Quality Assurance Project Plan

PBT Monitoring: Measuring PBDE Levels in Washington Rivers and Lakes

by
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September 2005

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Approvals

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Abstract

A Quality Assurance (QA) Project Plan is provided for analyzing polybrominated diphenyl ether (PBDE) flame retardants in selected rivers and lakes in Washington State. The goal of the study is to establish baseline conditions in freshwater areas that can be used in the future to evaluate the effectiveness of Washington's Interim PBDE Chemical Action Plan and other efforts to reduce PBDE inputs to the environment. PBDE concentrations will be determined in fish tissue samples from 20 lakes and water samples from 10 lakes. The study will be conducted during 2005-2006.

Background

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in a wide variety of everyday items including foam for seat cushions and carpet pads; automobile trim, telephone handsets, and kitchen appliances; wire coatings; and casings for TV sets, computers, and other home electronics. The Washington State Department of Ecology (Ecology) has identified PBDEs as persistent, bioaccumulative toxins (PBTs). Ecology and the Washington State Department of Health have prepared an Interim Chemical Action Plan identifying steps the state may take to reduce the threat of PBDEs in the environment (Peele, 2004).

Release of PBDEs to the environment occurs from landfills, electronics recycling, wastewater treatment plant effluents, stormwater runoff, and other sources. The three commercially produced PBDE mixtures are penta-BDE, octa-BDE, and deca-BDE. The sole U.S. producer of penta-BDE and octa-BDE has voluntarily agreed to stop production and sale by the end of 2004 and 2005, respectively. The continued use of deca-BDE, meanwhile, may depend on the results of current or future studies. Many manufacturers have stopped using penta-BDE and octa-BDE.

The major congeners in commercial PBDE mixtures include PBDE-47, -99, -100, -153, 154, and 209, with -47 and -99 accounting for the greatest percentage of residues found in environmental samples.

Table 1. Congener Constituents of Commercial PBDE Products

TetraDBE:	
PBDE-47	2,2',4,4'-tetrabromodiphenyl ether
PentaDBE:	
PBDE-99	2,2',4,4',5-pentabromodiphenyl ether
PBDE-100	2,2',4,4',6-pentabromodiphenyl ether
HexaDBE:	
PBDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether
PBDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether
DecaBDE:	
PBDE 209	2,2'3,3',4,4',5,5',6,6'-decabromodiphenyl ether

The Interim Chemical Action Plan has detailed information on use, environmental occurrence, health effects, and regulations pertaining to PBDEs. Briefly, the primary concern revolves around the observation that the levels of PBDEs in humans have been doubling every two to five years. If this rate continues, the levels in humans could reach those known to cause adverse effects in laboratory rodents (Peele, 2004). Certain PBDEs have been linked to neurotoxicity, impaired thyroid function, fetal toxicity, and tumor generation in animal experiments. Diet is the source of most of the PBDE body burden in humans, and fish have the highest PBDE levels among different types of food (Peele, 2004).

There is not very much data on PBDE levels in fish from Washington State rivers and streams, and no data on the levels in water. There are currently no state or federal fish tissue or water quality criteria for PBDEs.

PBDEs were first reported in Washington fish in 2001 when Ecology analyzed 16 samples of freshwater fish from various locations (Johnson and Olson, 2001). The method used in this study for PBDE analyses was in the method development stage and provided only concentrations of homologue groups (total tetra-BDE, total penta-BDE, etc.).

The concentrations of total PBDEs reported by Johnson and Olson ranged from 1.4 ug/Kg (wet weight) in rainbow trout collected in remote Douglas Creek to 1,250 ug/Kg in mountain whitefish from the Spokane River. The highest concentrations were found in areas draining urbanized/agricultural watersheds (Spokane, Yakima, and Snake rivers) compared to undeveloped watersheds (Douglas Creek, Rock Island Creek, and Soleduck River). There appeared to be substantial interspecies differences among fish species in their tendency to accumulate penta-BDEs, with relatively low levels in bottom feeders such as large-scale suckers and carp compared to rainbow trout and mountain whitefish. This finding has since been corroborated by other investigators (Rayne et al., 2003; Paul Peterman, USGS Columbia Environmental Research Center, personal communication, 3/30/200 email).

The bulk of the recent data on PBDEs in Washington State freshwater fish has been reported through Ecology's Washington State Toxics Monitoring Program (WSTMP; Seiders, 2003; Seiders and Kinney, 2004). The WSTMP has analyzed PBDE-47, -99, -100, -153, and -154. Most of the sampling has been done in smaller lakes and only PBDE-47, -99, and -100 have been detected. Concentrations were generally low, with total PBDEs (sum of detected congeners) ranging from 1 – 4 ug/Kg in the majority of samples.

In view of the limited data and potential for human health concerns, the Washington State Legislature provided funding during FY06 for the Ecology Environmental Assessment (EA) Program to conduct a statewide survey of PBDEs in selected rivers and lakes to better determine the current level of contamination. The survey will be conducted during 2005-2006 and include both fish and water samples.

Project Description

The EA Program will conduct a one-time survey to measure PBDE concentrations in fish from 20 Washington rivers, impoundments, and lakes. PBDEs in water samples from a subset of ten rivers and lakes will be determined using a semipermeable membrane device (SPMD) to absorb and concentrate PBDEs from water. The goal of the study will be to establish baseline conditions that can be used in the future to evaluate the effectiveness of Washington's Interim PBDE Chemical Action Plan and other efforts to reduce PBDE inputs to the environment.

Specific study objectives will be to:

1. Measure PBDE concentrations in three fish species from each of 20 waterbodies, analyzing composite fillet samples and limited numbers of whole fish composites.
2. Measure PBDE concentrations in water samples from each of ten representative fish collection sites.
3. Assess seasonal changes in water column PBDE levels at six sites.
4. Rank the waterbodies in terms of the level of PBDE contamination.
5. Identify spatial, species, and temporal patterns in the environmental distribution and accumulation of PBDEs.

Field work for the study will be conducted during August – April 2006. The following congeners will be analyzed: PBDE-47, -66, -71, -99, -100, -138, -153, -154, -183, -190, and -209. PBDEs will be analyzed at the Ecology Manchester Environmental Laboratory (MEL) by GC/MS SIM using EPA Method 8270.

Organization and Schedule

Name	Organization	Phone No.	Role
Art Johnson	EAP-WES-TSU	360-407-6766	Project co-lead, responsible for water sampling and final report
Keith Seiders	EAP-WES-TSU	360-407-6689	Project co-lead, responsible for fish sampling
Kristin Kinney	EAP-WES-TSU	360-407-7168	Field assistance
Casey Deligeannis	EAP-WES-TSU	360-407-7395	Field assistance
Brandi Lubliner	EAP-WES-TSU	360-407-7168	Field assistance
Dale Norton	EAP-WES-TSU	360-407-6765	Unit supervisor
Terri Spencer	Environmental Sampling Technologies	816-232-8860	SPMD prep. and extraction
Dolores Montgomery	Manchester Laboratory	360-871-8804	PBDE analyst
Dean Momohara	Manchester Laboratory	360-871-8808	Unit supervisor
Stuart Magoon	Manchester Laboratory	360-871-8801	Lab director
Cliff Kirchmer	EAP	360-407-6455	QA officer
Brandee Era-Miller	EAP-WES-TSU	360-407-6771	EIM data entry

Date	Task
August – Sept. 2005	Deploy/retrieve SPMDs; send to EST for extraction
August – Oct. 2005	Collect fish samples
October 2005	2005 SPMD extracts submitted to Manchester Laboratory
November 2005	Fish samples submitted to Manchester Laboratory
January 2006	All 2005 data reported to project co-leads
March – April 2006	Deploy/retrieve SPMDs; send to EST for extraction
April 2006	2006 SPMD extracts submitted to Manchester Laboratory
May 2006	All 2006 data reported to project co-leads
May 2006	Draft project report completed
AJOH0048	EIM study area ID
June 2006	EIM data entry completed
May 2006	Report draft to supervisor
May 2006	Report draft to client
June 2006	Report draft out for external review
June 2006	Final project report completed
General Information	
EIM User Study ID	AJOH0048
EIM Data Engineer	Brandee Era-Miller
EIM Study Name	PBT Monitoring: Measuring PBDE Levels in Washington
Report Lead Author	Art Johnson

Quality Objectives

Manchester Environmental Laboratory is expected to meet all quality control (QC) requirements of the analytical methods being used for this project. Recoveries of the decachlorobiphenyl (DCB) surrogate have been selected as significant, bottom-line measurement quality objectives (MQOs) for estimating the accuracy of the PBDE analysis. This study will also require a separate analysis of two PCB congeners (4 and 29) which are spiked into the SPMDs prior to deployment (see Background on SPMDs). DCB is also the surrogate in the PCB analysis and the same MQOs apply. The MQOs for all analyses being conducted for this project are shown in Table 2.

Table 2. Measurement Quality Objectives for 2005-2006 PBDE Study

Matrix	Analysis	MQO
Fish tissue	PBDEs	50-150% surrogate recovery
"	"	50-150% LCS* recovery
"	"	±50% duplicate precision
"	"	50-150% matrix spike recovery
"	"	±40% matrix spike RPD[†]
"	Lipids	80-120% LCS recovery
"	"	±20% duplicate precision
SPMD extract	PBDEs	50-150% surrogate recovery
"	"	50-150% LCS recovery
"	"	±50% duplicate precision
"	"	50-150% matrix spike recovery
"	"	±40% matrix spike RPD
"	PCB-4, -29**	50-150% surrogate recovery
"	"	50-150% LCS recovery
"	"	±50% duplicate precision
"	"	50-150% matrix spike recovery
"	"	±40% matrix spike RPD
Water	TSS	80-120% LCS recovery
"	"	±20% duplicate precision
"	TOC	80-120% LCS recovery
"	"	±20% duplicate precision
"	"	75-125% matrix spike recovery
"	"	±20% matrix spike RPD

*Laboratory Control Sample

[†]Relative Percent Difference

**Performance Reference Compounds for SPMDs

The lowest concentrations of interest for project samples are listed in Table 3. These are the lowest concentrations practically attainable within budget constraints of this project and should be sufficient to quantify the predominant PBDE congeners and ancillary parameters of interest in the majority of samples, based on comparable studies by the EA Program.

Table 3. Lowest Concentrations of Interest for 2005-2006 PBDE Study

Analysis	Matrix	Lowest Concentration of Interest
PBDEs	Fish tissue	0.5 ug/Kg, wet
Lipids	"	0.1%
PBDEs	SPMD extract	0.005 ng
PCB-4,-29*	"	50 ng
TSS	Water	1 mg/L
TOC	"	1 mg/L

*Performance Reference Compounds for SPMDs

Study Design

The waterbodies proposed for PBDE sampling are listed in Table 4. Their locations are shown in Figure 1.

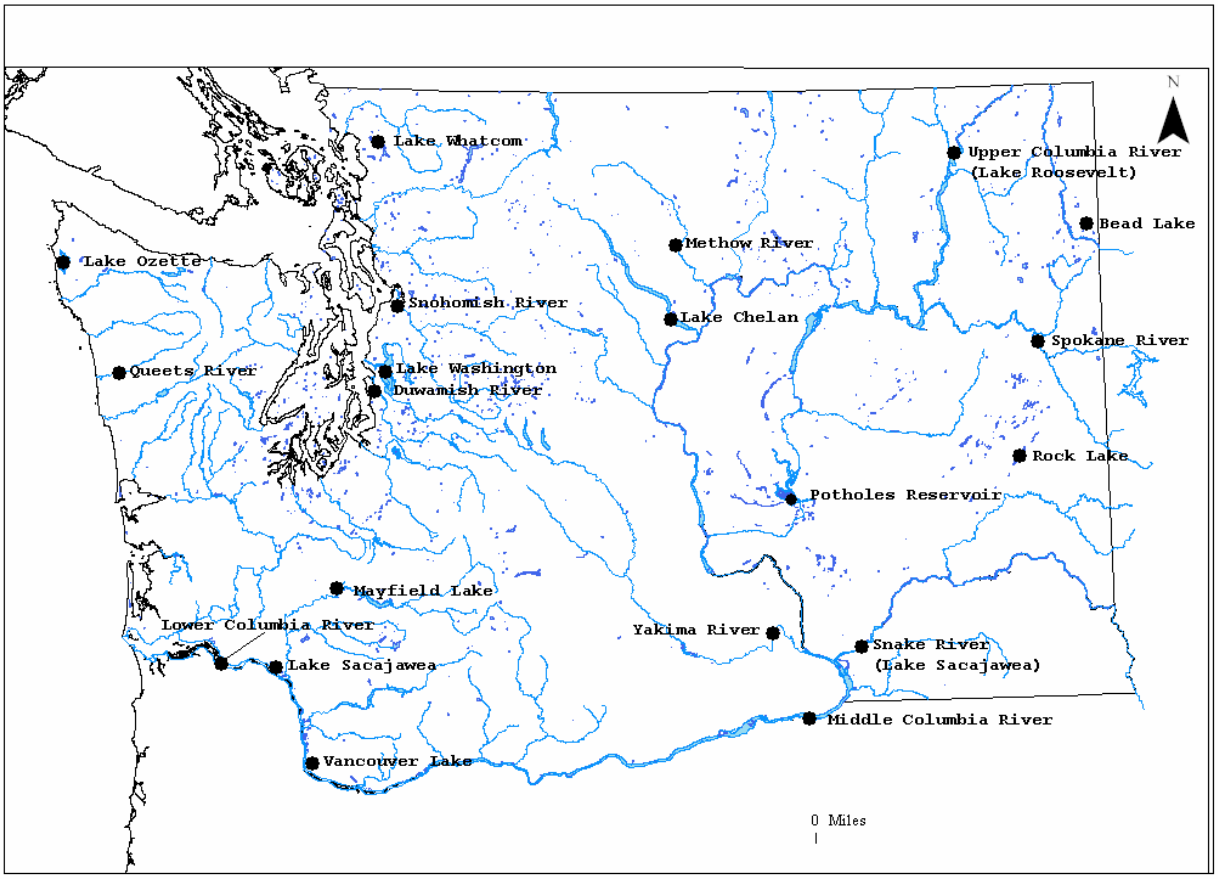


Figure 1. Rivers and Lakes Proposed for PBDE Sampling

Sampling will be focused primarily on waterbodies that drain large areas and are a significant fisheries resource. Ten rivers/impoundments and ten lakes were selected to represent a range of land-use types including urban, agricultural, and forested. An attempt was made to distribute the sampling effort equitably across the state. There is an emphasis on the Columbia River system, not only due to its size and importance but also because of reports of rapidly increasing PBDE levels in Columbia River fish in British Columbia (Rayne et al., 2003). Two rivers and two lakes were selected as likely representing present-day background for PBDEs, given their location and surrounding land use, as indicated in Table 4.

Several other major waterbodies were considered for sampling--Cowlitz River, Palouse River, Chehalis River, Wenatchee River, Banks Lake, Sprague Lake, and Medical Lake--but not selected because the WSTMP has recently collected fish at these locations for PBDE analysis. These data will be included in the project report for the present study.

Fish will be collected from all 20 sites listed in Table 4. An effort will be made to collect three species from each waterbody. Gamefish will be preferentially taken, with other less sought after species such as carp, suckers, or squawfish, and retained when needed to obtain the target sample size. Where possible, the species sampled will include both predators and bottom feeders to cover a range of trophic levels (EPA, 2000). The fish will be collected during August – October 2005. The lipid content of many species represents a reservoir for PBDEs and is generally highest at this time (EPA, 2000).

Table 4. Rivers and Lakes Proposed for 2005-2006 PBDE Study

Waterbody	Fish Samples	Water Samples	WRIA	County	Drainage Area (sq. miles)	Predominant Land Use
Rivers/Impoundments						
Spokane River	x	x*	54	Spokane	5,200	urban
Lower Columbia River	x	x*	25	Cowlitz	256,900	urban
Snohomish River	x		7	Snohomish	1,720	urban
Duwamish River	x	x*	9	King	483	urban
Snake River	x		33	Walla Walla	108,500	agriculture
Yakima River	x	x*	37	Benton	6,120	agriculture
Middle Columbia River	x	x	31	Benton	2,214,000	agriculture
Upper Columbia River	x	x	58	Stevens	64,500	forested
Methow River†	x		48	Okanogan	1,772	forested
Queets River†	x	x*	21	Jefferson	143	forested
Lakes						
Lake Washington	x	x*	8	King	472	urban
Vancouver Lake	x		28	Clark	39	urban
Lake Sacajawea	x		26	Cowlitz	6	urban
Lake Chelan	x		47	Chelan	924	agriculture
Rock Lake	x		54	Whitman	523	agriculture
Potholes Reservoir	x	x	41	Grant	4,551	agriculture
Lake Whatcom	x		1	Whatcom	56	forested
Mayfield Lake	x		26	Cowlitz	1,400	forested
Bead Lake†	x		62	Pend Oreille	9	forested
Lake Ozette†	x	x	20	Clallam	78	forested

*To be collected both summer-fall 05 and spring 06, otherwise summer-fall 05 only

†Background site

WRIA = Water Resources Inventory Area

Fillets will be analyzed for all species. Each tissue sample will consist of composited fillets from five individual fish. One whole-body composite each will be analyzed for five species, as whole fish is probably a worst-case sample for PBDEs. These data will be used to calculate a fillet: whole body ratio for PBDEs.

PBDE concentrations will be determined in water samples for ten of the waterbodies, as shown in Table 4. In light of the low concentrations anticipated in water, SPMDs will be used to sample and concentrate PBDEs.

In addition to filling the data gap that presently exists on PBDE concentrations in surface waters, the SPMD data complement the study in several other ways. A number of potentially confounding factors in interpreting fish tissue data such as migration, metabolism, species differences, and selective-depuration of PBDEs are not an issue with SPMDs. For these reasons and because of their standardized design, SPMDs from different sites or time periods may be more comparable than fish tissue samples. Also, the SPMD data can be used in conjunction with the fish tissue data to estimate site-specific bioaccumulation factors (BAFs) for PBDEs.

One SPMD array will be deployed at each of the 10 sites for approximate one month during August – September, 2005. For six waterbodies, as indicated in Table 4, a second set of SPMDs will be deployed during March – April 2006 to assess the magnitude of seasonal changes in PBDE levels as a result of runoff. Seasonality is being assessed in a limited number of rivers and lakes for budgetary reasons.

All project samples will be analyzed for PBDE-47, -66, -71, -99, -100, -138, -153, -154, -183, -190, and -209. (PBDE- 66, -71, -138, -190, and -183 are part of MEL's standard analytical suite.) The fish samples will also be analyzed for percent lipids, as this parameter may be useful for normalizing the data. Water samples for total suspended solids (TSS) and total organic carbon (TOC) and field measurements of conductivity will be taken at the beginning, mid-point, and end of the SPMD deployments to characterize water quality. Temperature will be recorded continuously at each SPMD site.

Background on SPMDs

SPMDs are passive samplers that mimic the biological uptake of hydrophobic organic compounds such as PCBs, organochlorine pesticides, and PBDEs. The passive uptake of these compounds is driven by membrane- and lipid-water partitioning. SPMDs measure the dissolved and, therefore, readily bioavailable fraction. SPMDs provide much lower detection limits than traditional water sampling techniques.

The device proposed for the present study was developed by the U.S. Geological Survey (USGS) and is 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 application can be found at wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm.

Each SPMD is composed of a thin-walled, layflat polyethylene tube (91 x 2.5 cm) filled with triolein, the major neutral lipid in fish (Figure 2). 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 20-30 days. The SPMDs are then extracted and analyzed for the chemicals of interest.

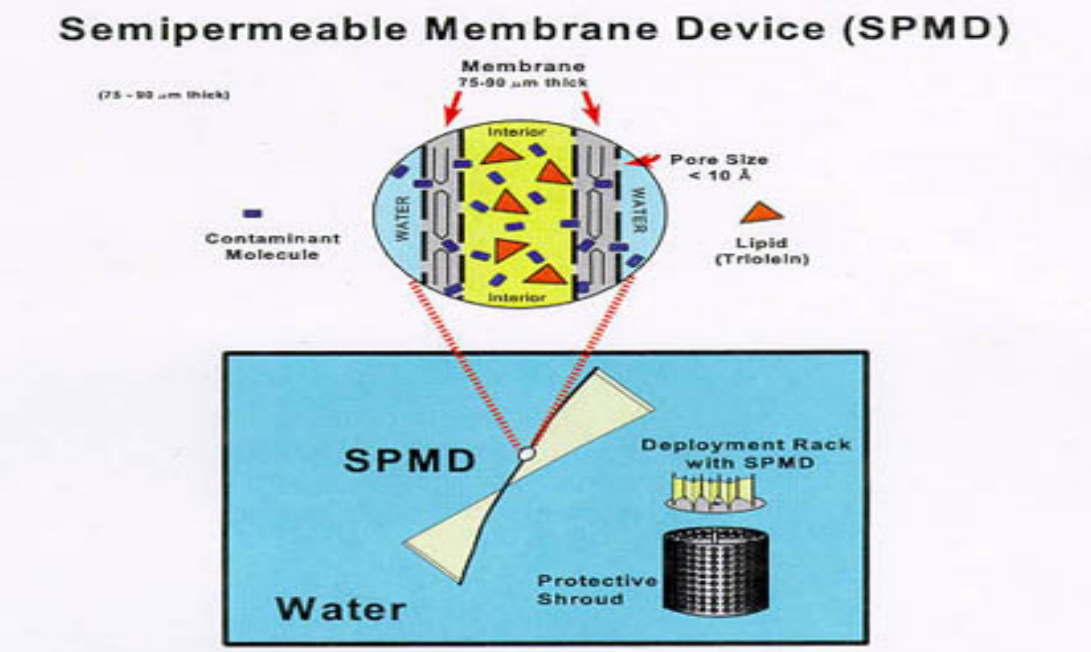
The absorbed amount is proportional to the local water concentration. Therefore, the environmental distribution and relative levels of contaminants such as PBDEs can be assessed by comparing the absorbed amounts among sites or within the same site for different sampling periods.

SPMDs can also provide a time-weighted average concentration for the chemicals of interest. Estimates of average dissolved concentration in the water are obtained using a combination of laboratory calibration data and Permeability/Performance Reference Compounds (PRCs) spiked into deployed SPMDs. At present, sampling rates have not been determined in the laboratory for PBDEs. However, because sampling rates correlate well with octanol-water partition coefficients (K_{ow}), PBDE sampling rates can be estimated from laboratory calibration data for similar compounds.

PRCs are analytically non-interfering compounds with moderate to relatively high fugacity (escape tendency). The loss rate of PRCs is proportional to the uptake of target compounds. PRC loss rates in the field are used to derive an exposure adjustment factor (EAF) to recalibrate for the effects of temperature, water velocity, and biofouling on SPMD sampling rates that have been determined in the laboratory. A high rate of PRC loss translates into a lower calculated water concentration for target compounds because the chemical residues in the SPMD represent a larger volume of water, and vice versa. The PRCs to be used in the present study are PCB-4, PCB-29, and C13-labeled PBDE-15.

A fundamental assumption of the PRC approach is that they can be used to predict EAFs for chemicals over a wide range of K_{ow}. Based on studies by Huckins et al. (2002), this assumption appears valid and the difference between measured concentrations of an analyte and the PRC-

derived estimates should be within a factor of two. Studies on other chemicals such as PCBs and chlorinated pesticides have shown the results are comparable to other low-level sampling methods such as solid-phase and liquid-liquid extraction (Ellis et al., 1995; Rantalainen et al, 1998; Hyne et al., 2004).



The lipid containing semipermeable membrane device (SPMD) and a typical deployment apparatus.

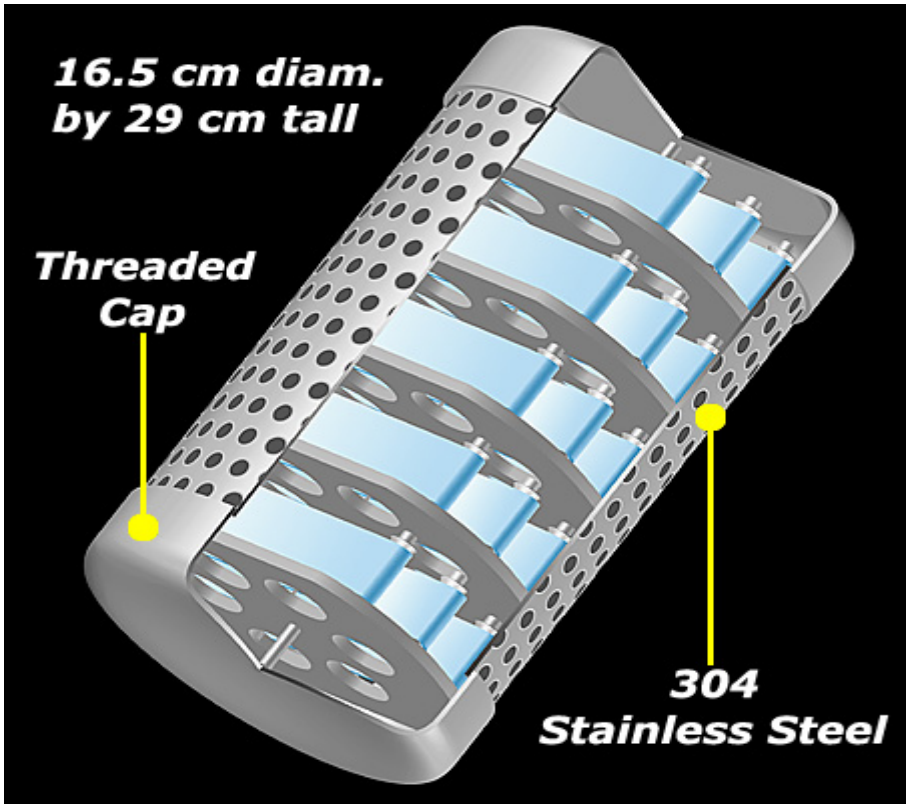


Figure 2. SPMD Device and Deployment Canister
(wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm)

Sampling Procedures

Fish

Fish will be collected by electroshocking or with gill nets or beach seines. Only legal size fish will be taken for chemical analysis. For species with no size limits, only those large enough to reasonably be retained for consumption will be taken. Fish selected for analysis will be killed by a blow to the head. Each fish will be given a unique identifying number and its length and weight recorded. The latitude and longitude of the sampling sites will be recorded from a Magellan 320 global positioning receiver (GPS).

Potential sources of sample contamination in the field will be identified and appropriate steps taken to minimize or eliminate them. The fish will not be allowed to come in contact with oils, grease, dirt or dust. Each fish will be rinsed with site water, individually wrapped in aluminum foil, put in waterproof plastic bags, and placed on ice for transport to Ecology headquarters, where the samples will be frozen pending preparation of tissue samples.

SPMDs

Deployment and retrieval procedures for SPMDs will follow the guidance in Huckins et al. (2000). Standard SPMDs (91 x 2.5 cm membrane containing 1 mL triolein) and the stainless steel canisters (16.5 x 29 cm) and spindle devices that hold the membranes during deployment will be obtained from EST. The SPMDs are preloaded onto the spindles by EST in a clean room and shipped in solvent-rinsed metal cans under argon atmosphere.

Five or six SPMD membranes will be used for each SPMD sample. Five membranes will be deployed in a single canister at sites that are secure from vandalism. Six membranes will be divided among two separately deployed canisters at sites where vandalism is a concern. The SPMDs will be kept frozen until deployed.

On arrival at the sampling site, the cans will be pried open, spindles slid into the canisters, and the device anchored and tethered in the waterbody. 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. Field personnel will wear nitrile gloves and not touch the membranes. The latitude and longitude of each SPMD site will be recorded from a Magellan 320 GPS.

The SPMDs will be deployed for approximately 30 days, as recommended by USGS and EST. 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.

Temperature data are required to determine dissolved PBDE concentrations, and TOC data can be used to estimate total concentrations. An Onset StowAway Tidbit will be attached to each

canister to monitor temperature. At the beginning, middle, and end of each deployment period TOC and TSS samples and conductivity measurements will be taken at each SPMD site. These samples will be collected in appropriate containers (Table 5).

Table 5. Field Procedures for Ancillary Water Quality Parameters for 2005-2006 PBDE Study

Parameter	Min. Sample Size	Container	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4^oC	7 days
TOC	50 mL	125 mL poly bottle	HCl to pH<2, 4^oC	28 days

The SPMDs will be shipped with a chain-of-custody record to EST by overnight Federal Express, in coolers with blue ice or ice in poly bottles. The water samples will be returned to Ecology Headquarters and held in a secure cooler for later transport with chain-of-custody record to MEL.

Measurement Procedures

Preparation of Fish Tissue Samples

Preparation of tissue samples will follow the guidance in EPA (2000). Techniques to minimize potential for sample contamination will be used. People preparing the samples will wear non-talc nitrile gloves and work on heavy duty aluminum foil or a polyethylene cutting board. The gloves and foil will be changed between samples; the cutting board will be cleaned between samples as described below.

The fish will be thawed enough to remove the foil wrapper and rinsed with tap water, then deionized water to remove any adhering debris. The entire fillet from one side of each fish will be removed with stainless steel knives and homogenized in a Kitchen-Aid or Hobart commercial blender. The fillets will be scaled and analyzed skin-on, except skin-off for species where the skin is not eaten (e.g., catfish, sturgeon). Fish for whole-body samples will be similarly prepared and homogenized in a Hobart commercial blender. The sex of each fish will be recorded and hard structures saved for age determination (scales, otoliths, opercles, dorsal, and/or pectoral spines as appropriate for each species). Aging will be done by WDFW, Olympia.

Five individual fish will be used for each composite sample. To the extent possible, the length of the smallest fish in a composite will be no less than 75% of the length of the largest fish (EPA, 2000). The composites will be prepared using equal weights from each fish. The pooled tissues will be homogenized to uniform color and consistency, using a minimum of three passes through the blender. The homogenates will be placed in 8 oz. glass jars with Teflon lid liners, cleaned to EPA (1990) QA/QC specifications.

Cleaning of resecting instruments, cutting boards, and blender parts will be done by washing in tap water with Liquinox detergent, followed by sequential rinses with tap water, de-ionized water, and pesticide-grade acetone. The items will then be air dried on aluminum foil in a fume hood before use.

The tissue samples will be re-frozen for shipment with chain-of-custody record to the MEL. The samples will be stored frozen at MEL until analyzed. Excess sample will be stored frozen at Ecology Headquarters.

Chemical Analyses

Table 6 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. Other methods may by used by MEL after consulting with the project co-leads.

Table 6. Laboratory Procedures for 2005-2006 PBDE Study

Analysis	Sample Matrix	Number of Field Samples	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical Method
PBDEs*	Fish tissue	65† in 11/05	<1-1,000 ug/Kg	0.5 - 1 ug/Kg	EPA 3540**	EPA 8270**
Lipids	"	65† in 11/05	0.1 - 10%	0.1%	extraction	EPA 608.5
PBDEs*	SPMD extract	14†† in 10/05	1-100 ng	0.005 ng	dialysis/GPC***	EPA 8270
PCB-4,-29	"	8†† in 5/06	50 - 1,000 ng	50 ng	"	EPA 8082
TSS	Whole water	48	1 - 1,000 mg/L	1 mg/L	N/A	EPA 160.2
TOC	"	48	1-10 mg/L	1 mgL	N/A	EPA 415.1

* PBDE-47, 66, 71, 99, 100, 138, 153, 154, 183, 190, 209 and C13 PBDE-15 (PRC)

† 30 of these samples to be submitted by the WSTMP

**SOPs 730012 v.1.3 and 730096 v.1.0, respectively

††including field replicates and field blanks (see Quality Control)

***EST SOPs E14, E15, E19, E21, E33, E44, E48

PBDEs will be analyzed by gas chromatography/mass sectrometry in selective ion monitoring mode (GC/MS SIM). MEL is currently in the process of validating a new GC/MS system. As the new analytical parameters are developed, MEL will update SOP 730096 v.1.o referenced in Table 6 above.

Achieving low detection limits is important to the success of this study. MEL will conduct the chemical analyses in a manner consistent with the required reporting limits.

EST will extract the SPMDs (referred to as dialysis), perform gel permeation chromatography (GPC) cleanup on the extracts, and ship the ampulated extracts to MEL. The dialysis method used by EST is a patented procedure, described in Huckins et al. (2000). EST's 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 extract. The PRCs PCB-4 and PCB-29 will be quantified in the SPMD extracts through a separate GC/ECD analysis (see Field QC). C13 PBDE-15 will be quantified in the PBDE analysis.

Excess fish tissue and SPMD extracts will be saved by MEL for a period of 60 days after reporting the data to the project co-leads. **A turn-around time of 45 days is required for project samples collected in 2005 and 30 days for the SPMD extracts from 2006.**

The total cost of analyzing samples for this project is estimated at $31,088 (Table 7). Ten of the fish collection sites (30 samples) are being sampled as part of routine monitoring being done by the WSTMP. WSTMP will cover the $6,592 cost of analyzed PBDEs and lipids in these fish samples, leaving a net cost of approximately $24,496 for the PBDE study. These costs are based on MEL's 50% discounted price; true cost is 2X.

Table 7. Lab Cost Estimate*

Analysis	Number of Samples†	Cost per Sample	Cost Subtotals
Fish Tissue Samples			
PBDEs	72	175	12,600
Lipids	68	31	2,108
SPMD Samples (2005)			
Membrane prep/extract at EST	- -	- -	6,022
PBDEs	19	125	2,375
PCBs	16	50	800
TOC	30	10	300
TSS	30	10	300
SPMD Samples (2006)			
Membrane prep/extract at EST	- -	- -	3,923
PBDEs	14	125	1,750
PCBs	11	50	550
TOC	18	10	180
TSS	18	10	180
		Total =	$31,088
		32 fish samples (+MS/MSD) analyzed through WSTMP =	$6,592
		Net =	$24,496

*Manchester Laboratory costs are the 50% discounted prices

†Including Manchester MS/MSD and laboratory duplicates, and EST blanks

Quality Control

Field

The field QC samples to be analyzed for this project are shown in Table 8. All field QC samples will be submitted blind to the laboratory.

Table 8. Field Quality Control Samples for 2005-2006 PBDE Study

Sample Type	Analysis	Replicates	Field Blanks
Fish tissue	PBDEs	*	N/A
"	Lipids	*	N/A
SPMDs	PBDEs/PCBs	3	2
Water	TSS	none	N/A
"	TOC	none	N/A

*composite samples are being analyzed
N/A = not applicable

No field QC samples will be analyzed in conjunction with the fish sampling. Field variability is being addressed by analyzing composite samples. Field blanks are not applicable to fish sampling.

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, PCB-29, and C13 PBDE-15 will be used as PRCs for this project. These congeners are not present in significant amounts in the environment. The spiking level will be 0.2 ug of each congener per SPMD membrane. MEL will provide the PRC spiking solution to EST.

Field replicates will provide estimates of the total variability in the SPMD data (field + laboratory). Replicate SPMDs will be deployed at two sites during the 2005 deployment and one site during the 2006 deployment. The Spokane River, Duwamish River, and Queets River SPMDs will be replicated since these are likely to provide a range of concentration levels.

Because SPMDs sample vapors while being exposed to air, a field 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 samplers 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. 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.

Laboratory

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

Table 9. Laboratory Quality Control Samples for 2005-2006 PBDE Study

Matrix	Analysis	Check Stnds/ LCS	Method Blanks*	Surrogate Spikes	Analytical Duplicates	MS/MSD
Fish tissue	PBDEs	1/batch	2/batch	all samples	3/project	2/batch
"	Lipids	1/batch	2/batch	- -	- -	- -
SPMD extracts	PBDEs	1/batch	2/batch	all samples†	- -	2/batch†
"	PCB-4,-29	1/batch	2/batch	all samples†	- -	2/batch†
Whole water	TSS	1/batch	1/batch	- -	- -	- -
"	TOC	1/batch	1/batch	- -	- -	- -

*Manchester laboratory blanks; see discussion for additional blanks prepared by EST

†to be spiked at EST

EST will prepare the following method blanks for each SPMD deployment: 1) A spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples. 2) A day-zero SPMD blank to serve as a reference point for PRC loss. 3) Three dialysis blank-SPMDs from the same lot as the project batch, to represent background during dialysis and cleanup. Three dialysis blanks are being analyzed in response to caution from USGS about the potential for a significant PBDE background in these samples (Walt Cranor, USGS/CERC Columbia, MO, 6/1/2005 email). (4) A day-zero blank SPMD, prepared just prior to dialysis, to serve as a control. 5) A reagent blank to assess contamination independent of the SPMDs.

Only the extract from the day-zero and dialysis blanks will be analyzed by MEL. The remaining blanks will be saved frozen at MEL in the event that the day-zero or dialysis blank results indicate significant contamination or other problems needing further investigation. MEL will also analyze their own method blanks with each batch of samples.

Manchester Environmental Laboratory will follow their routine practice of adding surrogates to the fish samples prior to extraction. EST will add surrogate compounds to each SPMD sample prior to dialysis. This will provide an estimate of accuracy for the entire analytical procedure. The surrogate will be decachlorobiphenyl. The spiking level will be 40 ng; one membrane will be spiked for each sample. MEL will supply the surrogate spiking solution to EST.

Dibromooctafluorobiphenyl (DBOB) will be the internal standard in the PBDE analyses of fish and water samples. DBOB will be added to the final SPMD extract.

Manchester Environmental Laboratory will analyze one spiked blank with each batch of SPMDs. Results from these samples will be used to verify that analytical precision is in control and that the level of bias due to calibration is acceptable. The spiked blank will include PBDE-47, 66, 71, 99, 100, 138, 153, 154, 183, 190, and 209.

Matrix spikes may provide an indication of bias due to interference from components in the sample and an estimate of precision. MEL will do a matrix spike and matrix spike duplicate (MS/MSD) with each batch of fish tissue samples. The spike will include PBDE-47, 66, 71, 99, 100, 138, 153, 154, 183, 190, and 209. For each dialysis batch, EST will do a MS/MSD of field quality SPMDs using target compounds. The spiking level will be approximately 40 ng for each of the PBDEs and 200 ng of PCB-1260. MEL will supply the matrix spiking solution to EST.

The analytical precision associated with the fish tissue data will be assessed with duplicate (split) samples. Three tissue composites will be analyzed in duplicate for the project. These will be selected to represent a range of contaminant levels and submitted blind to the laboratory. The laboratories will re-mix all fish tissue samples by stirring prior to sub-sampling for analysis.

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 with 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 blanks, surrogate compounds, and check standards included in the sample batch, as well as results for analytical duplicates and matrix spikes.

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 Validation Review procedure where data is reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

Audits

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

Reports

A draft technical report will be prepared for review by the client and other interested parties. This report will be completed in May 2006. A final technical report is anticipated by June 2006. The responsible staff member is Art Johnson.

The project data will be entered into EIM on, or before, June 2006. The responsible staff member is Brandee Era-Miller.

Data Verification and Validation

Manchester Environmental Laboratory will conduct a review of all laboratory data and case narratives. MEL will verify that methods and protocols specified in the QA Project Plan were followed; that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and that 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, results for surrogate recoveries and estimates of precision and bias will be compared to QC limits. The MQOs correspond to the laboratory's QC limits for this project. 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 and validate the data. 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 final project report.

Data Quality (Usability) Assessment

Once the data have been verified and validated, 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.

Data from the present study and all available and appropriate PBDE data from the WSTMP and other sources will be used in the analysis and assessment of PBDE concentrations in Washington State freshwater fish. The fish tissue data will be examined for site and species differences using bar graphs, percentile plots, and analysis of variance (ANOVA). If a correlation is found between PBDE concentrations and lipid content, the data will be normalized to percent lipid and re-examined. Figures will be prepared that show the spatial distribution of PBDE concentrations in Washington Sate freshwater fish.

The fish tissue data will be further analyzed by preparing box and whisker plots comparing results by land-use categories. Cluster analysis will be used to identify site and species patterns in accumulation of specific PBDE congeners.

The PBDE residues accumulated in the SPMDs will be used in conjunction with the fish tissue data to rank waterbodies with respect to contamination level. Seasonality will be assessed by comparing SPMD results for the summer-fall 2005 and spring 2006 deployment periods.

Dissolved PBDE concentrations in the water will be estimated from published SPMD laboratory calibration data for similar compounds. PRC loss rates and temperature data will be used to adjust laboratory determined sampling rates for in-situ conditions. These procedures are described in Huckins et al. (2000, 2002), Booij et al. (2003) and elsewhere. Total PBDE concentrations will be estimated using the relationship with TOC developed by Meadows et al. (1998).

The dissolved data will be used to estimate BAFs for PBDEs in Washington freshwater fish. The total data will be used in conjunction with Ecology and USGS stream gauging data to obtain order-of-magnitude estimates of PBDE loading in the seven Washington rivers sampled in the present study.

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