann-Kendall trend test for small sample sizes ($N<10$) and the Wilcoxon Rank Sum test will be used to test the null hypothesis that there is no temporal trend in the data vs. the alternate hypothesis of either an upward or downward trend over time. The Wilcoxon Rank Sum is not as robust with respect to outliers as Mann-Kendall, but has more statistical power. A minimum of four samples (four years for each monitoring period) are required for testing.

References

Anderson, C., A. K. Williamson, K. Carpenter, R. W. Black, F. Finella, J. Morace, G. Greg, and H. Johnson. 2005. Pesticides in Surface Waters of the Pacific Northwest -- Overview of USGS Regional Findings. Presentation at 5th Washington Hydrogeology Symposium, Tacoma, WA. April 12-14, 2005.

Coffin, C., R. Plotnikoff, and R. Anderson. 2006. Lower Yakima River Suspended Sediment Total Maximum Daily Load Study Water Quality Effectiveness Monitoring Report. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-114. www.ecy.wa.gov/biblio0603114.html

Coots, R. 2006. Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-113. www.ecy.wa.gov/biblio/0603113.html

Coots, R. and B. Era-Miller. 2006. Lake Chelan DDT and PCBs in Fish, Total Maximum Daily Load Study. Washington State Department of Ecology, Olympia, WA. Publication No. 05-03-014. www.ecy.wa.gov/biblio/0503014.

Davis, D., A. Johnson, and D. Serdar. 1995. Washington State Pesticide Monitoring Program: 1993 Fish Tissue Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 95-356. www.ecy.wa.gov/biblio/95-356.html

EPA. 2002. Columbia River Basin Fish Contaminant Survey, 1996-1998. EPA Region 10, Seattle, WA. EPA 910/R-02-006.

Ecology. 2006 (Draft). Multiyear PBT Chemical Action Plan Schedule. Washington State Department of Ecology, Olympia, WA. Publication No. 06-07-025. www.ecy.wa.gov/biblio/0607025.html

Ellis, G.S., J.N. Huckins, C.E. Rostad, C.J. Schmitt, J.D. Petty, and P. MacCarthy. 1995. Evaluation of Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Monitoring Organochlorine Contaminants in the Upper Mississippi River. Environ. Toxicol. Chem. 14:1875-1884.

Era-Miller. 2004. Verification of 303(d)-listed Sites in Northwest, Central, and Eastern Regions of Washington State. Washington State Department of Ecology, Olympia, WA. Pub. No. 04-03-035. www.ecy.wa.gov/biblio/0403035.html

Gray, D., K. Baldwin, and A. Johnson. 2006. Walla Walla River Chlorinated Pesticide and PCBs Total Maximum Daily Load. Washington State Department of Ecology, Olympia, WA. Pub. No. 05-10-079. www.ecy.wa.gov/biblio/0510070.html

Gries, T. 2006. Quality Assurance Project Plan: Using Sediment Profile Imaging (SPI) to Evaluate Sediment Quality at Two Puget Sound Cleanup Sites: Part I - Lower Duwamish Waterway. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-116. www.ecy.wa.gov/biblio/0603116.html.

Hallock, D. and W. Ehinger. 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. Pub. No. 03-03-200. www.ecy.wa.gov/biblio/0303200.html

Hardy, J. and D. McBride. 2004. Evaluation of Contaminants in Fish from Lake Washington King County, Washington. Washington State Department of Health, Olympia, WA.

Hopkins, B., D. Clark, M. Schlender, and M. Stinson. 1985. Basic Water Quality Monitoring Program: Fish Tissue and Sediment Sampling for 1984. Washington State Department of Ecology, Olympia, WA. Pub. No. 85-7. www.ecy.wa.gov/biblio/85-7.html

Huckins, J.N., J.D. Petty, and K. Booij. 2006. Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices. Springer Science and Business Media, New York, NY. 223 pp.

Huckins, J.N. et al. (in press). A Guide to the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants. USGS Columbia Environmental Research Center, Columbia MO. Am. Petrol. Inst. 4690.

Hyne, R., F. Pablo, M. Aistrope, A.W. Leonard, and N. Ahmad. 2004. Comparison of Time-Integrated Pesticide Concentrations Determined from Field-Deployed Passive Samplers with Daily River-Water Extractions. Environ. Toxicol. Chem. 23(9):2090-2098.

Johnson, A. 2006. Quality Assurance Project Plan: Chlorinated Pesticides, PCBs, and Dioxins in Yakima River Fish – 2006: Assessing Progress Toward TMDL Targets and Updating the Fish Consumption Advisory. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-111. www.ecy.wa.gov/biblio/0603111.html

Johnson, A. 2007. Standard Operating Procedure for Using Semipermeable Membrane Devices to Monitor Hydrophobic Organic Compounds in Surface Water. Washington State Department of Ecology, Environmental Assessment Program, Olympia, WA.

Johnson, A., B. Era-Miller, R. Coots, and S. Golding. 2004. A Total Maximum Daily Load Evaluation for Chlorinated Pesticides and PCBs in the Walla Walla River. Washington State Department of Ecology, Olympia, WA. Pub. No. 04-03-032. www.ecy.wa.gov/biblio/0403032.html

Johnson, A. and D. Norton. 2005. Concentrations of 303(d) Listed Pesticides, PCBs, and PAHs Measured with Passive Samplers Deployed in the Lower Columbia River. Washington State Department of Ecology, Olympia, WA. Pub. No. 05-03-006. www.ecy.wa.gov/biblio/0503006.html.

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

Joy, J. 2002. Upper Yakima River Basin Suspended Sediment and Organochlorine Pesticide Total Maximum Daily Load. Washington State Department of Ecology, Olympia, WA. Pub. No. 02-03-012. www.ecy.wa.gov/biblio/0203012.html.

Joy, J. and B. Patterson. 1997. A Suspended Sediment and DDT Total Maximum Daily Load Evaluation Report for the Yakima River. Washington State Department of Ecology, Olympia, WA. Pub. No. 97-321. www.ecy.wa.gov/biblio/97-321.html

LaFlamme, D. and D. Gilroy. 1996. Health Analysis of Chemical Contaminants in Lower Columbia River Fish. Washington State Department of Health, Olympia, WA.

Lombard, S. and C. Kirchmer. 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030. www.ecy.wa.gov/biblio/0403030.html.

Luross, J.M., M. Alaee, D.B. Sergeant, C.M. Cannon, D.M. Whittle, K.R. Solomon, and D.C.G. Muir. 2002. Spatial Distribution of Polybrominated Diphenyl Ethers (PBDEs) and Polychlorinated Biphenyls (PCBs) in Lake Trout from the Laurentian Great Lakes. Chemosphere 46:665-672.

McCarthy, K.A. and R.W. Gale. 1999. Investigation of the Distribution of Organochlorine and Polycyclic Aromatic Hydrocarbon Compounds in the Lower Columbia River Using Semipermeable Membrane Devices. U.S. Geological Survey, Water-Resources Investigation Report 99-4051.

Meadows, J.C., K.R. Echols, J.N. Huckins, F.A. Borsuk, R.F. Carline, and D.E. Tillitt, D.E. 1998. Estimation of Uptake Rates for PCB Congeners Accumulated by Semipermeable Membrane Devices and Brown Trout (*Salmo trutta*). Environ. Sci. Tech. 32:1847-1852.

Noren, K. and D. Meironyte. 2000. Certain Organochlorine and Organobromine Contaminants in Swedish Human Milk in Perspective of Past 20-30 years. Chemosphere 40:1111-1123.

Peterschmidt, M. 2004. Lower Okanogan River Basin DDT and PCBs Total Maximum Daily Load Submittal Report. Washington State Department of Ecology, Yakima WA. Pub. No. 04-10-043. www.ecy.wa.gov/biblio/0410043.html

Rantalainen, A.L., M.G. Ikonomou, and I.H. Rogers. 1998. Lipid-Containing Semipermeable Membrane Devices (SPMDs) as Concentrators of Toxic Chemicals in the Lower Fraser River, British Columbia. Chemosphere 37:1119-1138.

Rayne, S., M.G. Ikonomou, and B. Antcliffe. 2003. Rapidly Increasing Polybrominated Diphenyl Ether Concentrations in the Columbia River System from 1992 to 2000. Environ. Sci. Technol. 37(13):2847-2854.

Seiders, K. 2006. Quality Assurance Project Plan: Measuring Mercury Trends in Freshwater Fish in Washington State. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-103. www.ecy.wa.gov/biblio/0603103.html

Seiders, K., C. Deligeannis, and K. Kinney. 2006. Washington State Toxics Monitoring Program: Toxic Contaminants in Fish Tissue and Surface Water in Freshwater Environments, 2003. Washington State Department of Ecology, Olympia, WA. Pub. No. 06-03-019. www.ecy.wa.gov/biblio/0603019

Serdar, D. 2003. TMDL Technical Assessment of DDT and PCBs in the Lower Okanogan River Basin. Washington State Department of Ecology, Olympia, WA, Pub. No. 03-03-013. www.ecy.wa.gov/biblio/0303013.html

Serdar, D. and B. Era-Miller. 2004. DDT Contamination and Transport in the Lower Mission Creek Basin, Chelan County; Total Maximum Daily Load Assessment. Washington State Department of Ecology, Olympia, WA, Pub. No. 04-03-043. www.ecy.wa.gov/biblio/0403043.html

Serdar, D., K. Kinney, and P. Hallinan. 2006-draft. Spokane River PCBs Total Maximum Daily Load Water Quality Improvement Report. Washington State Department of Ecology, Olympia, WA, Pub. No. 06-03-024. www.ecy.wa.gov/biblio/0603024.html

She, J., M. Petreas, J. Winkler, P. Visita, M. McKinney, and D. Kopec. 2002. PBDEs in the San Francisco Bay Area: Measurements in Harbor Seal Blubber and Human Breast Adipose Tissue. Chemosphere 46:697-707.

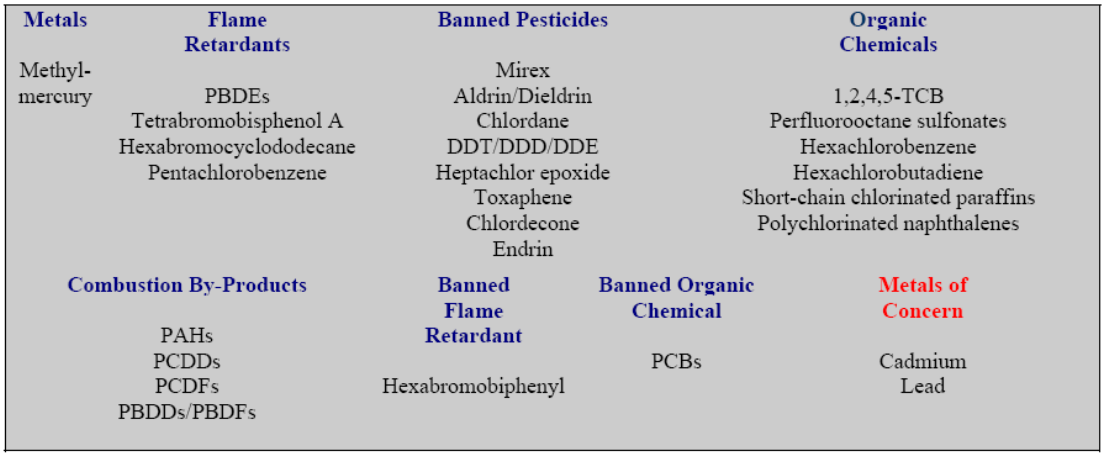
Tetra Tech. 1996. Assessing Human Health Risks from Chemically Contaminated Fish in the Lower Columbia River. Lower Columbia River Bi-State Program. Tetra Tech Inc., Bellevue, WA.

WDOH. 2003. Public Health Assessment: Lower Duwamish Waterway, Seattle, King County Washington. Washington State Department of Health, Olympia, WA.

Appendices

Appendix A. Chemicals and Chemical Groups on the PBT List (Ecology, 2006)

Figure 1. Chemicals and Chemical Groups on the PBT List.



Appendix B. Chemicals to be Analyzed in SPMD Samples Collected during 2007

Chlorinated Pesticides (MEL PEST2)
alpha-BHC
beta-BHC
gamma-BHC (lindane)
delta- BHC
Heptachlor
Aldrin*
Chlorpyriphos
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

Polybrominated Diphenyl Ethers*
PBDE-47
PBDE-66
PBDE-71
PBDE-99
PBDE-100
PBDE-138
PBDE-153
PBDE-154
PBDE-183
PBDE-190
PBDE-209

Polychlorinated Biphenyls*
Approximately 150 PCB congeners

*PBTs

.