Washington State Toxics Monitoring Program

Trends Monitoring for Chlorinated Pesticides, PCBs, and PBDEs in Washington Rivers and Lakes, 2007

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Cover photo: The Queets River (photo by Casey Deligeannis).

Washington State
Toxics Monitoring Program

Trends Monitoring for Chlorinated Pesticides, PCBs, and PBDEs in Washington Rivers and Lakes, 2007

by
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Statewide Coordination Section
Environmental Assessment Program
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Waterbody Numbers

Columbia River near Clatskanie	WA-CR-1010
Columbia River at McNary Dam	WA-CR-1026
Columbia River at Rock Island Dam	WA-CR-1040
Duwamish River	WA-09-1010
Lake Washington	WA-08-9340
Okanogan River	WA-49-1010
Queets River	WA-21-1030
Snohomish River	WA-07-1020
Spokane River	WA-54-1020
Walla Walla River	WA-32-1010
Wenatchee River	WA-45-1010
Yakima River	WA-37-1010

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Glossary, Acronyms, and Abbreviations

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

Bioaccumulate: Build up in the food chain.

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

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

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

Acronyms and Abbreviations

BHC	benzene hexachloride (alpha-, beta-, gamma (gamma- also known as Lindane)
CERC	Columbia Environmental Research Center (USGS)
CFS	cubic feet per second
CP	chlorinated pesticides
C_w	dissolved concentration
DDD	dichlorodiphenyldichloroethane (o,p' and p,p'; 2,4' and 4,4')
DDE	dichlorodiphenyldichloroethylene (o,p' and p,p'; 2,4' and 4,4')
DDMU	1-chloro-2, 2-bis (p-chlorophenyl) ethane (a breakdown product of DDE)
DDT	dichlorodiphenyltrichloroethane (o,p' and p,p'; 2,4' and 4,4')
DOC	dissolved organic carbon
EAF	exposure adjustment factor
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
EST	Environmental Sampling Technologies
GC-ECD	gas chromatography – electron capture detection
GC-MS	gas chromatography – mass spectrometry
GPS	Global Positioning System
HCB	hexachlorobenzene

K_{oc}	carbon-water partition coefficient
K_{ow}	octanol-water partition coefficient
MQO	measurement quality objectives
M_w	mass of water
ng/L	nanograms per liter (parts per trillion)
NTR	National Toxics Rule
PACE	PACE Analytical Laboratories
PBDE	polybrominated diphenylether
PBT	persistent bioaccumulative toxic
PAH	polycyclic aromatic hydrocarbon
PCA	pentachloroanisole
PCB	polychlorinated biphenyl
PCDD/Fs	polychlorinated dibenzo-p-dioxins and -furans
pg/L	picograms per liter (parts per quadrillion)
PRC	permeability/performance reference compounds
RM	river mile
RPD	relative percent difference
SPMD	semipermeable membrane device
T-DDT	Total DDT (sum of detected o,p’ and p,p’ isomers of DDT+DDE+DDD)
T-PBDE	Total PBDEs (sum of detected congeners)
T-PCBs	Total PCBs (sum of detected congeners)
TCDD	tetrachlorodibenzo-p-dioxin (most toxic of PCDD/Fs)
TMDL	Total Maximum Daily Load (cleanup plan)
TOC	total organic carbon
TSS	total suspended solids
ug/L	micrograms per liter (parts per billion)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WSTMP	Washington State Toxics Monitoring Program

Abstract

The Washington State Department of Ecology began implementing a trend monitoring program for persistent, bioaccumulative, toxic (PBT) chemicals in the spring of 2007. Semipermeable membrane devices (passive samplers) were deployed at 12 sites statewide for a one-month period during spring high-flow conditions and fall low-flow conditions. Sample sites represented a range of land use types including urban, agricultural, and mixed use, subject to present and historical contamination. Target analytes included chlorinated pesticides (CPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether flame retardants (PBDEs).

The PBT Trends Study is one component of the Washington State Toxics Monitoring Program. This report presents the results for 2007, the first year of monitoring.

Many chemicals were detected at high frequencies. PCBs were found in 100% of the samples. DDT and its metabolites, dieldrin, and endosulfan and its metabolites were found in over half of the samples. PBDEs were detected in 96% of the samples, primarily as penta-BDE (BDE-47, -99, -100). Pentachloroanisole (PCA) was found in 74% of the samples.

The widest varieties of chemicals were detected in the Walla Walla and Yakima Rivers. These rivers had higher concentrations of DDT compounds, dieldrin, toxaphene, chlorpyrifos, and endosulfan than most of the other sites sampled. The highest concentration of PCBs and PBDEs were found in the Spokane River.

Several samples did not meet (exceeded) one or more Washington State or EPA water quality criteria for the protection of human health or aquatic life. These were toxaphene in the Walla Walla River, dieldrin in the Yakima River, and PCBs in the Lower Columbia, Duwamish, and Spokane Rivers.

Recommendations include:

- Develop more rigorous quality-control procedures to improve the ability to detect temporal and spatial trends.
- Develop a standardized data management system.
- Incorporate additional PBTs, such as polycyclic aromatic hydrocarbons (PAHs), into the monitoring program.
- Conduct exploratory sampling to identify other waterbodies appropriate for trend monitoring.

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    - Upper Columbia River site at Rock Island Dam access: Randy Browley, Mike Simpson, Kirby Reinhardt, Kelly Hampton, and other officials.
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Introduction

The Washington State Department of Ecology (Ecology) initiated a persistent bioaccumulative toxic (PBT) reduction strategy for reducing toxic threats in 2000. Ecology identified and listed 27 substances at that time (Table 1). These chemicals degrade very slowly, tend to build up in animal tissues, and can have adverse health effects on humans, fish, and wildlife. Information about Ecology's PBT initiative can be found at www.ecy.wa.gov/programs/swfa/pbt/. These chemicals are targeted for cleanup, reduction, and elimination where possible.

Table 1. PBT Trends Monitoring Chemicals of Interest in 2007, taken from Ecology's PBT List (Ecology 2007).

Metals	**Flame Retardants**	**Banned Pesticides**	**Organic Chemicals**
Methy-Mercury	PBDEs Tetrabromobisphenol A Hexabromocyclododecane Pentachlorobenzene	Aldrin/Dieldrin Chlordane DDT/DDD/DDE Heptachlor Epoxide Toxaphene Chlordecone Endrin Mirex	1,2,4,5-TCB Perfluoro-octane Sulfonates Hexachlorobenzene Hexachlorobutadiene Short-chain chlor paraffin Polychlrned Naphthalenes
Combustion By Products	**Banned Flame Retardants**	**Banned Organic Chemicals**	**Metals of Concern**
PAHs PCDD PCD PBDD/PBDF	Hexabromobiphenyl	PCBs	Cadmium Lead

Ecology's Washington State Toxics Monitoring Program (WSTMP) was developed to investigate the occurrences and concentrations of toxic chemicals in the state's waterbodies. Developing a trend monitoring component for contaminants is a long-term objective of the program. A project plan was developed for a PBT Trends Study (Johnson 2007), and sampling began in 2007. Target analytes include chlorinated pesticides (CP), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) (Table 1).

The WSTMP has also initiated long-term studies for assessing mercury trends in fish and sediment in 2005 and 2006, respectively. Information about WSTMP can be found at www.ecy.wa.gov/programs/eap/toxics/wstmp.htm.

Monitoring for this PBT Trends Study began in 2007 and involved sampling two times a year at 12 sites: 11 major rivers and 1 lake. The sites were selected throughout the state for monitoring contaminants in waterbodies that have chemicals of concern. Standardized passive samplers were used to concentrate and quantify these chemicals over time, approximately one month. Passive samplers reduce the variability associated with conventional water samples and biological samples.

Contaminants Assessed

Brief descriptions of contaminants included in this monitoring program are presented below.

Chlorinated Pesticides

Chlorinated pesticides (CPs) include a number of legacy insecticides that do not degrade or metabolize easily, making them extremely persistent in the environment. They have low solubility in water but a strong affinity for lipids (fats), therefore accumulating to high concentrations in fatty tissue through the food chain (EPA 2000).

Many CPs are neurotoxins and may cause cancer (EPA 2000). Most were banned from use in the United States during the 1970s and 1980s as their hazards became evident (e.g., DDT). Other CPs currently used in agriculture appear to be less persistent in the environment. However, EPA recommends monitoring some of these because of their toxicity and potential to build up in tissue (e.g., chlorpyrifos and endosulfan).

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are chemically and physically stable synthetic organic compounds having excellent insulating properties. Hence, transformers and other electrical equipment, inks, paint, plastics, pesticide extenders, and a variety of other applications used PCBs. Manufacturing of PCBs in the United States ended in 1979 due to their toxicity and persistence in the environment.

PCBs have low solubility in water yet have a high affinity for sediments and animal fats allowing them to readily build up in the aquatic food chain (EPA 1999). Health effects from PCBs include toxicity to the nervous, endocrine, digestive, and immune reproductive systems. EPA currently classifies PCBs as a probable human carcinogen based on sufficient evidence in animal studies and inadequate, but suggestive, evidence in humans (IRIS 2009).

Individual PCB compounds, called congeners, differ from one another in the number and relative positions of chlorine atoms that they contain (1 to 10) (ATSDR 2000). Up to 209 different compounds are possible. Commercial PCB congener mixtures were known in the United States by the trade name Aroclor. Historically, many studies analyzed for PCB Aroclor mixtures, but increasingly more studies, including the present effort, are analyzing all the individual congeners for a more thorough assessment of toxicity potential. The term “T-PCBs” refers to the sum of individual congeners or Aroclors.

Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers (PBDEs) are a group of brominated organic compounds added as a flame-retardant to a variety of plastic and foam products such as electronic enclosures, wire insulation, adhesives, textile coatings, foam cushions, and carpet padding. Individual PBDE congeners differ by the number and position of bromine atoms (1 to 10) creating as many as 209 individual congener possibilities (ATSDR 2004). PBDEs are often categorized by the number of bromine atoms attached to the biphenyl rings: mono- through decabromo-congeners can exist.

Penta-BDE, Octa-BDE, and Deca-BDE are the three main types of PBDEs in consumer products worldwide, with North America having the highest volume of production (Ecology and WDOH 2006; ATSDR 2004). Commercial PBDE products are mixtures. The mixtures are named after the primary PBDE component. In this study, PBDE results refer to the individual compound and not the commercial mixtures.

PBDEs are ubiquitous in the environment, and concentrations in humans and wildlife are increasing throughout the world. The lower bromated congeners associated with the Penta formulation (e.g., PBDE-47, 99, 100, 153) are the most bioaccumulative and make up the brunt of the levels found in animals and humans. The highest levels of PBDEs in human tissue have been found in the U.S. and Canada (Ecology and WDOH 2006). PBDE-209 (Deca-BDE) is the most prevalent congener found in sediment and indoor dust. Deca-BDE can debrominate to lower congeners, but its contribution to the levels found in animals and humans is unclear.

Animal studies show that PBDEs can affect the thyroid, liver, immune system, nervous system, and endocrine system (Ecology and WDOH 2006; ATSDR 2004). EPA found available information inadequate to assess the carcinogenic potential of PBDE-47, 99 and 153 but found “suggestive” evidence regarding the potential for Deca-BDE to cause cancer in humans.

Monitoring Design

Monitoring Sites

Criteria for selecting monitoring sites included:

- Levels and types of contaminants reported in fish.
- 303(d) listings and Total Maximum Daily Load (TMDL) status[1].
- Potential for water quality improvement.
- Fish consumption advisories.
- Statewide distribution of the monitoring effort.
- Availability of a secure sampling site.

Figure 1 shows locations of the 12 sampling sites for this 2007 study.

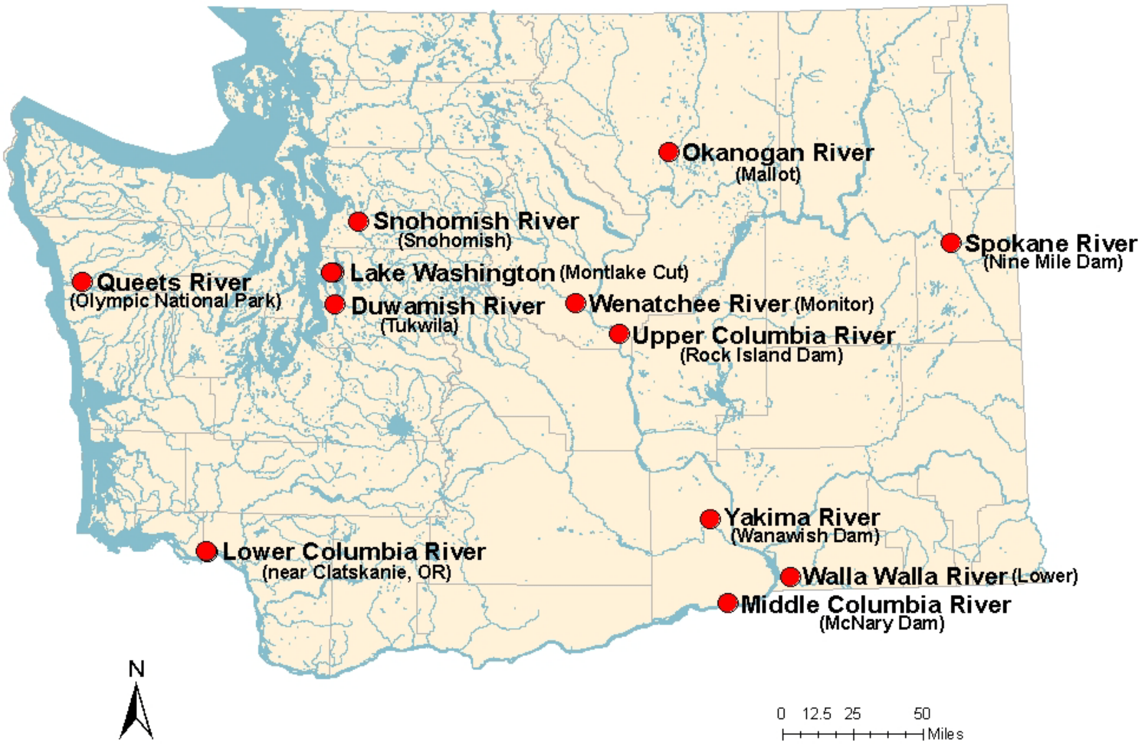

Figure 1. PBT Trends Monitoring Sites in 2007.

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[1] The 303(d) listings are federal Clean Water Act required listings. TMDLs are cleanup plans for impaired waters.

Eight monitoring sites were in the Columbia River drainage, three sites were in the Puget Sound basin, and a reference site was in the Olympic National Park. Because of the size of the Columbia River mainstem and the many PBT sources discharging into it, three monitoring sites were chosen to integrate the effects of upstream sources. Descriptions of the monitoring sites and a brief discussion of the chemicals of concern are in Appendix A.

Passive Sampling

A passive sampling technique using semipermeable membrane devices (SPMDs) was used to provide time-weighted average concentrations for the chemicals of interest. SPMDs were designed to mimic the bioconcentration (uptake) of organic pollutants from water by aquatic organisms without the variability introduced by movements, growth, and spawning of fish.

The amount of chemical absorbed by a SPMD is proportional to the local water column concentration. Variances from random and other short-term changes in water quality inherent with conventional sampling techniques are reduced. SPMDs concentrate chemicals to higher levels than in bottom sediment or suspended particulates. Trends in contaminant levels at a particular site can be assessed with SPMDs by directly comparing absorbed amounts over the monitoring period or by estimating water column concentrations. Detailed discussion on SPMDs can be found in Appendix B and C.

Sample Timing and Procedures

The SPMDs were deployed for approximately 28 days, from April 30 – June 4 (spring) and August 27 – September 2 (fall). Deployments during these periods captured typical seasonal high-flow (spring) and low-flow (fall) conditions for the rivers (Figure 2). For Lake Washington, these sampling events capture the higher water level (pre-stratification beginning in April) and the lower water level (strong stratification in the fall) (King County 2003). Studies in Washington have shown that peak levels of the target chemicals tend to occur during these periods (Johnson et al. 2004; 2005).

One sample per site per monitoring period was placed in a well-mixed location and away from known sources of the chemicals of interest. For deepwater sites, the SPMDs were positioned in the top 20 feet of the water column, above the summer thermocline. For shallow water, the SPMDs were placed approximately one foot above the bottom.

During each monitoring period, a replicate sampler was deployed in the Spokane River to assess variability in the field samples. A field trip blank was exposed during deployment and retrieval at the Queets River reference site to assess background air contamination during the spring and fall sampling events.

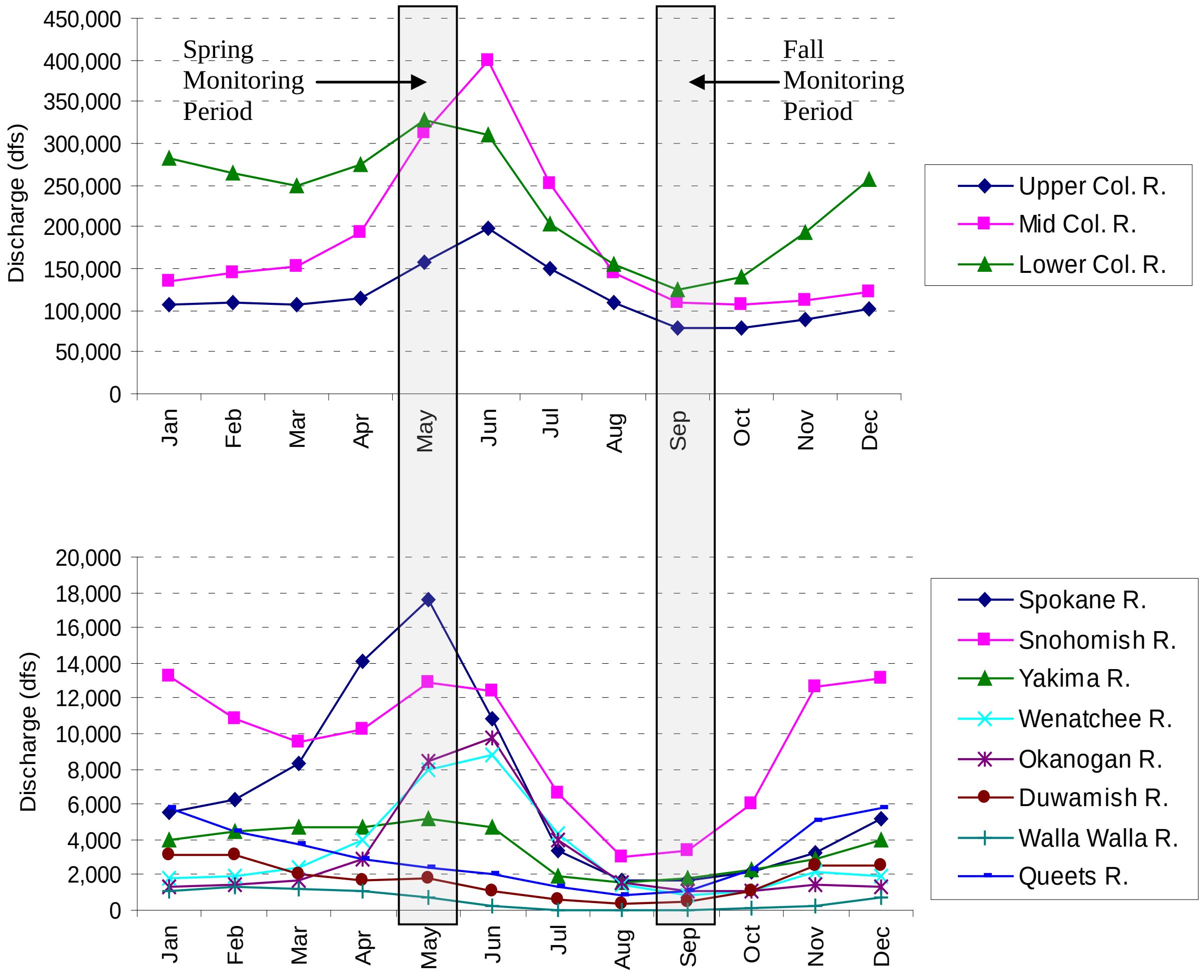


Figure 2. Annual Streamflow Pattern for the 11 River Monitoring Sites Showing Periods When SPMDs Were Deployed (http://waterdata.usgs.gov/wa/nwis/sw).

Chemical Analyses

Chemicals analyzed at each site included over 30 chlorinated pesticides or breakdown products, 209 PCB congeners, and 13 PBDE congeners. A complete list of target analytes is in Appendix D.

Temperature was monitored continuously during deployment. Total suspended solids (TSS) and total organic carbon (TOC) were determined at the beginning, middle, and end of each sampling period at each site. Conductivity was measured in the Duwamish and Snohomish Rivers to assess the influence of marine water at those locations.

Methods

Field Procedures

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

EST spiked each membrane with performance reference compounds (PRCs) consisting of 200 ng each of PCB-004, PCB-029, and PCB-050 prepared by PACE Laboratories. The SPMDs were preloaded onto the carriers by EST in a clean room and shipped frozen in solvent-rinsed metal cans filled with argon gas. One 30 cm x 16 cm stainless-steel sampling canister with five SPMD membranes was used per sampling site (Figure 3)

Figure 3. SPMDs Mounted on Carriers Inside a 5-membrane Canister. Shipping Cans in Background.

The cans with SPMDs were transported to the field on bottled ice. Upon arriving at the sampling site, an anchoring and tethering system was constructed for securing the SPMD canisters. The cans were pried open, carriers slid into the canister, and the device was secured in the water as quickly as possible to avoid air contamination. Field personnel wore nitrile gloves and avoided touching the membranes.

The SPMDs were deployed for approximately 28 days. All SPMDs were retrieved or accounted for during the 2007 spring and fall sampling events. SPMDs were checked for presence midway (two weeks) during the deployment. During the midcheck, the SPMDs were gently swished under water to remove loose sedimentation or biofouling. Retrieval procedure was essentially the reverse of deployment. The cans holding the SPMDs were sealed and kept at or near freezing for shipping to EST for extraction. Chain-of-custody procedures were maintained.

Onset StowAway® TidbiTs™ were used to monitor water and air temperatures to determine if SPMDs remained submerged during deployment. One TidbiT™ was attached to each SPMD canister and another TidbiT™ secured out of the water near the site. Data from TidbiTs™ showed that all samples remained submerged during deployment.

Grab samples for TOC, TSS, and salinity were collected at the beginning, middle, and end of each deployment sampling period (Table 2). These were preserved, cooled on ice, and shipped within the holding time to Ecology's Manchester Environmental Laboratory with a chain-of-custody record.

Salinity was collected for the estuarine rivers of Duwamish and Snohomish. Water temperature and conductivity were measured during each collection using a temperature/conductivity probe (Hanna DIST 5 pH/EC/TDS meter) or a water thermometer and Beckman conductivity meter. Flow data were obtained through Ecology's Environmental Assessment Program Stream Hydrology Unit, USGS, and other sources.

Latitude and longitude of each sampling location was determined from a hand-held GPS receiver (Garmin or Magellan) and checked using ESRI®ArcMap™ 9.2 (Appendix A).

Table 2. Field Procedures for Ancillary Water Quality Parameters.

Parameter	Minimum Sample Size	Container	Preservation	Holding Time
TSS	1000 mL	1 L poly bottle	Cool to 4ºC	7 days
TOC	50 mL	123 mL poly bottle	HCL to pH<2, 4ºC	28 days
Salinity	300 mL	500 mL poly bottle	Cool to 4ºC	28 days

Laboratory Procedures

Analysis

After retrieval from the field, the SPMD membranes required additional preparation and extraction (described below) by EST before further analysis by other laboratories. Manchester Environmental Laboratory analyzed pesticides and PBDEs from the cleaned-up extracts. Conventional water quality samples were also analyzed by Manchester. PCB congeners were analyzed by PACE Analytical Laboratories, a contractor. The methods used are shown in Table 3.

Table 3. Laboratory Procedures.

Analysis	Sample Matrix	Sample Preparation Method	Analytical Method
Chlorinated pesticides	SPMD extract	dialysis/GPC*	EPA 3620, 3665, 8081**
PCB congeners	SPMD extract	dialysis/GPC*	EPA 1668A
PBDEs	SPMD extract	dialysis/GPC*	EPA 8270***
TSS	whole water	N/A	EPA 160.2
TOC	whole water	N/A	EPA 415.1
Salinity	whole water	N/A	SM2520

*EST SOPs E14, E15, E19, E21, E32, E33, E44.
**Modifications of EPA SW-846.
***GC/MS SIM.

Extraction and Cleanup

Upon receiving the SPMDs, EST inspected and cleaned all membranes. Each of membranes was then spiked with surrogate compounds. These surrogates were 50 ng of each of PCB-014, PCB-078, and PCB-186 provided by PACE; as well as 80 ng of Manchester's combined pesticide and PBDE surrogates. Surrogates were added prior to extraction (referred to as dialysis). Recovery of the surrogates provides estimates of recovery of target compounds in each sample.

Once dialyzed, the extracts were combined into single sample and solvent exchanged to methylene chloride for gel permeation chromatography (GPC) cleanup. After GPC, the samples were solvent exchanged into hexane, split 50:50, and each fraction sealed in a 5-mL ampoule for transport to the laboratories. One ampoule was sent to Manchester. The other ampoule was sent by Manchester to PACE. Specified extraction and cleanup analytical methods are documented in standard operating procedures (SOPs) on file at Ecology Headquarters.

The Manchester ampoule was further split 50:50 for pesticide and PBDE analysis, resulting in 25% fraction for each. The PBDE extract fraction was solvent exchanged into iso-octane prior to analysis. The pesticide fraction was concentrated and then eluted through a macro Florisil® column. Following a solvent exchange concentration, the extracts were split and one portion was treated with concentrated sulfuric acid to remove interferences. Both portions were analyzed by dual column GC-ECD.

Half the original extract was sent to PACE for PCB analyses. Each extract was brought to a fixed volume and processed through a silica column (acidic, basic, and neutral) for cleanup. They were then concentrated, spiked with recovery standards, and analyzed.

Results were corrected for all dilutions and reported as 100% of extract (ng/sample). Because samples are composites of five SPMD membranes, residue results are discussed as ng/sample of five SPMDs unless otherwise noted.

Data Quality

Laboratory Case Narratives

Manchester Laboratory prepared written case narratives assessing the quality of the data collected during the 2007 spring and fall sampling events. These reviews include a description of analytical methods, assessment of holding times, calibration and verification and degradation checks, on-going precision and recovery assessments, method blanks, matrix spike/matrix spike duplicates (MS/MSD) recoveries, qualitative identification, laboratory control samples, surrogate recoveries, laboratory replicates, and internal standards checks. Case narratives are available from the author on request.

Most laboratory results for pesticides, PCBs, PBDEs, and conventional parameters met measurement quality objectives (MQO) requirements of this study (Johnson 2007). Exceptions were qualified as estimates. Appendix E summarizes data quality as described in the case narratives.

Field Quality Control Samples

Field Trip and Day0-Dialysis Blanks

Two types of blank samples were used to assess contamination during each sampling period: a field trip blank and a Day0-Dialysis blank. The field trip blank was used to determine contamination from air during deployment and retrieval. The Day0-Dialysis blank helped assess contamination during the creation and processing of SPMD membranes at the EST Laboratory.

The field trip blank consisted of five membranes manufactured at the same time. These blanks were taken to the field and exposed to the air for the average amount of time that the samples were exposed to air during deployment and retrieval. The field trip blank was returned to its can and held frozen until processed with the samples. The Day0-Dialysis blank contained five membranes manufactured at the same time as the samples but held frozen at EST during the sampling period and then processed with the samples at the end of the sampling period.

Gamma-BHC (Lindane) and certain PCB and PBDE congeners were detected in both the field and Day0-Dialysis blanks at almost identical levels, indicating laboratory contamination. Concentrations in the blanks were greater than 10% of the sample concentrations and often more than 50% above the samples. Therefore, field trip blank concentrations were subtracted from all the measured results in the field samples before calculating water column concentrations. The results of the field trip blank and the Day 0-Dialysis blank analysis are included in Appendix F.

Replicate Samples

A second SPMD assembly was deployed in the Spokane River for each sampling event (spring and fall) to provide an estimate of the total variability (field + laboratory) associated with the SPMD data. Results from the spring field replicate were unusable due to a laboratory accident. Results from the fall replicate are listed in Appendix G.

The pesticide, PCB, and PBDE residues in the replicates generally agreed within 20% relative percent difference (RPD)). RPDs for chlordane, technical chlordane, and T-PCBs were slightly higher (27%, 24%, and 29% respectively). Dissolved water column concentrations calculated from the residue data agreed with 30% RPD, except for 48% for T-PCBs. Precision of PRC recovery in the replicates was good (<12% RPD).

Concentration Estimation Methods

Dissolved Water Concentrations

SPMDs absorb the dissolved fraction of a chemical. Dissolved concentrations for the chemicals of interest were estimated using the SPMD residue data and the most current USGS Estimated Water Concentration Calculator Spreadsheet. This spreadsheet, updated November 18, 2007, was taken from the USGS website for Columbia Environmental Research Center (CERC) Integrative Passive Samplers (USGS, 2008). The data collected on chemical residues, exposure time, and PRC recovery were entered into the spreadsheet for the available analytes. These data are listed in Appendices F, H, and I. Appendix B describes SPMDs and the use of PRCs.

Prior to calculating water concentrations, data qualifiers were considered and field trip blank results were subtracted. The detection limit was used to calculate a “less-than” value for water column concentrations where a compound was not detected. For the tables and figures in this report, the qualifiers have been omitted for the sake of clarity, but the qualifiers are retained in the data appendices.

Several analytes are reported as summed values of detected compounds. T-DDT is the sum of o,p’- and p,p’- isomers of DDD, DDE, and DDT. T-chlordane is the sum of *cis* and *trans* chlordane, *cis* and *trans* nonachlor, and oxychlordane. Endosulfan is the sum of alpha (endosulfan I) and beta endosulfan (endosulfan II). Non-detect results were treated as zero when summing compounds for T-DDT, T-PCBs, total chlordane, and T-PBDEs.

Total Water Concentrations

Total water column concentrations were estimated from the dissolved concentrations using the equation from Meadows et al. (1998):

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

where:

- C_w is the dissolved concentration.
- TOC is total organic carbon.
- K_{oc} is the organic carbon-water equilibrium partition coefficient.
- Mw is the mass of water (1g/mL).

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

Results and Discussion

Flow Conditions

Flows at all 11 river sites were fairly typical when compared to historical flow data. Most sites were around the historical long-term monthly mean flow except for sites in eastern Washington. Flows at east-side locations were approximately 35% below average in the fall due to the low snow pack and the lack of precipitation in the mountains bordering Washington and Idaho that feed these systems. The Spokane and Walla Walla Rivers in particular were affected by reduced snow pack resulting in below average flows for both spring and fall. Flow data are provided in Appendix J.

General Chemistry

Ancillary water quality data for TSS, TOC, salinity, and conductivity are listed in Appendix K. Average TSS was generally higher in the spring than the fall ranging from 3-39 mg/L and 1-10 mg/L, respectively. Average TOC reflected the same high and low-flow conditions ranging from 1.0 – 4.8 mg/L (spring) and 1.0 – 3.0 mg/L (fall).

Exceptions included the Duwamish and Snohomish Rivers where the fall TSS and TOC results were slightly higher than the spring results. Both these sites are located upstream of the estuarine confluence with Puget Sound and are tidally influenced. Salinity was not detected at the Duwamish and Snohomish Rivers, indicating they were not influenced by marine water.

Dissolved PBT Concentrations

Table 4 shows summary statistics for the dissolved pesticide, PCB, and PBDE concentrations estimated from SPMDs deployed in the spring and fall of 2007. The concentrations are in picograms per liter (parts per quadrillion) and are considered estimations. Chemicals not detected were heptachlor, alpha-Benzenehexachloride (a-BHC), beta-Benzenehexachloride (b-BHC), delta-Benzenehexachloride (d-BHC), aldrin, endrin, endrin ketone, endrin aldehyde, mirex, and methoxychlor.

The complete data are in Appendix F (residue data) and L (dissolved data). The dissolved data are also available through the Ecology Environmental Information Management System (EIM) in searchable databases at www.ecy.wa.gov/.

Table 4. Summary Statistics (estimated dissolved, pg/L) for PBT Trends in 2007.
(< = detection limit for nondetects.)

Parameter	No. of Detections	Detection Frequency	Min	Max	Median	Mean	Standard Deviation	90th %
p,p'-DDT	12	52%	3.0	21	5.8	8.1	5.3	17
p,p'-DDE	14	61%	<4.4	161	33	37	40	75
p,p'-DDD	14	61%	2.4	155	14	20	31	30
o,p'-DDT	1	4%	<2.8	8.3	5.1	5.2	1.4	6.8
o,p'-DDE	1	4%	<2.8	<8.2	5.2	5.3	1.3	<6.8
o,p'-DDD	7	30%	<3.6	42	5.6	7.9	7.9	11
Total DDT[1]	15	65%	4.4	340	60	65	78	110
DDMU[2]	7	30%	<4.6	33	8.2	9.6	5.9	13
Dieldrin	13	57%	<9.8	71	13	20	16	39
Chlorpyrifos	7	30%	<20	3800	21	280	810	610
Endosulfan I	13	57%	<220	2660	310	590	620	1100
Endosulfan-II	4	17%	<460	1200	460	590	220	920
Endosulfan Sulfate	5	22%	<320	2700	320	480	500	720
Hexachlorobenzene (HCB)	14	61%	<3.6	34	6.6	9.0	7.9	16
Pentachloroanisole (PCA)	17	74%	<3.7	31	10	13	8.2	26
Toxaphene	5	22%	<81	1150	90	160	230	190
Total Chlordane[3]	6	26%	<3.2	23	6.1	7.8	4.4	13
Dacthal	1	4%	<18	30	19	20	2.6	20
Heptachlor Epoxide	2	9%	<11	19	12	13	1.8	14
Lindane	1	4%	<68	755	68	100	150	70
Total PCBs	23	100%	6.2	99	38	40	25	70
PBDE-47	22	96%	0.6	101	10	18	21	22
PBDE-49	3	13%	<1.0	5.3	2.3	2.6	1.0	3.6
PBDE-66	2	9%	<1.0	<3.7	2.3	2.3	0.7	<3.1
PBDE-99	19	83%	0.1	54	9.2	13	12	23
PBDE-100	20	87%	0.3	12	2.2	2.9	2.4	4.1
PBDE-138	1	4%	<4.0	<16	9.5	9.7	3.1	<13
PBDE-153	7	30%	0.1	<9.3	4.7	4.6	3.1	<7.6
PBDE-154	10	43%	0.4	<11	5.1	5.0	3.3	<8.8
PBDE-183	7	30%	1.0	<14	8.4	7.5	4.2	<11
PBDE-184	1	4%	<6.7	<28	16	17	5.4	<23
Total PBDEs	22	96%	0.9	180	21	35	40	62

1-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT. DDD = p,p'- dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.

2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.

3-Total Chlordane is the sum of cis- and trans- chlordane, dis- and trans- nonachlor, and oxychlordane.

A total of 23 samples were analyzed.

PCBs were detected in all samples. T-PCBs ranged from 6.2 to 99 pg/L with an average of approximately 40 pg/L.

DDT or its breakdown products were detected in 65% of the samples. DDE and DDD were detected in 61% of the samples, whereas the parent compound DDT was detected in 52%. Dieldrin was detected in 57% of the samples. Endosulfan and its metabolite were found in over 50% of the samples. These same pesticides were among the most frequently detected in SPMDs in a national study by USGS (Gilliom et al. 2006).

Pentachloroanisole (PCA), a microbial breakdown product of the wood preservative pentachlorophenol, was found in all of the spring samples and over 50% of the fall samples for a total of 74% of the samples. USGS found PCA to be the most frequently detected compound (71% detection frequency) in streams sampled in six U.S. metropolitan areas using SPMDs (Bryant et al. 2007).

PBDEs were detected in 96% of the samples. Penta-BDEs were most frequently detected: PBDE-47, -99, -100 had detection frequencies of 96%, 83%, and 87% respectively. This is consistent with other studies showing the distribution of commercial PBDEs and its breakdown products (Ecology and WDOH 2006, Johnson et al. 2006, and Hale et al. 2003). Most PBDE congeners were detected below or near the reporting limit, except for PBDE-47 and -99. PBDE-191, and -209 were not detected. These highly brominated PBDEs are large molecules and strongly associated with particulate. They are not likely to be detected using SPMDs due to the small pore size of the membranes.

Spatial Patterns

Figure 4 shows the number of different chemicals detected at least once at each site during 2007. There were 48 chemicals analyzed.

In Figure 4 and for the remainder of this report, the Spokane River fall results are reported as the average of two replicate samples unless otherwise stated.

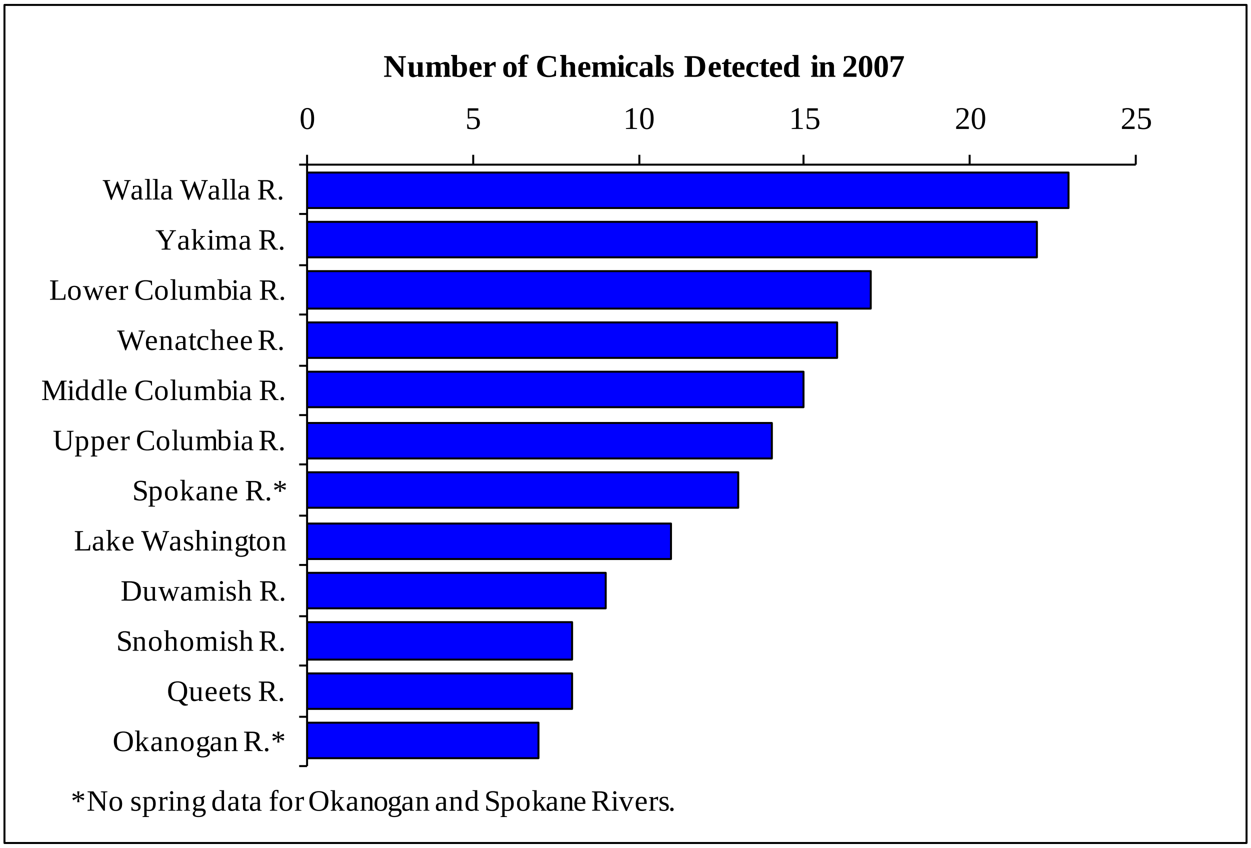


Figure 4. Number of Chemicals Detected During PBT Trends Monitoring, 2007.

The Walla Walla and Yakima Rivers had the greatest number of chemicals detected (23 and 22 respectively), followed by the Columbia and Wenatchee Rivers (17 and 16, respectively). The fewest chemicals were detected in the Snohomish, Queets, and Okanogan Rivers. The Spokane and Okanogan Rivers would most likely have had more detected chemicals if spring results were available.

Figure 5-12 compare estimated concentrations for T-DDT, T-PCBs, T-PBDEs, dieldrin, endosulfan, toxaphene, chlorpyrifos, and pentachloroanisole by location. Concentrations from spring and fall were averaged. Reporting limits were used for nondetections. Sites were ordered by highest to lowest concentrations for each chemical.

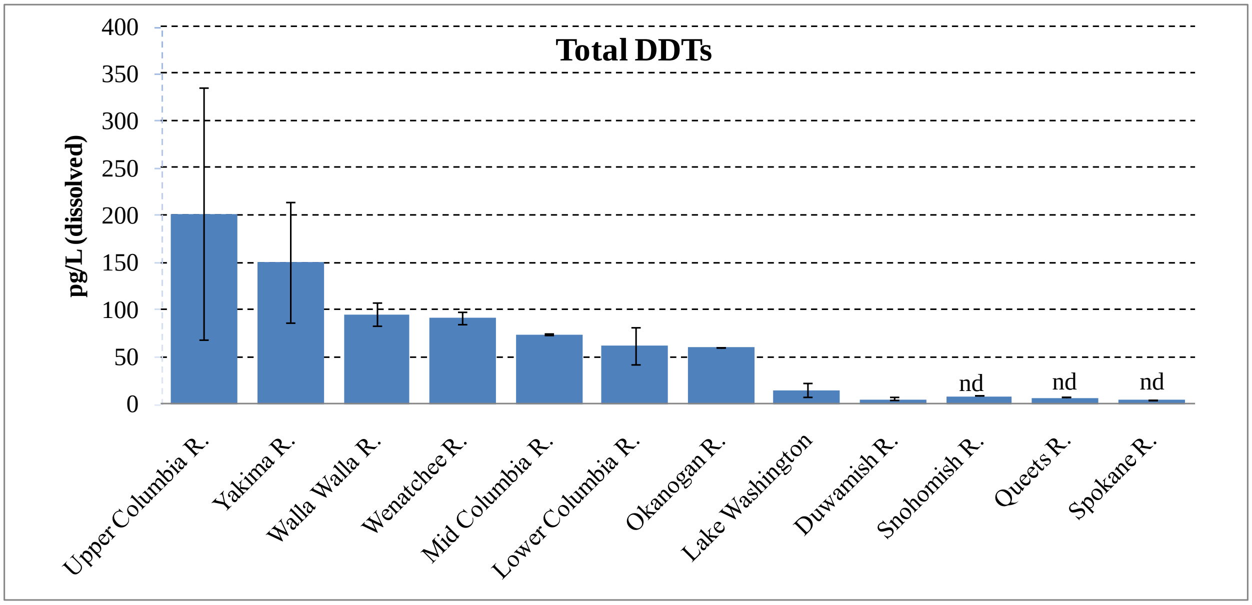


Figure 5. Average Estimated Concentrations of Total DDTs, 2007.
(nd = not detected; bars show maximum and minimum).

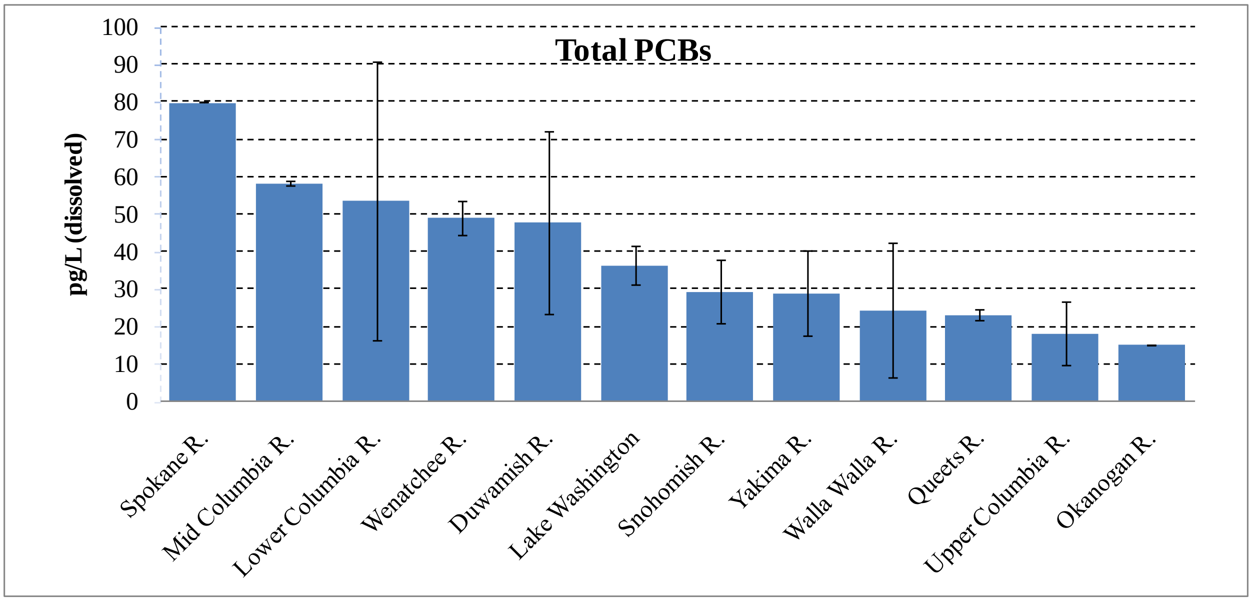


Figure 6. Average Estimated Concentrations of Total PCBs, 2007.
(nd = not detected; bars show maximum and minimum).

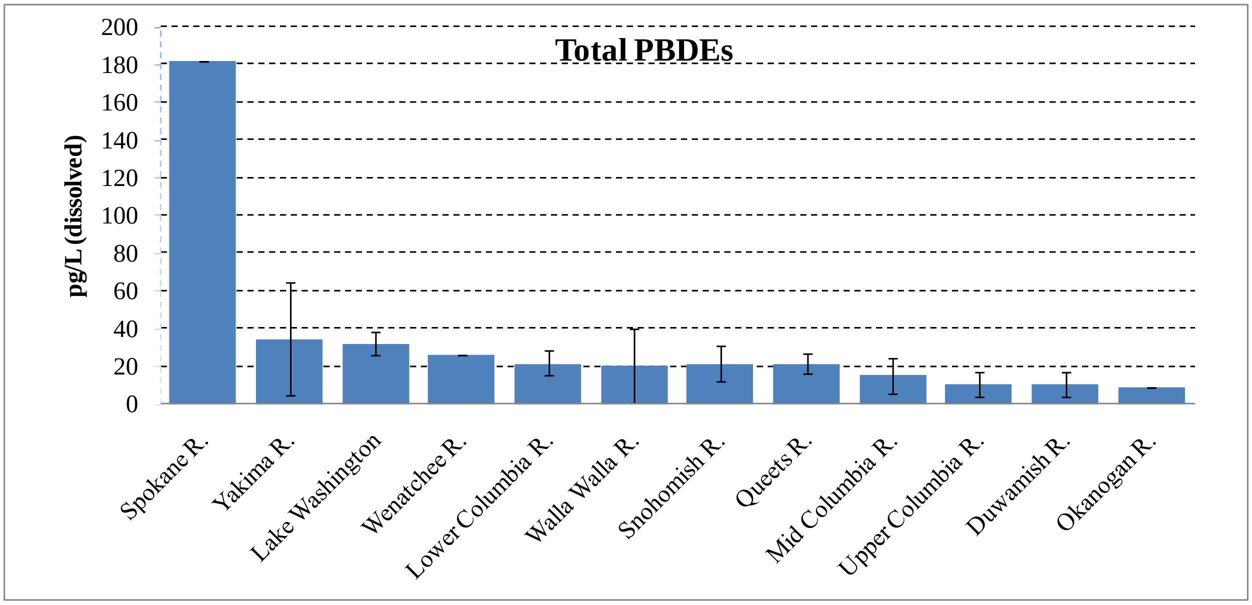


Figure 7. Average Estimated Concentrations of Total PBDEs, 2007.
(nd = not detected; bars show maximum and minimum).

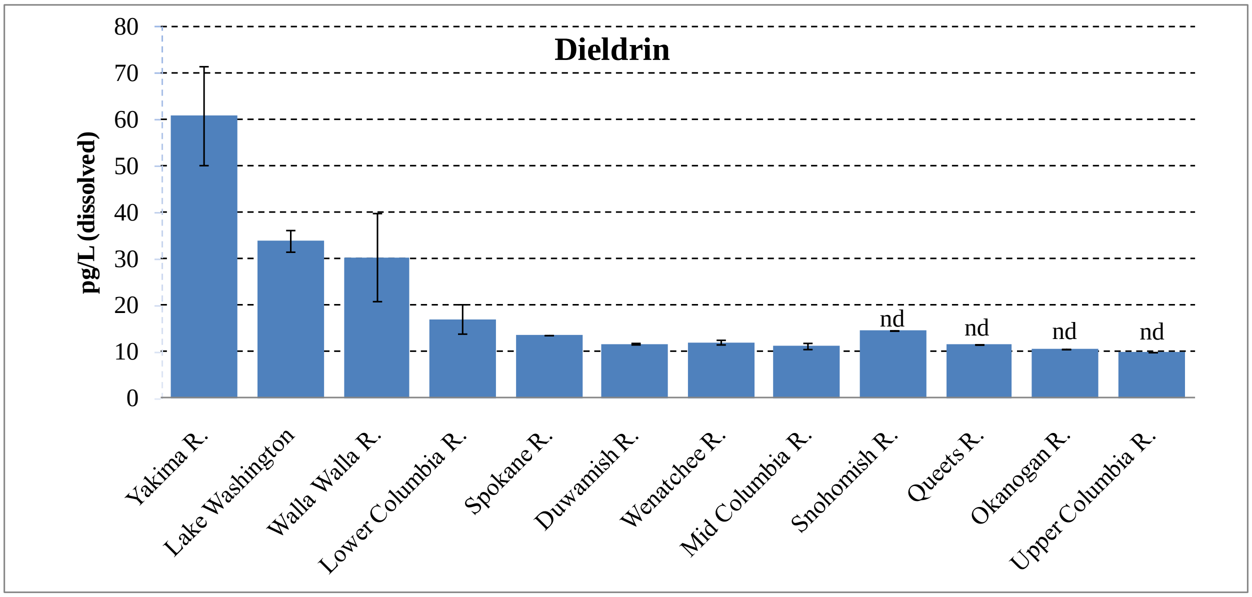


Figure 8. Average Estimated Concentrations of Dieldrin, 2007.
(nd = not detected; bars show maximum and minimum).

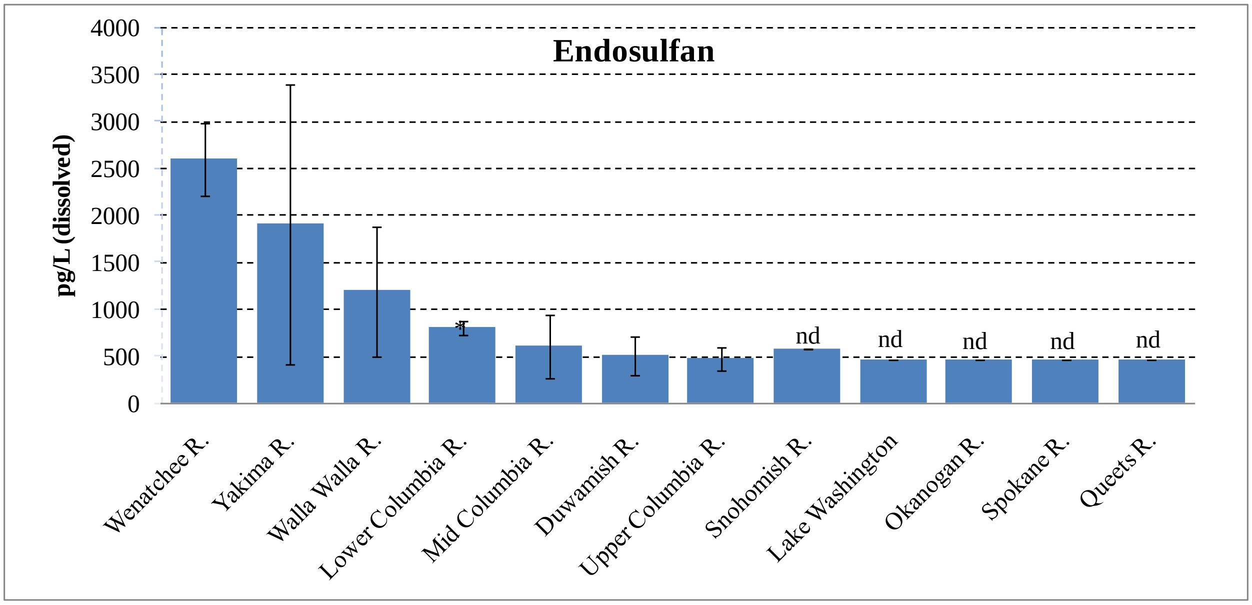


Figure 9. Average Estimated Concentrations of Endosulfan, 2007.
(nd = not detected; bars show maximum and minimum).

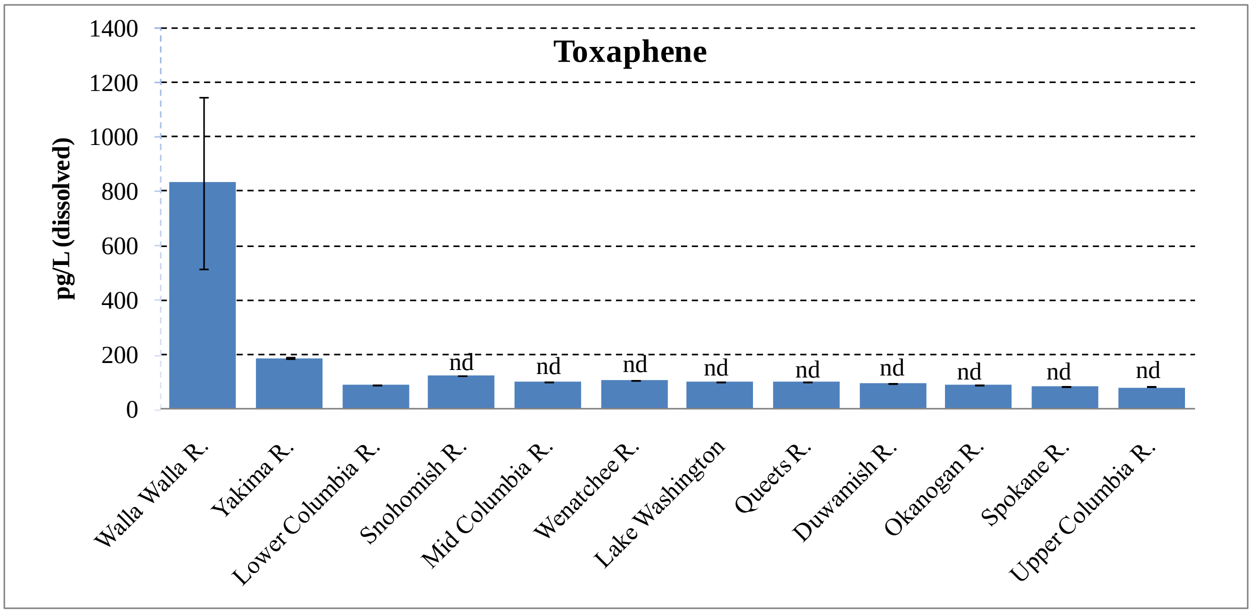


Figure 10. Average Estimated Concentrations of Toxaphene, 2007.
(nd = not detected; bars show maximum and minimum).

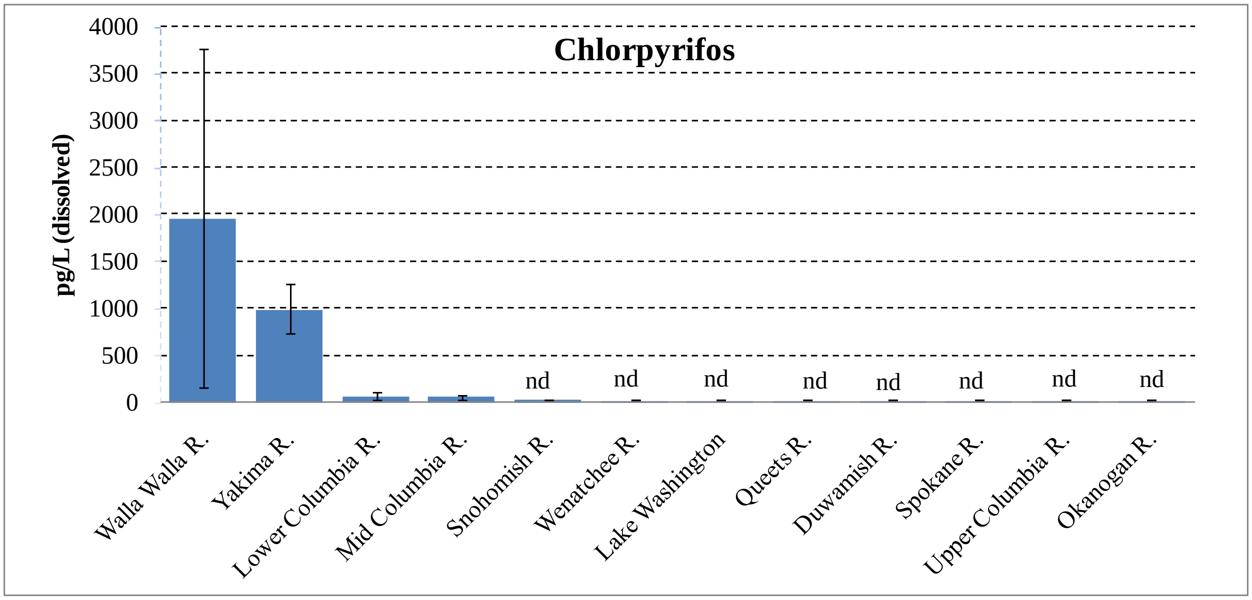


Figure 11. Average Estimated Concentrations of Chlorpyrifos, 2007.
(nd = not detected; bars show maximum and minimum).

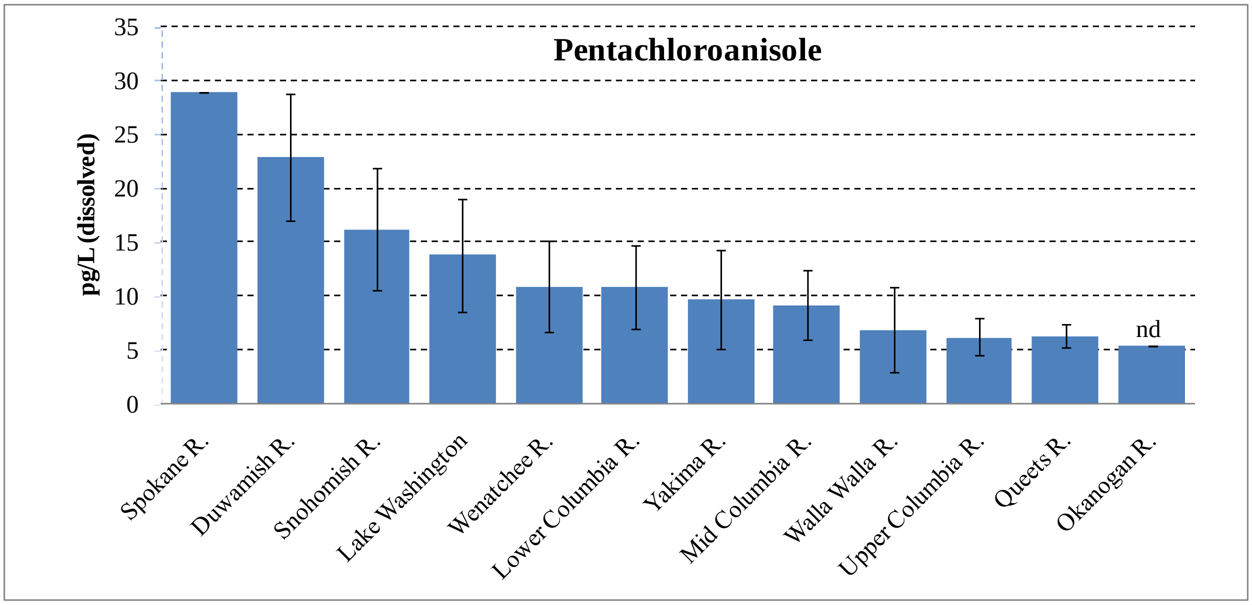


Figure 12. Average Estimated Concentrations of Pentachloroanisole, 2007.
(nd = not detected; bars show maximum and minimum).

Highest concentrations of T- DDT were found in the Upper Columbia, Yakima, Walla Walla, and Wenatchee Rivers. DDT compounds were not detected or detected at very low levels in Lake Washington and the Duwamish, Snohomish, Queets, and Spokane Rivers.

PCBs were detected at all sites. PCB concentrations were highest in the Spokane, Middle and Lower Columbia, Wenatchee, and Duwamish Rivers. These sites are known to have PCB problems.

PBDEs were detected at all 12 sites. Concentrations in the Spokane River were 1.5 times higher than in the other sites. An earlier Ecology study also reported the Spokane River as having the highest PBDE levels in the state (Johnson et al. 2006).

The Yakima, Walla Walla, and the Lower Columbia Rivers ranked in the top three for high toxaphene and chlorpyrifos levels and in the top four for endosulfan and dieldrin. The Wenatchee River also had high concentrations of endosulfan. Pesticide detections at these sites are likely due to upstream agriculture land use. Lake Washington had elevated concentrations of dieldrin, and the Middle Columbia River site had detections for dieldrin, endosulfan, and chlorpyrifos.

Pentachloroanisole was detected at all sites except the Okanogan River, which only had fall results available.

Seasonal Patterns

Several seasonal patterns were observed among the 12 sites. Overall, there were more chemicals detected in the spring than in the fall, except for in Lake Washington and the Duwamish River (Figure 13). In part, the differences in numbers of chemicals detected between seasons might be attributed to slightly lower detection limits in the fall for some chemicals. DDT compounds were undetected in the spring and found at low levels in the fall for Lake Washington and Duwamish River.

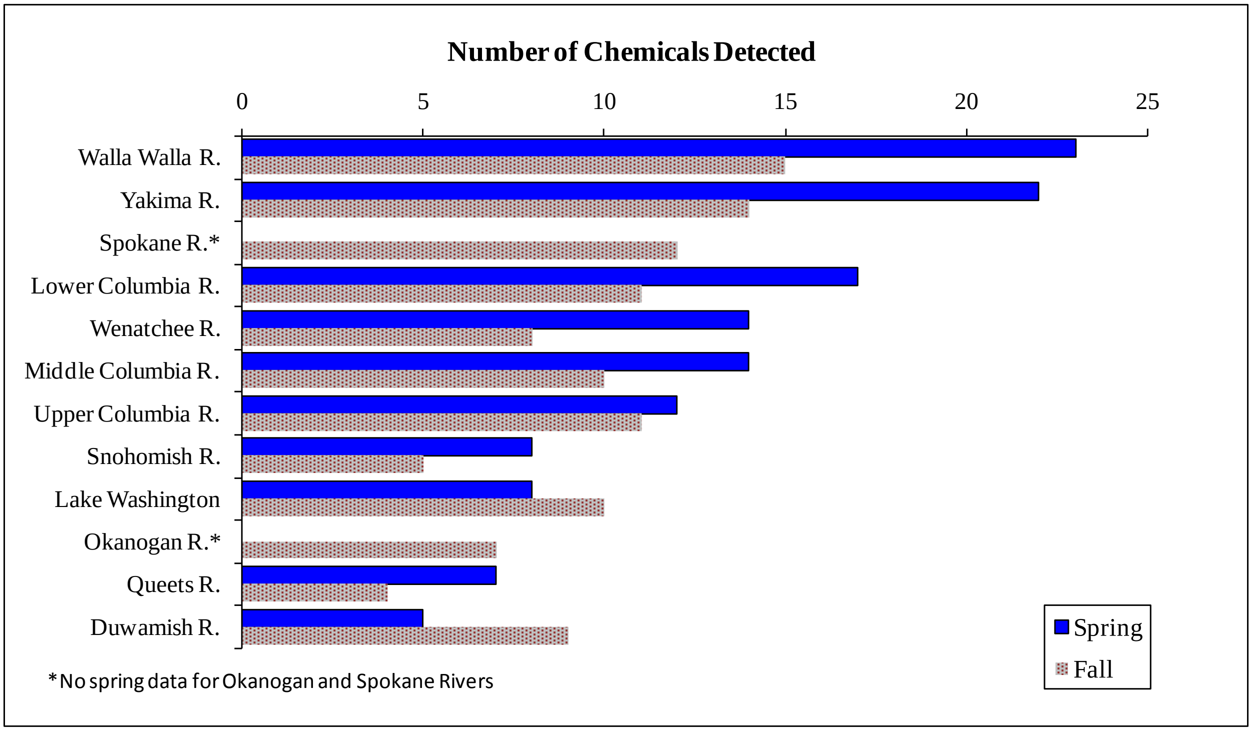


Figure 13. Number of Chemicals Detected in Spring Versus Fall, 2007.

Table 5 highlights those waterbodies where the highest concentrations were recorded in the spring and fall.

Table 5. Location of Maximum Concentrations Observed in 2007.

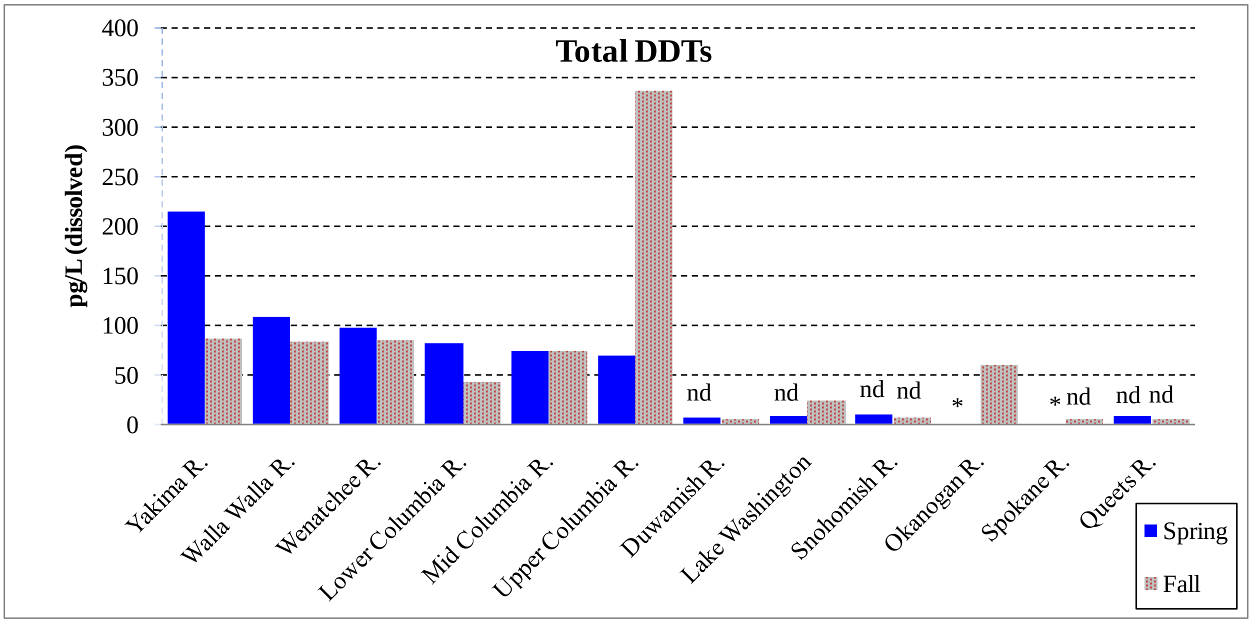
Parameter	pg/L[4]	Spring Location
Spring		
Chlorpyrifos	3800	Walla Walla R.
Toxaphene	1150	Walla Walla R.
Hexachlorobenzene (HCB)	34	Walla Walla R.
Total Chlordane[1]	23	Walla Walla R.
Heptachlor Epoxide	19	Walla Walla R.
Lindane	755	Walla Walla R.
Dacthal	30	Mid Columbia R.
Endosulfan I	2660	Yakima R.
Endosulfan-II	1200	Walla Walla R.
Fall		
Endosulfan Sulfate	2700	Walla Walla R.
Pentachloroanisole (PCA)	29	Spokane R.
Dieldrin	71	Yakima R.
DDMU[2]	33	Upper Columbia R.
Total DDT[3]	340	Upper Columbia R.
Total PCBs	80	Spokane R.
Total PBDEs	182	Spokane R.

1-Total Chlordane is the sum of cis- and trans- chlordane, dis- and trans- nonachlor, and oxychlordane.
2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
3-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT.
DDD = p,p'-dichlorodiphenyldichloroethane.
DDE = p,p'-dichlorodiphenyldichloroethylene.
DDT = p,p'-dichlorodiphenyltrichloroethane.
4-Estimated dissolved concentrations.

The highest pesticides concentrations were found mostly in the spring in the Walla Walla, Yakima, and Mid-Columbia Rivers. The Upper Columbia and the Spokane Rivers had the highest concentrations for T-DDT, T-PCBs, and T-PBDEs in the fall, respectively.

EPA identified sources of legacy pesticides coming from disturbed contaminated soils and runoff from farmland, roads, construction sites, and stormwater (EPA 2009). The Yakima, Walla Walla and Middle Columbia Rivers drain large agricultural areas with historical pesticide use. The soil disturbance (spring tilling), spring runoff, and irrigation may help explain the elevated pesticide concentrations found in these rivers (Joy 2002, Joy et al. 1997, and Johnson et al. 2004). In a national water quality report for pesticides in streams and groundwater, USGS reported the highest concentrations of pesticides across the nation were detected during the growing season and the lowest were detected during the winter (Gilliom et al. 2006).

Figure 14 shows T-DDT, T-PCB, and T-PBDE levels for spring and fall of 2007, ordered from the highest to lowest concentrations observed in the spring.



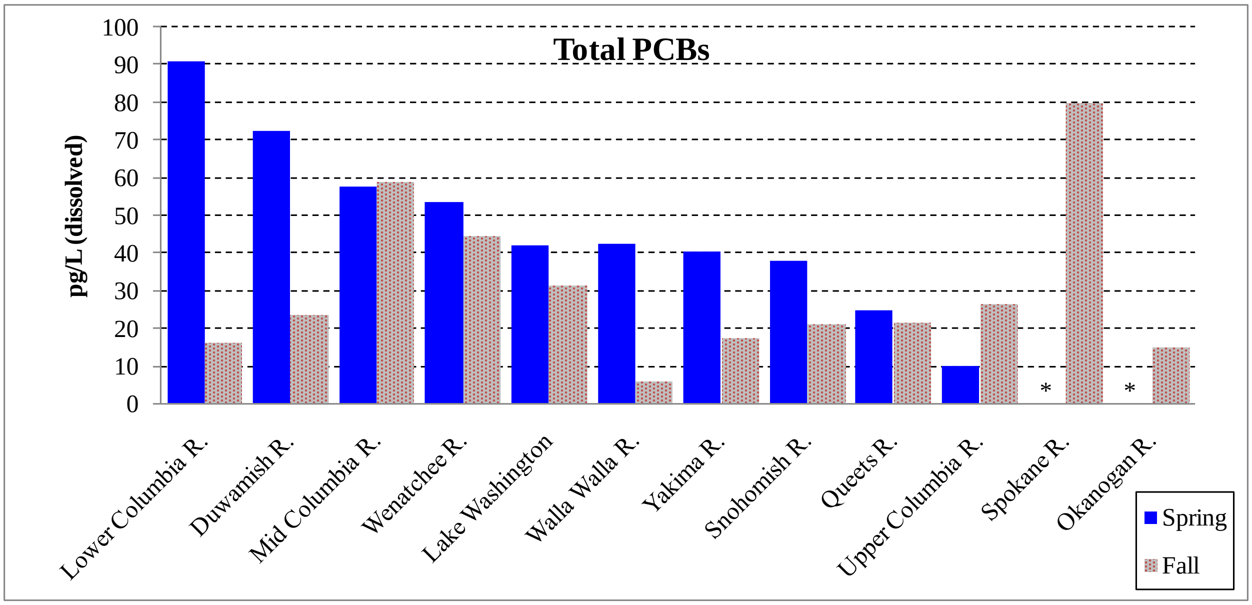


Figure 14. Estimated Concentration of Dissolved Total DDT, Total PCBs, and Total PBDEs, 2007 (nd = not detected, * = no data.)

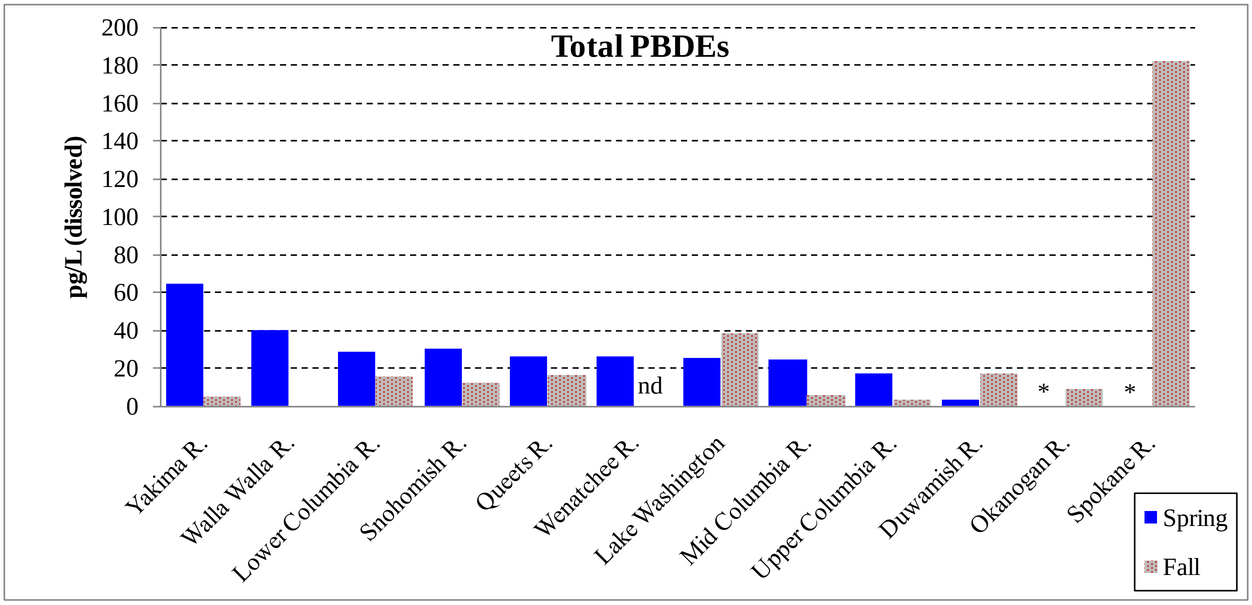


Figure 14 (cont.). Estimated Concentration of Dissolved Total DDT, Total PCBs, and Total PBDEs, 2007 (nd = not detected, * = no data.)

Concentrations of DDT and PCB compounds were highest in the spring at most sites. Exceptions include the Upper Columbia River for T-DDT and T-PCBs, and the Middle Columbia River for T-PCBs. T-DDT in the Upper Columbia River fall sample was over four times the level found in the spring sample. It seems unlikely that runoff can fully explain this difference, so other factors are suspected. The Yakima and Wenatchee Rivers ranked second and third highest for T-DDT (215 and 97 pg/L respectively) from the spring.

Differences between PCB concentrations in the spring and fall were less clear. Results suggest a lowering of PCB levels at most sites in the fall. More variability was associated with the PCB data than for other target compounds (28% RPD for residues and 48% for dissolved concentrations in the field replicate).

Although PBDEs showed excellent precision (<5% RPD for both residue and dissolved concentrations), no seasonal trends were observed. So far in this 2007 monitoring program, only one replicate has been used. However, PBDEs were found in Ecology's statewide PBDE assessment to have substantial seasonal variation (Johnson et al. 2006). The higher concentrations of PBDEs found in the Spokane River were consistent with earlier findings pointing to Spokane as a possible hot spot (Johnson et al. 2006).

Total PBT Concentrations

Chlorinated organic compounds discharged to surface waters partition between dissolved and particulate fractions. Data on total water concentrations and relative amounts of dissolved and total fractions may have implications for contaminant loading and for source control. Total concentrations were estimated from the dissolved concentrations as described earlier. Estimated total water concentrations of pesticides, PCBs, and PBDEs for individual samples can be found in Appendix M.

Table 6 summarizes estimates of the dissolved fraction of target compounds for the 2007 sampling periods. These are listed in descending order of the dissolved fraction. Dissolved versus total concentrations were estimated only where there were at least two detections.

Results show that greater than 90% of endosulfan, dieldrin, toxaphene, and chlorpyrifos appeared to be in dissolved form. Approximately 66-84% of heptachlor epoxide, PCA, DDMU, HCB, DDT, and DDD would be dissolved. DDE would be split between dissolved and particulate fractions (range 36–62%), whereas 64% of T-PCBs were bound to particulates. An earlier Ecology SPMD study in the Lower Columbia River found similar results for dissolved fractions of dieldrin (99%), DDD and DDT (70 – 80%), DDE (52%), and T-PCBs (35%) (Johnson et al. 2005).

Due to their large molecular size and a strong tendency to partition to particles, high molecular weight PBDEs such as PBDE-191 and -209 have low accumulation in SPMDs. As suggested in a North America PBDE study by Hale et al. (2003), the bulk of the environmental burden of these chemicals will eventually reside in either the sediments or soil. However, these molecules have been found to degrade to lower brominated PBDE species (Ecology and WDOH 2006).

Table 6. Estimates of the Dissolved Fraction of Pesticides, PCBs, and PBDEs, 2007.

Parameter	% Dissolved*			N**
	Mean	Minimum	Maximum	
Endosulfan-II	99.7	99.6	99.9	4
Endosulfan Sulfate	99.6	99.5	99.8	5
Endosulfan I	99.5	99.2	99.7	13
Dieldrin	96.5	95.2	98.1	13
Toxaphene	94.3	93.6	95.2	5
Chlorpyrifos	92.3	90.8	93.7	7
Heptachlor Epoxide	84.4	83.9	85.0	2
Pentachloroanisole (PCA)	80.9	72.3	89.1	17
p,p'-DDT	79.1	72.7	88.1	12
DDMU[1]	76.6	71.1	83.7	7
Hexachlorobenzene HCB)	70.8	60.6	79.8	14
p,p'-DDD	65.9	58.3	79.7	14
p,p'-DDE	44.5	36.3	61.6	14
Total PCBs	36.4	24.6	50.4	23
PBDE-66	51.0	51.0	51.1	2
PBDE-49	48.0	38.0	53.2	3
PBDE-47	44.4	32.1	59.5	22
PBDE-100	23.9	15.2	36.1	20
PBDE-99	19.5	12.2	30.3	19
PBDE-153	8.4	5.2	13.8	7
PBDE-154	5.6	3.1	9.0	10
PBDE-183	1.0	0.7	3.5	7

*Dissolved Concentration / Total Concentration x 100 = % Fraction.
**N = number of samples with detected analytes.
1-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.

Comparison with Water Quality Standards

Federal and state agencies and tribes adopt water quality criteria to protect waterbodies for designated uses (e.g. public water supply, protection of fish and wildlife, and recreational or agricultural purposes). Results from this 2007 study were compared to the water quality standards and recommended criteria described below. The criteria for Washington State are regulatory whereas the EPA criteria are current recommendations (Ecology 2006a). The Washington and EPA criteria for the chemicals of concern in this study are listed in Appendix N.

Washington Water Quality Standards

Chapter 173-201A WAC established water quality standards for surface waters consistent with public health, public enjoyment, and the protection of fish, shellfish, and wildlife resources. The criteria are thresholds that, when exceeded, may lead to regulatory action.

The federal Clean Water Act requires that the waterbodies that exceed water quality standards be put on a list (known as the 303(d) list) for development of a water cleanup plan specific for the pollutant causing the problem. The cleanup plan results from a Total Maximum Daily Load (TMDL) study and public involvement process. Ecology uses the TMDL program to control sources of the particular pollutant in order to bring the waterbody back into compliance with the water quality standards.

Washington State's water quality standards for toxic substances (WAC 173-201A-040[5]) define human-health-based water quality criteria by referencing 40 CFR 131.36, also known as the National Toxics Rule or NTR (EPA 1992). Risk-based criteria for carcinogenic substances are based on a risk-level of 10^{-6}. The risk level estimates the number of additional cancer cases that would be caused by long-term exposure to a specific contaminant. At a risk level of 10^{-6}, one person in a million would be expected to contract cancer due to long-term exposure to a specific contaminant. These risks state upper-bound estimates, while true risks may be as low as zero. Some chemicals in this study, such as endosulfan and chlorpyrifos, are not carcinogens. These compounds have a reference dose below which adverse health effects are not expected.

Washington's protection for aquatic life define criteria for toxic substances (WAC 173-201A-240) as not to be above natural background levels which have the potential either singularly or cumulatively to adversely affect water uses or public health. Toxic substances should also be below levels that could cause short-or long-term toxicity to the most sensitive biota (plants and animals).

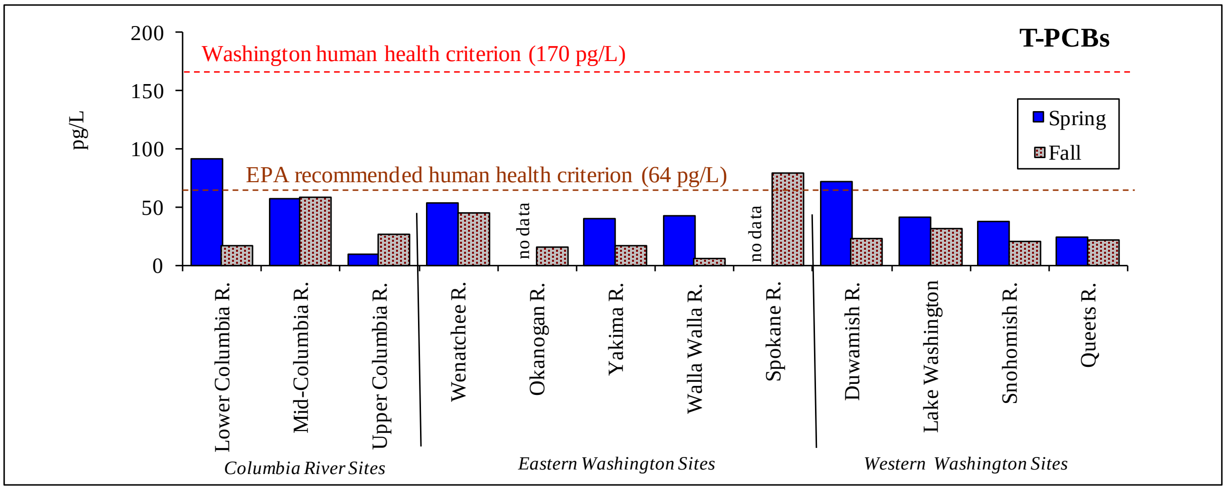
EPA Recommended Water Quality Criteria

EPA recommends use of their current updates (EPA 2006) when revising criteria for individual states. Several guidelines have been updated based on new information and were included in this report to show the importance of recommended changes. Although these EPA criteria are not regulatory, they can be used by state, tribal, and local health jurisdictions for human health risk evaluations. The EPA criteria include protection for human health and aquatic life.

Human Health Criteria

Results from this 2007 study were compared to the Washington State and EPA criteria for protecting human health and aquatic life. The dissolved concentrations were used for comparison to human health criteria based on human fish consumption because the dissolved form more accurately reflects the chemical fraction available for bioconcentration by fish (EPA 2000). Washington's human health criteria for "water plus fish consumption" values (Appendix N) were compared to dissolved results. Total concentrations were compared to the aquatic life criteria, following accepted practice.

The waterbodies monitored in 2007 met water quality criteria for most of the chemicals of concern. Significant exceptions included PCBs, dieldrin, and toxaphene. Figure 15 compares the estimated dissolved concentrations of T-PCBs, dieldrin, toxaphene, and DDT metabolites (DDE, and DDD) with the Washington and EPA human health criteria.



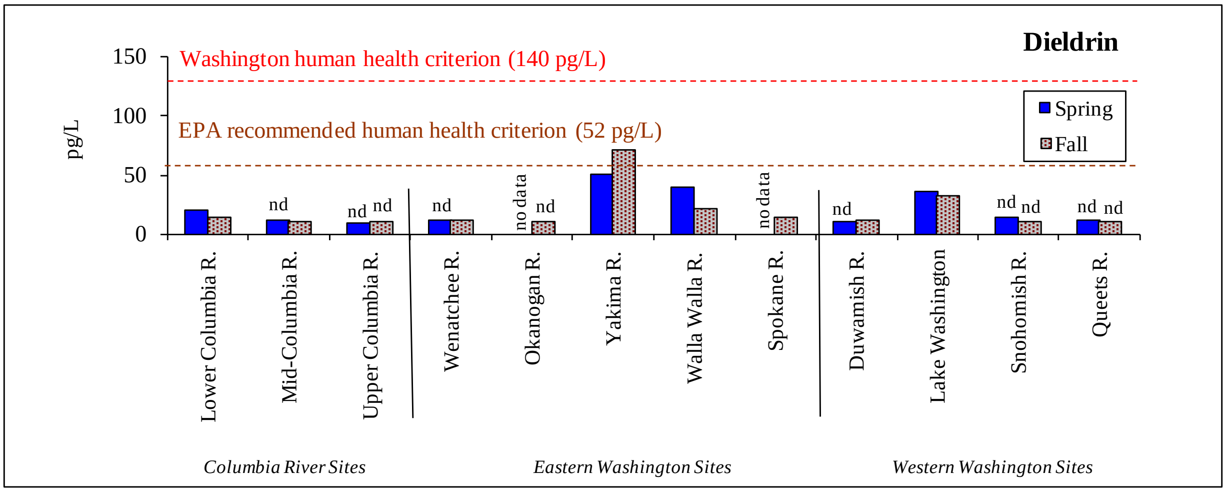


Figure 15. Estimated Dissolved Concentrations of T-PCBs, Dieldrin, Toxaphene, DDE, and DDD Compared with Washington and EPA Human Health Criteria. (nd = not detected.)

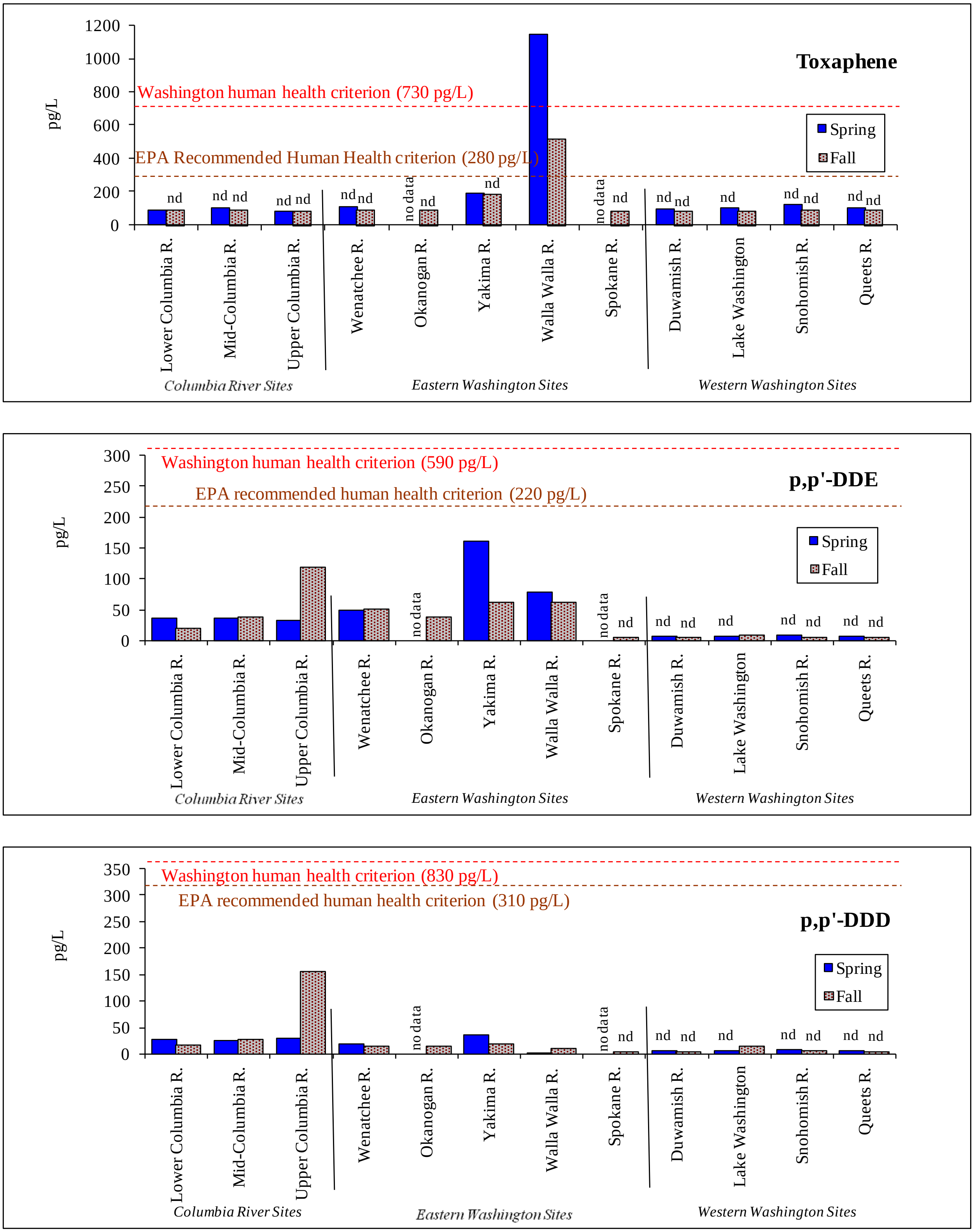


Figure 15 (cont.). Estimated Dissolved Concentrations of T-PCBs, Dieldrin, Toxaphene, DDE, and DDD Compared with Washington and EPA Human Health Criteria. (nd = not detected.)

PCBs were detected at all sites in both spring and fall of 2007 with three sites exceeding the EPA recommended human health criterion of 64 pg/L. These sites were the Lower Columbia (91 pg/L, spring), the Duwamish River (72 pg/L, spring), and the Spokane River (80 pg/L, fall).

Although the Washington human health criterion for dieldrin (140 pg/L) was not exceeded, the Yakima River exceeded the EPA recommended human health criterion (52 pg/L) in the fall with a concentration of 71 pg/L. The spring sample was 50 pg/L.

An Ecology Yakima River TMDL study conducted by Johnson (2008) in 2007 at the same site reported similar results for dieldrin in the spring (60 pg/L), but not in the fall (16 pg/L). Johnson found higher levels of dieldrin in water samples upstream (river mile 55) of this study's site. Dieldrin consistently exceeded criteria in the second half of the irrigation season in the Yakima River during low flows (last half of June through August). This 2007 PBT Trends Study sampled during September, after this period.

Toxaphene exceeded several criteria in the Walla Walla River. The Washington human health criterion of 730 pg/L was exceeded in the spring (1,150 pg/L), and the EPA recommended human health criterion of 280 pg/L was exceeded in the fall (510 pg/L).

High concentrations of toxaphene were reported in the Pine Creek tributary of the Walla Walla River during the 2003-2004 Walla Walla TMDL study. Johnson (2004) found estimates of up to 40,000 pg/L from SPMDs indicating Pine Creek as a significant source of toxaphene loading into the Walla Walla River.

No T-DDT or metabolites exceeded Washington's or EPA's human health criteria. The Yakima River neared the 220 pg/L EPA recommended human health criterion in the spring with a concentration of 160 pg/L for DDE. A higher concentrations of DDD was observed at the Upper Columbia River site in the fall (155 pg/L), but was below Washington human health criterion (830 pg/L) and EPA recommended human health criterion (310 pg/L).

Aquatic Life Criteria

Figure 16 compares estimated total concentrations of toxaphene and T-DDT with Washington and EPA chronic aquatic life criteria. The acute criteria were not exceeded.

The Walla Walla River exceeded Washington's aquatic life criterion for toxaphene (200 pg/L) in the spring (1220 pg/L) and fall (550 pg/L). Toxaphene concentrations in the Yakima River were at Washington's aquatic criterion of 200 pg/L: 200 pg/L in the spring and 190 pg/L in the fall.

Johnson (2008) found 363 pg/L of toxaphene in the Yakima River during the Yakima River TMDL study. The difference between results from this present study and the TMDL study can be attributed to different octanol-water partition coefficients (log K_{ow}[2]) used for estimating the dissolved concentration. (See Appendix B and C for discussion on SPMDs.) Recalculating the

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[2] Octanol-water partition coefficient, a measure of a chemical's tendency to associate with the organic fraction in water.

TMDL data using the log K_{ow} used in the present study gives a concentration of 201 pg/L (dissolved), which agrees well with this present study's results.

No T-DDT exceeded aquatic life benchmarks (1000 pg/L), but DDE and DDD were observed to be major contributors to T-DDT.

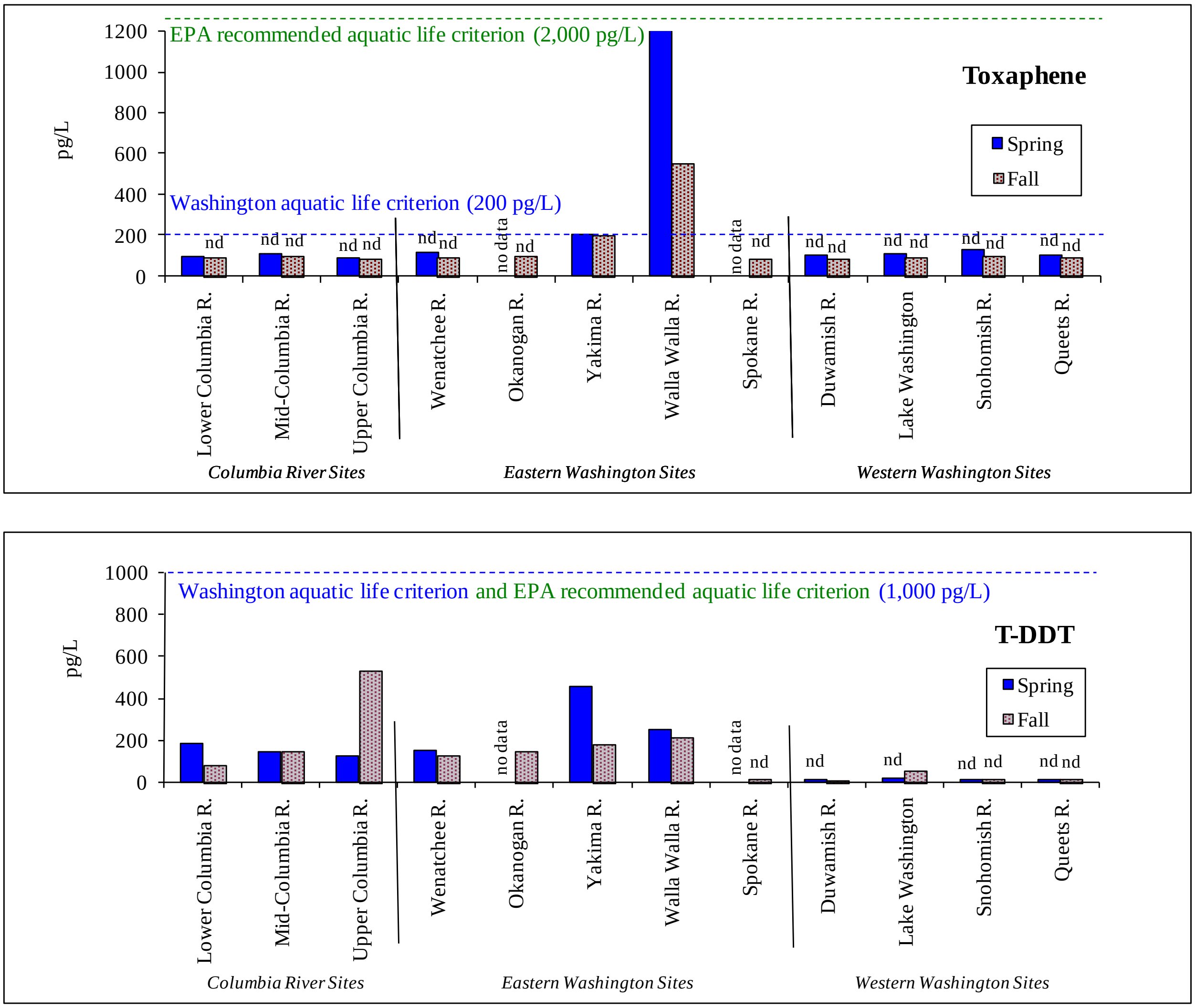

Figure 16. Estimated Total Concentrations of Toxaphene and T-DDT Compared with Washington and EPA Chronic Aquatic Life Criteria. (nd = not detected).

Comparison to Previous Data

Other Ecology studies have used passive sampling technology (SPMDs) at sites that shared locations with this 2007 study, but comparisons of data are confounded by differences in sampling and processing methods. Differences include:

- Varied requirements for numbers of samples, replicate, and blanks (i.e. multiple or one for establishing representativeness and estimating variability).
- Different correction processes among studies for blank contamination (i.e. use of field or Day0-Dialysis, or other blanks in residual or dissolved results).
- Changes in the USGS Estimated Water Concentration Calculator spreadsheet for estimating water concentrations, including the use of PRCs and updated log K_{ow}s for determining sampling rates.

Because of these differences, detailed comparisons were limited to the Yakima River Toxics TMDL study (Johnson 2008). Ecology's Yakima River TMDL and this study used SPMDs at the same location for spring and fall in the Yakima River at Wanawish Dam in 2007.

Yakima River Toxics TMDL Study

Results between this current 2007 PBT Trends Study and the Yakima River Toxics TMDL (Johnson 2008) were comparable because both studies had the same sampling requirements, analytical methods, and similar sampling timeframes at the same site. The spring sampling was staggered by about one week: the PBT Trends Study started and ended one week earlier than the Yakima TMDL. The Yakima TMDL fall sampling was about one month later. Results close to detection limits were not comparable because this study's detection limits were twice that of the Yakima TMDL study.

Table 7 shows the estimated dissolved concentrations for pesticides in the Yakima River for 2007.

Both studies had relatively similar results for most chemicals. T-DDT values were similar and showed the same spring and fall pattern. Spring results were 220 pg/L for PBT Trends compared to 228 pg/L for the Yakima TMDL. Fall T-DDT results were 86 pg/L for PBT Trends compared to 64 pg/L for the Yakima TMDL. Dieldrin and chlorpyrifos levels showed a similar pattern. Overall, Yakima River fall concentrations were less in October – November than in August – September. Dieldrin, chlorpyrifos, and the endosulfans showed a larger spread as the values increased.

Table 7. Estimated Dissolved Concentrations of Detected Pesticides in the Yakima River, 2007 (pg/L).

Pesticide	PBT Trends	TMDL in the Yakima River[1]	PBT Trends	TMDL in the Yakima River[1]
	April - May		Aug - Sept	Oct - Nov
p,p'-DDT	17	20	4.6	<2.3
p,p'-DDE	161	158	63	51
p,p'-DDD	36	40	18	13
o,p'-DDT	<4.6	5.4	<3.7	<2.3
o,p'-DDE	<4.6	3.6	<3.7	<2.3
o,p'-DDD	<4.7	1.3	<3.6	<2.3
Total DDT[2]	220	228	86	64
Dieldrin	50	60	71	16
Chlorpyriphos	1200	1083	729	117
Endosulfan I	2660	3098	420	398
Endosulfan-II	740	1017	<460	<231
Endosulfan Sulfate	510	635	790	<159
Hexachlorobenzene (HCB)	8.7	<8.6	<3.6	<5.3
Pentachloroanisole (PCA)	14	<12	6	<13
Toxaphene[3]	190	193	184	56
Total Chlordane[4]	4.9	11.9	<4.0	<2.4
Dacthal	<19	56	<19	<9.3
Heptachlor Epoxide	<12	7.5	<11	<5.8
T-PCBs	40	45	17	9.1

1. (Johnson 2008).
2. Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT.
   DDD = p,p'-dichlorodiphenyldichloroethane.
   DDE = p,p'-dichlorodiphenyldichloroethylene.
   DDT = p,p'-dichlorodiphenyltrichloroethane.
3. The Yakima TMDL toxaphene results were re-estimated using the 2007 PBT Trends log Kow value (4.73). Original results for the Yakima TMDL were 363 pg/L (spring) and 104 pg/L (fall) using log Kow 4.36.
4. Total chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

< = detection limit where compound not detected. Non-detects were treated as zero in summed totals. Rounding differences may cause slight variation compared to results reported elsewhere.

U = not detected at or above reported result.

UJ = not detected at or above reported estimated result.

J = estimated concentration.

Comparisons of toxaphene results are complicated because each study used different log K_{ow}s in the spreadsheet calculator. The Yakima TMDL study used a log K_{ow} of 4.36, whereas this PBT Trends Study used a log K_{ow} of 4.73. Finding a representative log K_{ow} for toxaphene is problematic because there are many combinations of the chemical compound resulting in thousands of chemical properties.

The Yakima TMDL toxaphene residues were re-estimated for dissolved concentrations using the 2007 PBT Trends log K_{ow} value (4.73) in Table 7. When re-estimated, toxaphene concentrations followed a pattern similar to T-DDT and other pesticides. This pattern had higher concentrations in the spring and decreasing concentrations the later the sampling took place in the fall: 190 pg/L (PBT Trends) versus 193 pg/L (Yakima TMDL) in the spring, and 184 pg/L (PBT Trends) versus 56 pg/L (Yakima TMDL) in the fall.

Original dissolved toxaphene concentrations for the Yakima TMDL were 363 pg/L (spring) and 104 pg/L (fall). The dissolved results of 363 pg/L from the Yakima TMDL and 184 pg/L from this PBT Trends Study had identical residue amounts of 240 ng/5-SPMDs. The use of different log K_{ow}s illustrates how large apparent differences in dissolved water concentrations can be attributed to data reduction methods.

PCBs were found at low concentrations in the Yakima River TMDL and this study. Spring results for both studies agreed very well. The fall PCB values showed a wider spread as did other pesticides discussed above.

Conclusions

Eleven Washington rivers and one large urban lake were sampled for this 2007 PBT Trends Study. Data are reported for the first year of this long-term trends program.

Major findings from this first year of monitoring are as follows:

Chemicals Detected

A range of chlorinated pesticides, PCBs, and PBDEs were detected:

- The most frequently detected compounds were PCBs and PBDEs which were detected at all 12 monitoring sites. Most detected PBDEs were of the penta- group (PBDE-47, -99, -49, -100). Dissolved concentrations ranged from 6.2 to 99 pg/L for PCBs; and 0.9 to 180 pg/L for PBDEs.
- The largest number of chemicals was detected in the Walla Walla and Yakima Rivers.
- Three pesticides and their breakdown products were found in over half the samples: DDT, dieldrin, and endosulfan. Generally, pesticide metabolites were detected more frequently and in higher concentration than the parent compound.
- Pentachloroanisole (PCA), from the wood preservative pentachlorophenol, was found in all the spring samples and over half of the fall samples.

Chemical Concentrations

Maximum concentrations for individual chemicals were present in the following waterbodies:

- T-DDT in the Upper Columbia River.
- T-PCBs in the Spokane River.
- Dieldrin in the Yakima River.
- Toxaphene in the Walla Walla River.
- Chlorpyrifos in the Walla Walla River.
- Endosulfan in the Wenatchee River.
- PBDEs in the Spokane River.

More of the chemicals listed above were detected in the spring than in the fall. An exception was PBDEs, which appear to vary seasonally. Toxaphene, lindane (gamma-BHC), and chlorpyrifos were observed in spring samples at much higher levels than in fall samples.

Several samples did not meet (exceeded) Washington State or EPA water quality criteria for the protection of human health and aquatic life:

- PCBs exceeded the EPA recommended criteria for human health in the spring samples from the Lower Columbia and Duwamish Rivers, and in the fall sample from the Spokane River.

Other studies show that these three sites have high concentrations of PCBs from historical contamination.

- Dieldrin exceeded the EPA recommended criterion for human health in the Yakima River fall sample.
- Toxaphene exceeded the Washington human health, EPA recommended human health, and Washington aquatic life criteria in the Walla Walla River spring sample. The Walla Walla River fall sample exceeded the EPA recommended human health and the Washington aquatic life criteria. The Yakima River spring and fall samples also had elevated concentrations of toxaphene but did not exceed any criteria. Similar findings from other studies of these two rivers indicated pollutants from local sources and agricultural land uses.

First Year Study Assessment

Results from the first year of monitoring (2007) indicate that this sample design can detect trends in some freshwater bodies for the chemicals highlighted above. For other locations or other chemicals, levels may be too low to identify baseline concentrations. The value of the program will become clearer as additional data accumulate.

Improvements to the PBT Trends program are needed in three areas:

1. Identifying and reducing sources of PCBs and PBDEs in field and laboratory blanks.
2. Increasing the frequency of replicate samples and field blanks.
3. Exploratory sampling to identify other waterbodies appropriate for trend monitoring.

Recommendations

As a result of this 2007 PBT Trends Study, the following recommendations are made.

- Increase the number of blanks and replicate samples to allow assessment of site-specific contamination and variability.
- Identify and reduce sources of PCBs and PBDEs in SPMD preparation and analytical processes.
- Conduct exploratory sampling to identify other waterbodies appropriate for trend monitoring.
- Incorporate additional PBTs, such as PAHs, into the monitoring program.
- Pursue other methods for assessing higher brominated PBDEs that do not accumulate in SPMDs, such as sampling sewage sludge, freshwater sediments, or suspended particulates.
- Develop a centralized data management system for SPMD data. This should include standardizing reporting elements for SPMD studies and a database.
- Revise the Quality Assurance Project Plan for this study to reflect future changes expected to the project.
- Discontinue monitoring salinity in the Duwamish and Snohomish Rivers.

References

Alvarez, D., 2008. Personal communication. USGS Columbia Environmental Research Center. Leader, Passive Sampling Group. Columbia, MO.

ATSDR, 2000. Toxicological Profile for Polychlorinated Biphenyls (PCBs). Agency for Toxic Substances and Disease Registry. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. www.atsdr.cdc.gov/toxprofiles/tp17.html. Accessed March 2009.

ATSDR, 2004. Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers (PBBs and PBDEs). Agency for Toxic Substances and Disease Registry. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. www.atsdr.cdc.gov/toxprofiles/tp68.html. Accessed March 2009.

Braekevelt, E., S.A. Tittlemier, and G.T. Tomy, 2003. Direct Measurement of Octanol-water Partition Coefficients of Some Environmentally Relevant Brominated Diphenyl Ether Congeners. Chemosphere 51:563-567.

Bryant, W.L., S.L. Goodbred, T.L. Leiker, L. Inouye, and B.T. Johnson, 2007. Use of Chemical Analysis and Assays of Semipermeable Membrane Devices Extracts to Assess the Response of Bioavailable Organic Pollutants in Streams to Urbanization in Six Metropolitan Areas of the United States. U.S. Geological Survey Scientific Investigations Report 2007-5113, 46 p., 2 app. http://pubs.water.usgs.gov/sir2007-5113. Accessed March 2009.

City of Spokane, 2008. DMR Data for the Riverside Park Water Reclamation Facility (RPWRF).

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/95356.html.

Ecology, 2006a. Water Quality Standards for Surface Waters of the State of Washington Chapter 173-201A WAC. Washington State Department of Ecology, Olympia, WA. Publication No. 06-10-091. www.ecy.wa.gov/programs/wq/swqs/index.html.

Ecology, 2006b. Water Quality Program Policy 1-11: Assessment of Water Quality for the Clean Water Act Sections 303(d) and 305(b) Integrated Report. September 6, 2006. Water Quality Program, Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/programs/wq/303d/wqp01-11-ch1Final2006.pdf. Accessed November 2008.

Ecology, 2007. Multiyear PBT Chemical Action Plan Schedule. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/biblio/0707016.html. Accessed March 2009.

Ecology and WDOH, 2006. Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Final Plan. Washington State Department of Ecology and Washington State Department of Health, Olympia, WA. Ecology Publication No. 05-07-048. www.ecy.wa.gov/biblio/0507048.html.

EPA, 1992. National Toxics Rule. Office of Water and Office of Science and Technology, U.S. Environmental Protection Agency, Washington, D.C. 40 CFR 131.36. Federal Register, Vol. 57, Issue: 246. p. 60848 (57 FR 60848), December 22, 1992. www.epa.gov/waterscience/standards/rules/ntr.html#sectionA. Accessed March 2009.

EPA, 1999. Polychlorinated Biphenyls (PCBs) Update: Impact on Fish Advisories. U.S. Environmental Protection Agency. Office of Water, Washington D.C. EPA-823-F-99-019.

EPA, 2000. Guidance for assessing chemical contaminant data for use in fish advisories – Volume 1; Field sampling and analysis. Third Edition. U.S. Environmental Protection Agency. Office of Water, Washington D.C. EPA-823-B-00-007. Accessed March 2009. www.epa.gov/waterscience/fishadvice/volume1/.

EPA, 2006. National Recommended Water Quality Criteria. Office of Water and Office of Science and Technology, U.S. Environmental Protection Agency, Washington, D.C. EPA-822-R-02-047. www.epa.gov/waterscience/criteria/wqctable. Accessed March 2009.

EPA, 2009. Columbia River Basin: State of the River Report for Toxics. U.S. Environmental Protection Agency. Washington, D.C. Region 10. http://yosemite.epa.gov/r10/ecocomm.nsf/Columbia/SoRR/. Accessed March 2009.

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

Gilliom, R.J., J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, and D.M. Wolock, 2006. The Quality of Our Nation's Waters. Pesticides in the Nation's Streams and Ground Water, 1992-2001: U.S. Geological Survey Circular 1291, 172 p.

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. Publication No. 05-10-079. www.ecy.wa.gov/biblio/0510079.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. Publication No. 06-03-116. www.ecy.wa.gov/biblio/0603116.html.

Hale, R.C., M. Alaee, J.B. Manchester-Neesvig, H.M. Stapleton, and M.G. Ikonomou, 2003. Polybrominated Diphenyl Ether Flame Retardants in the North American Environment. Environment International; 29. pp. 771-779.

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. Publication No. 85-7. www.ecy.wa.gov/biblio/857.html.

Huckins, J.N., J.D. Petty, and K. Booij, 2006. Monitors of Organic Chemicals in the Environment; Semipermeable Membrane Devices: New York, Springer.

Huckins, J.N., J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booij, D.A. Alvarez, W.L. Cranor, R.C. Clark, and B.B. Mogensen, 2002. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. Environmental Science Technology 36(1):85-91.

IRIS, 2009. Integrated Risk Information System. U.S. Environmental Protection Agency. Washington, D.C. http://cfpub.epa,gov/ncea/iris/index.cfm. Accessed March 2009.

Johnson, A., 2001. An Ecological Hazard for PCBs in the Spokane River. Washington State Department of Ecology, Olympia, WA. Publication No. 01-03-015. www.ecy.wa.gov/biblio/0103015.html.

Johnson, A., 2007. A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program – Quality Assurance Project Plan. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-104. www.ecy.wa.gov/biblio/0703104.html.

Johnson, A., 2008. Personnel communication. Yakima River Chlorinated Pesticides and PCBs TMDL (unpublished). Project Code 07-078-02. Washington State Department of Ecology, 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. Publication 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. Publication 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. Publication 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. Publication 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. Publication No. 97-321. www.ecy.wa.gov/biblio/97321.html.

Karickhoff, S.W., 1981. Semi-empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere 10(8):833-846.

King County, 2003. Lake Washington Existing Conditions Report. Sammamish/Washington Analysis and Modeling Program. Dept. of Natural Resources and Parks. Water and Land Resources Division. Seattle, WA. http://green.kingcounty.gov/lakes/reports/lk_wa_exist.htm. Accessed March 2009.

King County, 2005. Lake Washington. Seattle, WA. http://green.kingcounty.gov/wlr/waterres/lakes/LakeWashington.aspx. Accessed March 2009.

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, 1998. Estimation of Uptake Rates for PCB Congeners Accumulated by Semipermeable Membrane Devices and Brown Trout (*Salmo trutta*). Environmental Science Technology 32:1847-1852.

Meylan, W.M. and P.H. Howard, 1995. Atom/fragment contribution method for estimating octanol-water partition coefficients. J. Pharm. Sci. 84: 83-92.

Parsons, 2007. Spokane River PCB TMDL Stormwater Loading Analysis Final Technical Report. Accessed through Ecology website in March 2008. www.ecy.wa.gov/programs/wq/tmdl/spokaneriver/pcb/SpokaneSWLoading-FinalTechRpt.pdf.

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

Rayne, W., 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. http://pubs.acs.org. Accessed March 2009.

Seiders, K., C. Deligeannis, and P. Sandvik, 2007. Washington State Toxics Monitoring Program: Contaminants in Fish Tissue from Freshwater Environments in 2004 and 2005. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-024. www.ecy.wa.gov/biblio/0703024.html.

Serdar, D. and A. Johnson, 2006. PCBs, PBDEs, and Selected Metals in Spokane River Fish, 2005. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-025. www.ecy.wa.gov/biblio/0603025.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. Publication No. 06-03-024. www.ecy.wa.gov/biblio/0603024.html.

Tetra Tech, 1996. The Health of the River 1990-1996 Integrated Technical Report. Lower Columbia River Bi-State Program. Tetra Tech Inc., Bellevue, WA. www.lcrep.org/lib_bistate.htm. Accessed March 2009.

USGS, 2008. CERC Integrative Passive Samplers. U.S. Geological Survey. http://wwwaux.cerc.cr.usgs.gov/SPMD/index.htm. Accessed March 2009.

WDOH, 2006. Washington State Department of Health. Fish Advisories. www.doh.wa.gov/ehp/oehas/fish/fishadvisories.htm. Accessed March 2009.

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Appendices

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Appendix A. Monitoring Site Descriptions and Historical Contaminant Information

Table A-1. Sample Site Descriptions, PBT Trends 2007.

Site Name	County	Sampling Dates		Site Description	Latitude Decimal Degrees [1]	Longitude Decimal Degrees [1]	WBID [2] WA-	WRIA Number	EIM "User Location ID" [3]
		Deployed	Retrieved						
Duwamish/Green River	King	5/1/07 8/27/07	5/29/07 9/24/07	Duwamish River at Foster Golf Links in Tukwila, river mile (RM)10.	47.4825	-122.2614	WA- 09-1010	9	SPMDTR-DUWAM
Lower Columbia R near Clatskanie	Columbia (OR)	4/30/07	5/28/07	Columbia River near Clatskanie, OR, RM 54. Upstream side of dock at Portland General Electric Beaver Generating Station.	46.1822	-123.1772	WA- CR-1010	25	SPMDTR-LCR1
Lower Columbia R near Clatskanie	Wahkiakum	8/28/07	9/25/07	Columbia River near Clatskanie, OR, RM 54. Anchored to USGS Dolphin across river from Beaver Generating Station.	46.1849	-123.1876	WA- CR-1010	25	SPMDTR-LCR2
Mid Columbia R at McNary Dam	Benton	5/3/07 8/29/07	5/31/07 9/26/07	Columbia River at McNary Dam near Umatilla, OR, RM 292.0.	45.9394	-119.2972	WA- CR-1026	31	SPMDTR-MCR
Okanogan R	Okanogan	5/2/07 8/28/07	5/30/07 9/25/07	Okanogan River at Malott, RM 17, right bank, private property.	48.2806	-119.7050	WA- 49-1010	49	SPMDTR-OKAN
Queets R	Jefferson	5/4/07 8/30/07	6/4/07 9/27/07	Queets River in Olympic National Forest, 2 mi les up Queets River Road, RM 11.5.	47.5522	-124.1978	WA- 21-1030	21	SPMDTR-QUEETS
Snohomish R[4]	Snohomish	5/7/07 8/27/07	6/4/07 9/24/07	Snohomish River at Snohomish, behind visitor's center, RM 12.5.	47.9108	-122.0992	WA- 07-1020	7	SPMDTR-SNOHO
Spokane R at Nine Mile Dam[5]	Spokane	5/4/07 8/30/07	6/1/07 9/27/07	Upstream side off Spokane River's Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA- 54-1020	54	SPMDTR-SPOK
Spokane R Replicate Sample at Nine Mile Dam[5]	Spokane	5/4/07 8/30/07	6/1/07 9/27/07	Upstream side off Spokane River's Nine Mile Dam, RM 58.1.	47.7747	-117.5444	WA- 54-1020	54	SPMDTR-SPOK
Upper Columbia R at Rock Island Dam	Chelan-Douglas	5/2/07 8/28/07	5/30/07 9/25/07	Columbia River at Rock Island Dam, RM 453.5, 10 miles south of Wenatchee.	47.3439	-120.0939	WA- CR-1040	44	SPMDTR-UCR
Walla Walla R	Walla Walla	5/3/07 8/29/07	5/31/07 9/26/07	Walla Walla River, about 5 miles east of Wallula Junction, RM 9.	46.0709	-118.8268	WA- 32-1010	32	SPMDTR-WALLA
Washington L	King	5/1/07	5/29/07	Lake Washington, in Seattle, at the lake's outlet near Webster's Point.	47.6475	-122.2758	WA- 08-9350	8	SPMDTR-LKWA1

Site Name	County	Sampling Dates		Site Description	Latitude Decimal Degrees [1]	Longitude Decimal Degrees [1]	WBID [2] WA-	WRIA Number	EIM "User Location ID" [3]
		Deployed	Retrieved						
Washington L	King	8/27/07	9/24/07	Lake Washington , in Seattle, at Montlake Cut, right bank, east of University of Washington Marina.	47.6475	-122.3019	WA- 08-9350	8	SPMDTR-LKWA2
Wenatchee R	Chelan	5/3/07 8/27/07	5/31/07 9/24/07	Wenatchee River, about 5 miles NW of Wenatchee, RM 7.1, Old Monitor Rd. Bridge.	47.5007	-120.4257	WA- 45-1010	45	SPMDTR-WEN
Yakima R at Wanawish Dam	Benton	5/3/07 8/29/07	5/31/07 9/26/07	Yakima River, 12 mi NW of Richland, RM 18.0. Diversion structure at Wanawish Dam (formally Horn Rapids Dam), right bank.	46.3783	-119.4181	WA- 37-1010	37	SPMDTR-YAK

1 - North American Datum 1983 is horizontal datum for coordinates.
2 - Ecology's Waterbody Identification Number (WBID).
3 - Site identification as used in Ecology's Environmental Information Management (EIM) system.
4 - Sampler was compromised by low tides and redeployed a week later at this site.
5 - Spokane spring sampling was compromised due to lowering of the water level at the dam. Underwater membranes combined.

Following is an overview of contaminant data for 12 monitoring sites.

1. Lower Columbia River near Clatskanie, Oregon

Elevated levels of chlorinated pesticides (CPs) and PCBs have been reported in the Lower Columbia River (Tetra Tech, 1996) (Johnson and Norton, 2005) (McCarthy et al., 1999). Increasing concentrations of PBDEs were found Ecology's statewide study for detecting PBDEs found in Ecology's statewide PBDE (Johnson et al. 2006). Fish consumption advisories for CPs, PCBs, and DDT as well as water quality violations for CP, DDE, dieldrin, and PAHs, are listed by Oregon and Washington.

2. Middle Columbia River at McNary Dam

Elevated levels of CPs and PCBs have been reported in fish tissue water quality violations for p,p' DDE, aldrin, chlordane, dioxin, and PCBs have led to 303(d) listings in the area between Rock Island Dam and McNary Dam.

3. Upper Columbia River at Rock Island Dam

The WSTMP found elevated concentrations of PCBs and DDT in fish tissue near Rock Island Dam. 303(d) listed contaminants for the upper Columbia River area included DDTs and PCBs. Known sources of CPs and PCBs enter the Columbia River above Rock Island Dam from Wenatchee, Okanogan, Spokane, and Lake Chelan tributaries. Concentrations of PBDEs have also been reported (Rayne et al., 2003; Seiders et al., 2007; Johnson et al., 2006).

4. Lower Green/Duwamish River

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

5. Lake Washington

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

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

6. Snohomish River

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

7. Wenatchee River

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

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

8. Okanogan River

Ecology has consistently found high levels of DDT in fish tissue from the Okanogan River. A TMDL evaluation was conducted for DDT and PCB compounds in 2004, and a cleanup plan is in place (Peterschmidt, 2004).

9. Yakima River at Wanawish Dam

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

10. Walla Walla River

Elevated levels of DDT compounds, dieldrin, toxaphene, chlordane, hexachlorobenzene, heptachlor epoxide, and PCBs have been reported in fish tissue (Davis et al., 1995; Johnson et al., 2004). A TMDL has been completed and a cleanup plan developed for CP and PCBs (Johnson et al., 2004; Gray et al., 2006). Fish consumption advisories currently exist for PCBs in this river (WDOH, 2006).

11. Spokane River at Nine Mile Dam

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

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

12. Queets River

This site was chosen for a reference site. It was also used as reference for the 2005-2006 PBDE survey (Johnson et al., 2006).

Appendix B. Semipermeable Membrane Devices

In order to effectively sample the expected low-water-column concentrations, a passive sampling technique employing semipermeable membrane devices (SPMDs) was used to concentrate and quantify the chemicals of interest.

SPMDs were designed to mimic the bioconcentration (uptake) of organic pollutants from water by aquatic organisms and SPMDs can sample up to 10 liters of water a day depending on the compound in question (Meadows et al., 1998; Huckins et al., 2006). There are more than 180 peer-reviewed publications in the open scientific literature where SPMDs have been used for detecting chemical contaminants in the environment (Huckins et al., 2006).

Analytes targeted for this project were suitable for monitoring using SPMDs because SPMDs can take up a wide range of organic compounds generally with log $K_{ow} \geq 3$ (octanol-water partition coefficient, which is a measure of bioaccumulation potential). When placed in water, dissolved lipophilic organic compounds diffuse through the membrane and are concentrated over time.

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

- SPMDs measure long-term average concentrations of chemicals. Therefore, random fluctuations are smoothed and representation of the data is improved.
- Standardized SPMD design yields good reproducibility, improving comparisons within and between sampling sites.
- Large chemical residues accumulated in SPMDs give a strong analyte signal, translating into parts-per-trillion detection limits or lower.
- SPMDs are relatively easy compared to most other low-level sampling techniques.
- A wide range of chemicals can be sequestered by each SPMD, reducing the cost of sampling efforts.

Disadvantages of SPMDs compared to other sampling methods are: (1) an increased chance of data gaps due to vandalism or loss of the SPMDs in the waterbody; and (2) contamination from air while the membranes are prepared, deployed, retrieved, and transported to the laboratory.

Total chemical concentrations determined from SPMDs are estimates based on organic carbon-water equilibrium partitioning. The dissolved component is the assumed fraction available for uptake by fish. This is not a significant drawback in the present 2007 PBT Trends Study because the study is driven by human health concerns for fish consumption (Johnson, 2007).

PRCs

The amount of chemical absorbed by an SPMD is proportional to the local water column concentration and is representative of that chemical’s environmental bioavailability. To account for the effects of temperature, water velocity, and biofouling on absorption, permeability/ performance reference compounds (PRCs) were used as an in-situ calibration method. PRCs are (analytically) non-interfering compounds with moderate to high tendency to escape. The rate of PRC loss during an exposure is related to the uptake of the target compound. The assumption that PRCs with log K_{ow}s ≤ 5.0 can be used to predict an exposure adjustment factor (EAF) of chemicals with much higher log K_{ow}s appears valid based on studies performed by Huckins et al. (2002). These studies showed that the difference between measured concentrations of an analyte and the PRC-derived estimates were within a factor of 2.

200 ng/SPMD of PCB-004, PCB-029, and PCB-050 (log K_{ow} 4.65, 5.60, and 5.63 respectively) were used as PRCs for all analytes in this study. These PCBs are not found in significant amounts in commercial PCB mixtures or environmental samples. Huckins et al. (2006) showed that PRC-derived sampling rates can be used to calculate reasonably accurate relative sampling rates for PCBs, PAHs, HCHs/chlorobenzenes, and organochlorine (and other hydrophobic) pesticides. Even in biofouled SPMDs, although there is limited evidence, PRCs and corresponding native compounds have been found to be similarly reduced, and their sampling rates were within 1.5 fold of each other (Huckins et al. 2006).

For typical SPMD deployments of 3 to 6 weeks, PRCs with low log K_{ow} values tend to dissipate to below the detection limit. Extrapolation for low log K_{ow} compounds (less than the PRCs) typically have attained a substantial degree of equilibrium, resulting in water column concentration estimates insensitive to uncertainties in the sampling rates (Huckins et al. 2006).

The dissipated amount for PRCs with high log K_{ow} values is usually too small to quantify. Extrapolating PRC-based sampling rates for high log K_{ow} (log $K_{ow\ >}$7) compounds was argued that the decrease in sampling rates with increasing molecular size is small enough to be neglected or can be calculated by accounting for sorption to DOC.

The uncertainty factor for estimating concentrations of compounds in water using PRCs in this study was calculated from the antilog of the standard deviation of the log-based a_{oPRC} values: the intercept values of PRCs. The uncertainties of the estimated concentrations in water were about ± 1.5 fold, ranging from 1.15 to 1.74.

Log K_{ow}s

Analytes missing log K_{ow}s in the USGS spreadsheet included toxaphene, aldrin, endrin ketone, endrin aldehyde, DDMU, chlordane, and PBDEs. Values for log K_{ow}s found in literature were used. If multiple log K_{ow} values were found, a mean value was selected following the USGS technique. This technique uses the t test at 95% confidence for rejection of outliers (USGS, 2008; Alvarez, 2008).

Where no log K_{ow}s were found in literature, log K_{ow}s were calculated using an atom/fragment calculation developed by Syracuse Research Corporation (Meylan et al. 1995). Braekevelt et al. (2003) compared experimental and calculated PCB log K_{ow}s (PCB-180, -202, 2-6, and -209). They found that calculated values for the lower range log K_{ow}s (e.g. 7.36-8.27) were fairly close to experimental values (e.g. 7.36), whereas in the higher end of the range (e.g. 8.91-10.2), the calculated values were considerably higher than the experimental values (e.g. 8.27), often by over an order of magnitude. Braekevelt explains that the fragmented values are determined empirically from small molecules. Therefore, minor differences can result in large errors when multiple fragments are added. Mid to lower log K_{ow}s (4.8-6.3) were calculated for endrin ketone, endrin aldehyde, DDMU, and chlordane (technical).

Some log K_{ow}s were estimated using similar chemicals. Log K_{ow}s from PBDE-47, -69, -183, -190 log K_{ow}s were used for analytes PBDE-49, -71, -184, -191 respectively since these data were missing from the above described methods as of the date of this printing. This estimation seemed reasonable based on other PBDE congeners that are consecutive to each other having similar log K_{ow}s. USGS estimated the log K_{ow} for chlorpyrifos from Endrin because of its proximity in log K_{ow} values (USGS, 2008).

Because of the uncertainties previously stated, all calculated water concentrations should be considered estimates. Log K_{ow}s used in calculating water concentration can be found in Appendix C.

Log K_{ow}s for the USGS Estimated Water Concentration spreadsheet should be available for additional analytes in future upgrades. The equations behind the spreadsheet and 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).

Appendix C. Log K_{ow}s Used in the USGS Estimated Water Concentration Calculator Spreadsheet for the 2007 PBT Trends Study

Table C-1. Log K_{ow}s Used in the USGS Data Calculation Spreadsheet of Water Concentrations for the 2007 PBT Trends Study.

Organochlorine Pesticides	**Log K_{ow}**	**Reference**
p,p'-DDT	5.5	a
p,p'-DDE	6.1	a
p,p'-DDD	5.8	a
o,p'-DDT	5.6	a
o,p'-DDE	5.6	a
o,p'-DDD	6.1	a
DDMU	5.5	e
Dieldrin	4.6	a
Chlorpyrifos	4.9	f
Endosulfan I	3.8	a
Endosulfan-II	3.5	e
Endosulfan Sulfate	3.6	e
Hexachlorobenzene (HCB)	5.7	a
Pentachloroanisole (PCA)	5.5	b, e
Toxaphene	4.7	a
Chlordane (technical)	6.3	e
trans-Chlordane	5.38	a, c, d, e
cis-Chlordane	5.4	a, c, d, e
Dacthal	4.26	e
trans-Nonachlor	6.35	c, e
cis-Nonachlor	6.2	c, e
Heptachlor	5.19	a
Heptachlor Epoxide	4.51	a
alpha-Benzenehexachloride (a-BHC)	3.9	a
beta-Benzenehexachloride (b-BHC)	3.86	a
delta-Benzenehexachloride (d-BHC)	4.12	a
Lindane	3.71	a
Aldrin	6.0	e, i
Endrin	4.6	a
Endrin ketone	5.0	e
Endrin aldehyde	4.8	e
Mirex	6.9	a
p,p'-Methoxychlor	4.6	a
Oxychlordane	5.48	e

Individual PBDE Congeners	**Log K_{ow}**	**Reference**
IUPAC No.		
47	6.2	h, j
49	6.2	f
66	6.3	j
71	6.0	f, j
99	6.8	h, j
100	6.6	h, j
138	7.6	j
153	7.2	h, j
154	7.4	h, j
183	7.7	h, j
184	8.3	f
191	8.4	f, j
209	10.0	j

PCBs	**Log K_{ow}**	**Reference**
Total PCB	6.38	g

If multiple log K_{ow} values were found in the literature, a mean value was selected using the t test at 95% Confidence for rejection of outliers (USGS 2008 and Alvarez 2008).

[a] Mackay, D.; Shiu, W-Y; Ma, K-C Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume V, Lewis Publishers, Boca Raton, 1997.

[b] Oliver, B.G.; Niimi, A.J. Environ. Sci. Technol., 1985, 19:9, 842-849.

[c] Simpson, C.D.; Wilcock, R.J.; Smith, T.J.; Wilkins, A.L.; Langdon, A.G. Bull. Environ. Contam. Toxicol., 1995, 55:1, 149-153.

[d] Veith, G.D.; DeFoe, D.L.; Bergstedt, B.V. J. Fish Res. Board Can., 1979, 36, 1040-1048.

[e] Syracuse Research Corporation, On-Line Log K_{ow} Estimator (KowWin), http://esc.syrres.com/interkow/logkow.htm.

[f] Chlorpyrifos, PBDE-49, -71, -184, and -191 values estimated from Endrin (USGS 2008), PBDE-47, -69, -183, and -190 respectively, due to their proximity in Log K_{ow} values.

[g] Hawker, D.W. and Connell, D.W. Environ. Sci. Technol, 1988, 22, 382-387.

[h] Braekevelt, E., S.A. Tittlemier, and G.T. Tomy, 2003. Direct Measurement of Octanol-water Partition coefficients of Some Environmentally Relevant Brominated Diphenyl Ether Congeners. Chemosphere 51 (7):563-567.

Rantalainen, A.L., W. Cretney, and M.G. Ikonomou, 2000. Uptake Rates of Semipermeable Membrane Devices (SPMDs) for PCDDs, PCDFs, and PCBs in Water and Sediment. Chemosphere 40 (2): 147-158.

[i] Mackay, D.; Shiu, W-Y; Ma, K-C Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume IV, Lewis Publishers, Boca Raton, 2006.

[j] Mackay, D.; Shiu, W-Y; Ma, K-C Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume III, Lewis Publishers, Boca Raton, 2006.

Appendix D. Chemicals Analyzed in SPMD Samples

Table D-1. Chemicals 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-49
PBDE-66
PBDE-71
PBDE-99
PBDE-100
PBDE-138
PBDE-153
PBDE-154
PBDE-183
PBDE-184
PBDE-191
PBDE-209

*PBTs as defined by Ecology.

**Polychlorinated Biphenyls

Approximately 150 PCB congeners
(and remainder as co-eluting groups).

Appendix E. Data Quality Summary

Laboratory Case Narrative Summary

Manchester Laboratory prepared written case narratives assessing the quality of the data collected during the 2007 spring and fall sampling events. These reviews include a description of analytical methods, assessment of holding times, calibration and verification checks, degradation checks, on-going precision and recovery assessments, method blanks, matrix spike/matrix spike duplicate recoveries, qualitative identification, laboratory control samples, surrogate recoveries, laboratory replicates, and internal standards checks. Case narratives are available upon request. An overview of the data quality for the 2007 PBT Trends Study is summarized below.

Pesticides

All calibration checks were within Quality Control (QC) limits with a few exceptions of undetected results which were qualified as undetected estimates (UJ). Endosulfan II in the spring samples for the Yakima (sample number 07284807) and Walla Walla Rivers (07284809) may be biased high because the continuing calibration verification was reported above the acceptable QC limit. These results were qualified as an estimate (J).

Recoveries of pesticide surrogates spiked into the fall 2007 samples from the Lower Columbia River (07404800), Lake Washington (07404802), Yakima River (07404807), and Spokane River (07404810) were below the acceptable QC limits of 50-150%. These results may be biased low and were qualified as an estimate (J).

Qualitative identification was made for all pesticide analytes in the 2007 spring sampling and for most analytes in the fall sampling although several analyte results were qualified as estimates (J) having a relative percent difference (RPD) greater than 40%. Chromatographic interferences precluded proper identification for endosulfan II at the Lower and Middle Columbia River (07404800 & 07404808), Beta-BHC at Duwamish River (07404801), and DDMU at Lower Columbia River (07404800), Lake Washington (07404802), Okanogan River (07404806), Middle Columbia River (07404808), and Spokane River (07404810). These were qualified as estimates at a reporting limit raised to the level of the interference (UJ).

Analytes spiked before extraction for evaluation of the dialysis process, termed “Matrix Spike,” resulted in most recoveries within the QC limit of 50-150%. For both spring and fall sampling events, analytes that had recoveries below the QC limit included d-BHC, chlorpyrifos, endrin aldehyde, endosulfan sulfate, and dacthal. For only the fall samples, methoxychlor was below the QC limit. These results may be biased low and were qualified as estimates (J).

Concentrations of technical chlordane and toxaphene were determined using 3-10 of the most prominent homologs for averaging and comparing to a commercial standard. Because these analytes are subject to weathering (processes in the environment that degrade) the homologues, the pattern ratios are rarely the same as the commercial standards. Therefore, if the homologs exceeded 40% RPD, the results were reported as estimated concentrations (J). Most of the 2007 spring and fall samples were estimated.

PCBs

All surrogate and matrix spike recoveries were within the acceptable QC range of 50-150%. The fall matrix spike sample resulted in an elevated concentration of PCB-004 due to the membrane being spiked with PRCs. Once calculated for the addition of the analyte, the percent recovery was well within the QC limit.

Low levels of certain compounds were detected in the laboratory blanks in both spring and fall samples and maybe, at least partially, attributed to the background. Concentrations in most samples were greater than ten times that of the corresponding method blank results, which was considered insignificant relative to the native concentration detected in the sample. The exceptions included some compounds in the matrix spike, which were qualified as not detected at or above the reported result (UJ).

PCB-011 was not only found in the matrix spike but also in eight field samples and the manufacturing blank for the fall sampling at concentrations less than ten times that of the blank. The concentration level of PCB-011 found in the method blank was about ten times higher than the other PCBs found. The sample results were qualified the same as not detected at or above the reported result (UJ).

Internal standard recoveries were all within QC limits for all labeled compounds except for six results in the fall samples for PCB-001. These were qualified as estimates (J).

Almost all congeners met the isotopic abundance ratio and retention time criteria for positive identification. The exceptions were flagged but were included in the totals for corresponding homologs.

Laboratory spike samples were recovered within the QC limits (30-140%) showing high accuracy. Spiked duplicates had RPDs of less than 7% for both spring and fall, indicating good precision.

Field Quality Control Samples

SPMDs

All SPMDs were retrieved or accounted for during the 2007 spring and fall sampling events. SPMDs were checked for presence midway (two weeks) during the deployment. During the midcheck, the SPMDs were gently swished under water to remove loose sedimentation or biofouling.

A second deployment was necessary at the Snohomish River because of air exposure due to low tides in the spring. Fresh SPMDs from the same batch as the original SPMDs were deployed two weeks later.

The Okanogan River SPMD was compromised in the spring sampling due to heavy sedimentation. The whole canister containing the membranes was buried. No replacement was available.
The Spokane River SPMD and its field replicate were combined in the spring sampling due to the water being drawn down at the dam, exposing the top half of each five-membrane canister to the air. Only the submerged, bottom membranes were used to assure integrity. Unfortunately, this sample was rejected because of an accident in the laboratory resulting in > 60% loss of extract.

Replicate Samples

Two SPMD canisters (five membranes in each canister) were deployed in the Spokane River for each sampling period in 2007 (spring and fall) to estimate total variability (field + laboratory). The spring field replicate was unusable as mentioned above. Results from the fall replicate sample are listed in Appendix G.

The pesticide, PBDE, and PCB residue results per SPMD agreed fairly well and were relatively close to the QC limit of 20% RPD. RPDs for chlordane, trans-chlordane, and T-PCBs were somewhat elevated (27%, 24% and 29% respectively). Precision of PRC recovery was good (<12% RPD).

Field Trip and Day0-Dialysis Blanks

One blank with five membranes was manufactured for each of the spring and fall sampling periods. The field trip blank was used to assess air contamination during the deployment and retrieval of the SPMDs in the field. The Day0-Dialysis blank was used to assess contamination during the manufacturing and processing at EST laboratory.

The field trip blank sealed in an argon-filled stainless steel can was opened. The can was then swished back and forth for mixing in the air for the average amount of time the field samples were exposed during deployment. (In one field trip blank exposure, the membranes were carefully taken out of the can for air exposure).The blank was resealed and stored frozen until retrieval. During retrieval of the samples, the field trip blank was taken back into the field, opened, and exposed to the air for the average amount of time the field samples were exposed during retrieval. The blank was prepared, processed, and analyzed the same as the field samples.

The Queets River was chosen for the blank exposure for the 2007 sampling events. Total time the blank was exposed to air was close to two minutes for each spring and fall sampling event.

Using a single field trip blank in one field location may not appropriately represent potential air contamination for all sites statewide. It is also difficult to address the uncertainty of the data results from a single sample. Additional blanks will be used at other sites in the future.

The Day0-Dialysis blank, manufactured identical to the field samples, was held frozen at EST during the sampling period. After the sampling period, EST exposed the blank to the same air time and laboratory handling procedures used during the processing of the field samples.

The results of the field trip blank and the Day0-Dialysis blank analysis are in included in Appendix F. Gamma-BHC (Lindane), PBDE-47, -99, -100, -153, -154, -184, and certain PCB congeners were detected in the spring field blank, whereas only PBDE-47, -99, -100, and certain PCB congeners were detected in the fall field blank. These same compounds were detected in the Day0-Dialysis blank manufactured at the same time as the field-deployed SPMDs at almost identical levels of concentrations. The Day0-Dialysis blank remained at the manufacturing laboratory, which indicates a contamination source at the laboratory. Contaminant concentrations in the Day0-Dialysis blanks were found at levels much greater than 10% of the sample levels, with most over 50% of the sample concentration. Therefore, field trip blank concentrations were subtracted from the measured results in the field samples before calculating water column concentrations.

TidbiTs

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

Upon retrieval, the data were downloaded and charted for comparing the water and air temperature. If the SPMDs were compromised by being out of the water, a spike in water temperature appeared on the graph and followed the same temperature values as the air during the time period the SPMDs were exposed to the air.

All results used in this study were from SPMDs that remained submerged during the monitoring period. Although the initial deployment of the spring sampling of the Snohomish River was exposed to air due to low tides (Figure E-1), another set of SPMDs were deployed for 28 days, the same length of time as the other samples.

Because of water drawdown on the Spokane River in the spring, the top half of the Spokane and Spokane replicate SPMD samplers were exposed to air. This was not apparent from the TidbiTs™ as they were attached to the bottom of the canister rather than the top. During future deployments, TidbiTs™ were attached to the top of the canister to assess any compromises.

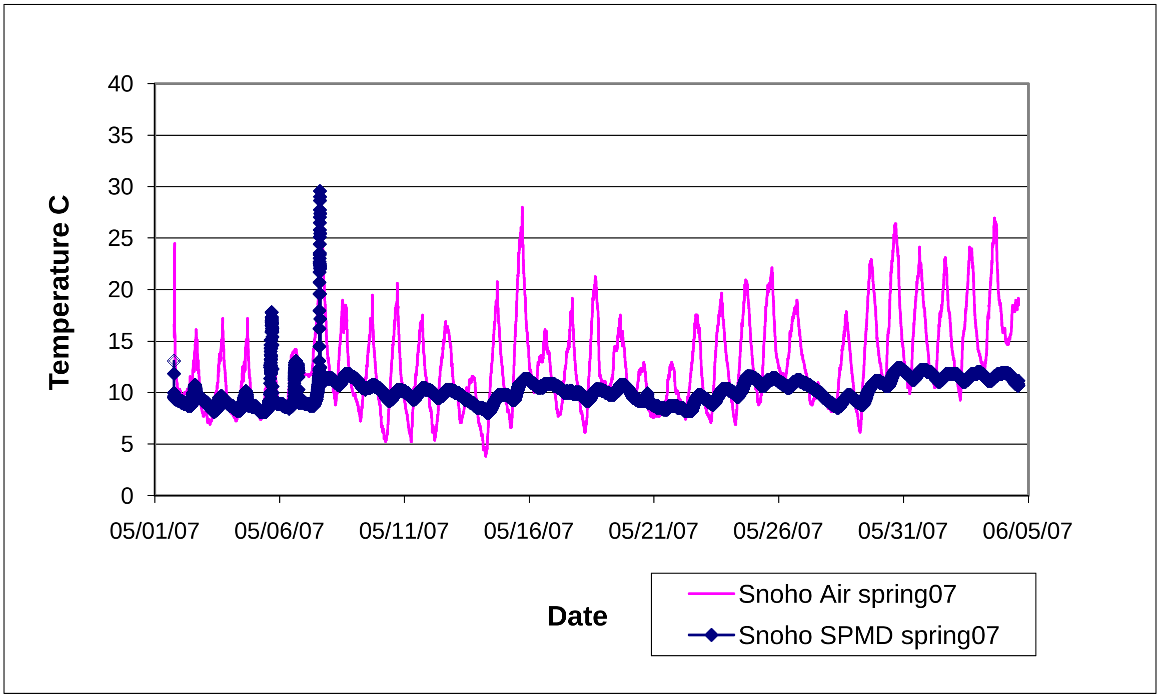

Figure E-1. Snohomish River TidbiT Temperature Monitoring. Spiked SPMD Temperature Resulted From Low Tides Exposing SPMDs to Air.

Appendix F. Pesticide and PCB Residues in SPMD Extracts

Table F-1. Pesticides and PCBs Measured in SPMD Extracts, April – May 2007 (ng/5-SPMDs).

Site:	Lower Columbia River	Duwamish River	Lake Washington	[†]Snohomish River	Wenatchee River	Upper Columbia River	*Okanogan River
Sample number:	7284800	7284801	7284802	7284803	7284804	7284805	784806
p,p'-DDT	12 J	10 U	10 U	10 U	28 J	12 J	no data
p,p'-DDE	74	10 U	10 U	10 U	60	75	"
p,p'-DDD	61	10 U	10 U	10 U	24	71	"
o,p'-DDT	10 U	10 U	10 U	10 U	11	10 U	"
o,p'-DDE	10 U	10 U	10 U	10 U	10 U	10 U	"
o,p'-DDD	23	10 U	10 U	10 U	10 U	10 U	"
DDMU	21 J	10 U	10 U	10 U	10 U	26	"
Dieldrin	20	10 U	31	10 U	10 U	10 U	"
Chlorpyrifos	54 J	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"
Endosulfan I	33	14	10 U	10 U	93	27	"
Endosulfan-II	10 U	10 U	10 U	10 U	20	10 U	"
Endosulfan Sulfate	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"
Hexachlorobenzene (HCB)	36	13 J	10 U	10 U	14 J	14 J	"
Pentachloroanisole (PCA)	32 J	45 J	27 J	26 J	22	18 J	"
Toxaphene	110 J	100 U	100 U	100 U	100 U	100 U	"
Chlordane (technical)	100 U	100 U	100 U	100 U	100 U	100 U	"
trans-Chlordane	12 U	10 U	10 U	10 U	10 U	10 U	"
cis-Chlordane	10 U	10 U	10 U	10 U	10 U	10 U	"
Dacthal	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"
trans-Nonachlor	10 U	10 U	10 U	10 U	10 U	10 U	"
cis-Nonachlor	10 U	10 U	10 U	10 U	10 U	10 U	"
Heptachlor	10 U	10 U	10 U	10 U	10 U	10 U	"
Heptachlor Epoxide	10 U	10 U	10 U	10 U	10 U	10 U	"

Site:	Lower Columbia River	Duwamish River	Lake Washington	†Snohomish River	Wenatchee River	Upper Columbia River	*Okanogan River
Sample number:	7284800	7284801	7284802	7284803	7284804	7284805	784806
a-BHC: alpha-Benzenehexachloride	10 U	10 U	10 U	10 U	10 U	10 U	"
b-BHC: beta-Benzenehexachloride	10 U	10 U	10 U	10 U	10 U	10 U	"
d-BHC: delta-Benzenehexachloride	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"
Lindane: gamma-Benzenehexachloride	10 U	11	10 U	10 U	11	10 U	"
Aldrin	10 U	10 U	10 U	10 U	10 U	10 U	"
Endrin	10 U	10 U	10 U	10 U	10 U	10 U	"
Endrin ketone	10 U	10 U	10 U	10 U	10 U	10 U	"
Endrin aldehyde	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"
Mirex	10 U	10 U	10 U	10 U	10 U	10 U	"
p,p'-Methoxychlor	10 U	13 UJ	10 U	10 U	10 U	10 U	"
Oxychlordane	10 U	10 U	10 U	10 U	10 U	10 U	"
Total PCB	260 J	180 J	140 J	120 J	140 J	100 J	"

U = not detected at or above reported result
UJ = not detected at or above reported estimated result
J = estimated concentration

† Four SPMD membranes per composite
* SPMD field compromised by sedimentation or water drawdown
**Data Rejected. Spokane River extract >60% lost in lab accident

Table F-1. (continued)

Site:	Yakima River	Middle Columbia River	Walla Walla River	†*Spokane River	Queets River	*RepSpok	Field Trip Blank	Day 0 Dial
Sample number:	7284807	7284808	7284809	7284810	7284811	7284812	7284813	7284820
p,p'-DDT	36 J	10 U	31	10 UJ	10 U	no data	10 U	10 U
p,p'-DDE	340	49	140	10 UJ	10 U	"	10 U	10 U
p,p'-DDD	80	38	4.7	10 UJ	10 U	"	10 U	10 U
o,p'-DDT	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
o,p'-DDE	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
o,p'-DDD	10 U	15	19 J	10 UJ	10 U	"	10 U	10 U
DDMU	29	13 J	24 J	10 UJ	10 U	"	10 U	10 U
Dieldrin	50	10 U	38	10 UJ	10 U	"	10 U	10 U
Chlorpyrifos	600 J	40 J	1800 J	10 UJ	10 UJ	"	10 UJ	10 UJ
Endosulfan I	120	43	33	10 UJ	10 U	"	10 U	10 U
Endosulfan-II	16 J	10 U	25 J	10 UJ	10 U	"	10 U	10 U
Endosulfan Sulfate	16 J	10 UJ	17 J	10 UJ	10 UJ	"	10 UJ	10 UJ
Hexachlorobenzene (HCB)	19 J	15 J	66 J	14 J	10 U	"	10 U	10 U
Pentachloroanisole (PCA)	29 J	19 J	19 J	25 J	11 J	"	10 U	10 U
Toxaphene	230 J	100 U	1300 J	120 UJ	100 U	"	100 U	100 U
Chlordane (technical)	100 U	100 U	120 J	100 UJ	100 U	"	100 U	100 U
trans-Chlordane	10 J	10 U	16	10 UJ	10 U	"	10 U	10 U
cis-Chlordane	10 U	10 U	13	10 UJ	10 U	"	10 U	10 U
Dacthal	10 UJ	15 J	10 UJ	10 UJ	10 UJ	"	10 UJ	10 UJ
trans-Nonachlor	10 U	10 U	12 J	10 UJ	10 U	"	10 U	10 U
cis-Nonachlor	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Heptachlor	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Heptachlor Epoxide	10 U	10 U	16	10 UJ	10 U	"	10 U	10 U

Site:	Yakima River	Middle Columbia River	Walla Walla River	†*Spokane River	Queets River	*RepSpok	Field Trip Blank	Day 0 Dial
Sample number:	7284807	7284808	7284809	7284810	7284811	7284812	7284813	7284820
a-BHC: alpha-Benzenehexachloride	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
b-BHC: beta-Benzenehexachloride	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
d-BHC: delta-Benzenehexachloride	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"	10 UJ	10 UJ
Lindane: gamma-Benzenehexachloride	10 U	10 U	130	10 UJ	11	"	15	18
Aldrin	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Endrin	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Endrin ketone	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Endrin aldehyde	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	"	10 UJ	10 UJ
Mirex	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
p,p'-Methoxychlor	17 UJ	10 U	10 UJ	10 UJ	10 U	"	10 U	10 U
Oxychlordane	10 U	10 U	10 U	10 UJ	10 U	"	10 U	10 U
Total PCB	160 J	160 J	160 J	72 J	120 J	"	85 J	100 J

U = not detected at or above reported result
UJ = not detected at or above reported estimated result
J = estimated concentration

† Four SPMD membranes per composite
* SPMD field compromised by sedimentation or water drawdown
**Data Rejected. Spokane River extract >60% lost in lab accident

Table F-2. Pesticides and PCBs Measured in SPMD Extracts, August – September 2007 (ng/5-SPMDs).

Site:	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River
Sample Number:	7404800	7404801	7404802	7404803	7404804	7404805	7404806
p,p'-DDT	10 J	10 J	10 UJ	10 U	38 J	25 J	13 J
p,p'-DDE	78 J	10 U	20 J	10 U	92	260	66
p,p'-DDD	63 J	10 U	34 J	10 U	27	360	29
o,p'-DDT	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
o,p'-DDE	10 UJ	10 U	10 UJ	10 U	10 U	15 J	10 U
o,p'-DDD	15 J	10 U	10 UJ	10 U	10 U	94	10 U
DDMU	22 UJ	14 UJ	40 UJ	10 U	18 UJ	72 J	11 UJ
Dieldrin	15 J	12	32 J	10 U	11	10 U	10 U
Chlorpyrifos	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Endosulfan I	10 UJ	32	10 UJ	10 U	50	16	10 U
Endosulfan-II	19 UJ	10 U	10 UJ	10 U	24	10 U	10 U
Endosulfan Sulfate	10 UJ	10 UJ	10 UJ	10 UJ	24 J	10 UJ	10 UJ
Hexachlorobenzene (HCB)	15 J	12	10 UJ	10 U	10 U	11 J	10 U
Pentachloroanisole (PCA)	21 J	39	22 J	20	10 U	10 U	10 U
Toxaphene	120 UJ	100 U	100 UJ	100 U	100 U	100 U	100 U
Chlordane (technical)	100 UJ	100 U	140 J	100 U	100 U	100 U	100 U
trans-Chlordane	10 UJ	10 U	11 J	10 U	10 U	10 U	10 U
cis-Chlordane	10 UJ	10 U	11 J	10 U	10 U	10 U	10 U
Dacthal	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
trans-Nonachlor	10 UJ	10 U	11 J	10 U	10 U	10 U	10 U
cis-Nonachlor	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Heptachlor	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Heptachlor Epoxide	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U

Site:	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River
Sample Number:	7404800	7404801	7404802	7404803	7404804	7404805	7404806
a-BHC: alpha-Benzenehexachloride	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
b-BHC: beta-Benzenehexachloride	10 UJ	23 UJ	10 UJ	10 U	10 U	10 U	10 U
d-BHC: delta-Benzenehexachloride	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Lindane: gamma-Benzenehexachloride	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Aldrin	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Endrin	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Endrin ketone	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Endrin aldehyde	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Mirex	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
p,p'-Methoxychlor	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Oxychlordane	10 UJ	10 U	10 UJ	10 U	10 U	10 U	10 U
Total PCBs	160 J	150 J	170 J	130 J	170 J	150 J	120 J

U = not detected at or above reported result.
UJ = not detected at or above reported estimated result.
J = estimated concentration.

Table F-2. (continued)

Site:	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok	Field Trip Blank	Day 0 Dial
Sample Number:	7404807	7404808	7404809	7404810	7404811	7404812	7404813	7404820
p,p'-DDT	12 J	10 U	13 J	10 UJ	10 U	10 U	10 UJ	10 U
p,p'-DDE	170 J	70	180	10 UJ	10 U	10 U	10 UJ	10 U
p,p'-DDD	51 J	54	33	10 UJ	10 U	10 U	10 UJ	10 U
o,p'-DDT	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
o,p'-DDE	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
o,p'-DDD	10 UJ	14	13 J	10 UJ	10 U	10 U	10 UJ	10 U
DDMU	26 J	20 UJ	30 UJ	11 UJ	10 U	10 U	10 UJ	10 U
Dieldrin	75 J	10	22 J	14 J	10 U	13	10 UJ	10 U
Chlorpyrifos	350 J	17 J	74 J	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Endosulfan I	19 J	12 J	23	10 UJ	10 U	10 U	10 UJ	10 U
Endosulfan-II	10 UJ	17 UJ	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Endosulfan Sulfate	25 J	10 UJ	85 J	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Hexachlorobenzene (HCB)	10 UJ	10	88	16 J	10 U	15	10 UJ	10 U
Pentachloroanisole (PCA)	15 J	10 U	10 U	67 J	10 U	59	10 UJ	10 U
Toxaphene	240 J	100 U	680 J	100 UJ	100 U	100 U	100 UJ	100 U
Chlordane (technical)	100 UJ	100 U	100	170 J	100 U	130	100 UJ	100 U
trans-Chlordane	10 UJ	10 U	10	14 J	10 U	11	10 UJ	10 U
cis-Chlordane	10 UJ	10 U	11	10 J	10 U	10 U	10 UJ	10 U
Dacthal	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
trans-Nonachlor	10 UJ	10 U	14	10 UJ	10 U	10 U	10 UJ	10 U
cis-Nonachlor	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Heptachlor	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Heptachlor Epoxide	10 UJ	10 U	11 J	10 UJ	10 U	10 U	10 UJ	10 U

Site:	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok	Field Trip Blank	Day 0 Dial
Sample Number:	7404807	7404808	7404809	7404810	7404811	7404812	7404813	7404820
a-BHC: alpha-Benzenehexachloride	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
b-BHC: beta-Benzenehexachloride	10 UJ	10 U	10 U	10 UJ	10 U	10 UJ	10 UJ	10 U
d-BHC: delta-Benzenehexachloride	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 U	10 UJ	10 UJ
Lindane: gamma-Benzenehexachloride	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Aldrin	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Endrin	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Endrin ketone	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Endrin aldehyde	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Mirex	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
p,p'-Methoxychlor	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ	10 UJ
Oxychlordane	10 UJ	10 U	10 U	10 UJ	10 U	10 U	10 UJ	10 U
Total PCBs	140 J	200 J	120 J	300 J	140 J	220 J	99 J	100 J

U = not detected at or above reported result.
UJ = not detected at or above reported estimated result.
J = estimated concentration.

Table F-3. PBDEs Measured in SPMD Extracts, April – May 2007 (ng/5-SPMDs).

Site:	Lower Columbia River	Duwamish River	Lake Washington	†Snohomish River	Wenatchee River	Upper Columbia River	*Okanogan River
Station Number:	7284800	7284801	7284802	7284803	7284804	#7284805	784806
PBDE-47	53	26	38	35	33	37	*
PBDE-49	4 U	4 U	4 U	4 U	4 U	4 U	*
PBDE-66	4 U	4 U	4 U	4 U	4 U	4 U	*
PBDE-71	4 U	4 U	4 U	4 U	4 U	4 U	*
PBDE-99	31	19 U	29	29	28	32	*
PBDE-100	8.5	5.1 U	7.4	7.7	7.2	9.2	*
PBDE-138	8 U	8 U	8 U	8 U	8 U	8 U	*
PBDE-153	4.3 J	8 U	4.7 J	4.7 J	4.6 J	4.4 J	*
PBDE-154	4.4 J	8 U	3.9 NJ	3.8 J	4.1 J	3.5 J	*
PBDE-183	3.8 J	8 U	8 U	3.7 J	4 J	8 U	*
PBDE-184	8 U	8 U	8 U	8 U	8 U	8 U	*
PBDE-191	16 U	16 U	16 U	16 U	16 U	16 U	*
PBDE-209	100 U	100 U	100 U	100 U	100 U	100 U	*
Total PBDEs	100 J	26 J	83 J	84 J	81 J	86 J	*

U = not detected at or above reported result.
NJ = approximate tentative identification.
J = estimated concentration.
† Four SPMD membranes per composite.
* SPMD field compromised by sedimentation or water drawdown.

Table F-3. (continued)

Site:	Yakima River	Middle Columbia River	Walla Walla River	†*Spokane River	Queets River	*RepSpok	Field Trip Blank	Day 0 Dial
Station Number:	7284807	7284808	7284809	7284810	7284811	7284812	7284813	7284820
PBDE-47	66	37	54	69	35	**	21	50
PBDE-49	6.2	4 U	4 U	4 U	4 U	**	4 U	4 U
PBDE-66	4 U	4 U	4 U	4 U	4 U	**	4 U	4 U
PBDE-71	4 U	4 U	4 U	4 U	4 U	**	4 U	4 U
PBDE-99	37	28	35	35	31	**	19	51
PBDE-100	9.4	7.3	9.8	8.9	7.7	**	5	12
PBDE-138	8	8 U	8 U	8 U	8 U	**	8 U	8 U
PBDE-153	5 J	4.4 J	4.8 J	3.7 J	4.1 J	**	4.6 J	7.3 J
PBDE-154	8 U	4 J	4.3 J	4.2 J	3.7 J	**	3 J	5.1 J
PBDE-183	5.4 J	2.5 J	6.4 J	8 U	3.7 J	**	3 J	4.8 J
PBDE-184	8	8 U	8 U	8 U	8 U	**	8 U	8 U
PBDE-191	16 U	16 U	16 U	16 U	16 U	**	16 U	16 U
PBDE-209	100 U	100 U	100 U	100 U	100 U	**	100 U	100 U
Total PBDEs	140 J	83 J	110 J	120 J	85 J	**	56 J	130 J

U = not detected at or above reported result.
J = estimated concentration.
† Four SPMD membranes per composite.
**Data Rejected. Spokane River extract >60% lost in lab accident.

Table F-4. PBDEs Measured in SPMD Extracts, August – September 2007 (ng/5-SPMDs).

Site:	Lower Columbia River		Duwamish River		Lake Washington		Snohomish River		Wenatchee River		Upper Columbia River		Okanogan River	
Station Number:	7404800		7404801		7404802		7404803		7404804		7404805		7404806	
PBDE-47	59		40		49		31		19		26		29	
PBDE-49	4	U	4	U	4	U	4	U	4	U	4	U	4	U
PBDE-66	4	U	4	U	4	U	4	U	4	U	4	U	4	U
PBDE-71	4	U	4	U	4	U	4	U	4	U	4	U	4	U
PBDE-99	26		26		49		20		11		14		18	
PBDE-100	9.9		6.6		8.9		5.4		4	U	4.8		5.4	
PBDE-138	8	U	8	U	8	U	8	U	8	U	8	U	8	U
PBDE-153	8	U	8	U	4.4	J	8	U	8	U	8	U	8	U
PBDE-154	8	U	8	U	8	U	8	U	8	U	8	U	8	U
PBDE-183	8	U	8	U	8	U	8	U	8	U	8	U	8	U
PBDE-184	8	U	8	U	8	U	8	U	8	U	8	U	8	U
PBDE-191	8	U	8	U	8	U	8	U	8	U	8	U	8	U
PBDE-209	100	U	100	U	100	U	100	U	100	U	100	U	100	U
Total PBDEs	95	J	72	J	110	J	56	J	30	J	45	J	52	J

U = not detected at or above reported result.
J = estimated concentration.

Table F-4. (continued)

Site:	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok	Field Trip Blank	Day 0 Dial
Station Number:	7404807	7404808	7404809	7404810	7404811	7404812	7404813	7404820
PBDE-47	31	29	21	230	39	210	20	21
PBDE-49	4 U	4 U	4 U	11	4 U	9.9	4 U	4 U
PBDE-66	4 U	4 U	4 U	5	4 U	6.2	4 U	4 U
PBDE-71	4 U	4 U	4 U	4 U	4 U	4 U	4 U	4 U
PBDE-99	14	15	9	100	21	100	14	14
PBDE-100	5	4 U	5	26	5	25	4 J	4
PBDE-138	8 U	8 U	8 U	8 U	8 U	8 U	8 U	8 U
PBDE-153	8 U	8 U	8 U	5.6 J	8 U	6.1 J	8 U	8 U
PBDE-154	8 U	8 U	8 U	5.3 J	8 U	4.9 J	8 U	8 U
PBDE-183	8 U	8 U	8 U	8 U	8 U	7.3 J	8 U	8 U
PBDE-184	8 U	8 U	8 U	8 U	8 U	8 U	8 U	8 U
PBDE-191	8 U	8 U	8 U	8 U	8 U	8 U	8 U	8 U
PBDE-209	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U
Total PBDEs	50 J	44 J	35 J	380 J	65 J	370 J	37 J	40 J

U = not detected at or above reported result.
J = estimated concentration.

Appendix G. Field Replicate Results

Table G-1. Field Replicate Results, August – September 2007.

Residue Accumulated in SPMD (ng/5-SPMDs)						Estimated Water Column Concentration pg/L)				
Parameter	Spokane River		RepSpok		RPD %	Spokane River		RepSpok		RPD %
p,p'-DDT	10	UJ	10	U		4.6	UJ	4.6	U	
p,p'-DDE	10	UJ	10	U		4.7	UJ	4.6	U	
p,p'-DDD	10	UJ	10	U		4.4	UJ	4.4	U	
o,p'-DDT	10	UJ	10	U		4.5	UJ	4.5	U	
o,p'-DDE	10	UJ	10	U		4.5	UJ	4.5	U	
o,p'-DDD	10	UJ	10	U		4.6	UJ	4.6	U	
DDMU	11	UJ	10	U		5.0	UJ	4.6	U	
Dieldrin	14	J	13		7	14	J	13		7
Chlorpyrifos	10	UJ	10	UJ		21	UJ	21	UJ	
Endosulfan I	10	UJ	10	U		220	UJ	220	U	
Endosulfan-II	10	UJ	10	U		460	UJ	460	U	
Endosulfan Sulfate	10	UJ	10	UJ		320	UJ	320	UJ	
Hexachlorobenzene (HCB)	16	J	15		6	7.1	J	6.6		7
Pentachloroanisole (PCA)	67	J	59		13	31	J	27		14
toxaphene	100	UJ	100	U		82	UJ	82	U	
Chlordane (technical)	170	J	130		27	82	J	62		28
trans-Chlordane	14	J	11		24	6.7	J	5.2		25
cis-Chlordane	10	J	10	U		4.8	J	4.7	U	
Dacthal	10	UJ	10	UJ		19	UJ	19	UJ	
trans-Nonachlor	10	UJ	10	U		5.0	UJ	4.9	U	
cis-Nonachlor	10	UJ	10	U		4.7	UJ	4.7	U	
Heptachlor	10	UJ	10	U		5.2	UJ	5.2	U	
Heptachlor Epoxide	10	UJ	10	U		12	UJ	12	U	

Residue Accumulated in SPMD (ng/5-SPMDs)				**Estimated Water Column Concentration pg/L)**		
Parameter	Spokane River	RepSpok	RPD %	Spokane River	RepSpok	RPD %
a-BHC: alpha-Benzenehexachloride	10 UJ	10 U		47 UJ	47 U	
b-BHC: beta-Benzenehexachloride	10 UJ	10 UJ		47 UJ	47 U	
d-BHC: delta-Benzenehexachloride	10 UJ	10 U		25 UJ	25 UJ	
Lindane: gamma-Benzenehexachloride	10 UJ	10 U		68 UJ	68 U	
aldrin	10 UJ	10 U		4.5 UJ	4.5 U	
Endrin	10 UJ	10 U		9.5 UJ	9.5 U	
endrin ketone	10 UJ	10 U		6.1 UJ	6.1 U	
endrin aldehyde	10 UJ	10 UJ		7.5 UJ	7.5 UJ	
Mirex	10 UJ	10 U		6.5 UJ	6.4 U	
p,p'-Methoxychlor	10 UJ	10 UJ		9.8 UJ	9.8 UJ	
Oxychlordane	10 UJ	10 U		4.6 UJ	4.6 U	
Total PCBs	300 J	220 J	29	99 J	61 J	48

J = estimated concentration.
U = not detected at or above reported result.
UJ = not detected at or above reported estimated result.

Table G-2. Field Replicate Results, August – September 2007.

Residue Accumulated in SPMD (ng/5-SPMDs)				**Estimated Water Column Concentration (pg/L) (dissolved)**		
Parameter	Spokane River	RepSpok	RPD %	Spokane River	RepSpok	RPD %
PBDE-47	230	210	9	100	90	12
PBDE-49	11	9.9	12	5.3	4.7	13
PBDE-66	5	6.2	21	2.4	3.0	21
PBDE-71	4 U	4 U		1.8 U	1.8 U	
PBDE-99	100	100	3	54	52	4
PBDE-100	26	25	2	12	12	0
PBDE-138	8 U	8 U		8.1 U	8.1 U	
PBDE-153	5.6 J	6.1 J	9	4.3 J	4.7 J	8
PBDE-154	5.3 J	4.9 J	8	4.7 J	4.3 J	9
PBDE-183	8 U	7.3 J	9	9.0 U	8.2 J	10
PBDE-184	8 U	8 U		14 U	14 U	
PBDE-191	8 U	8 U		15 U	15 U	
PBDE-209	100 U	100 U		600 U	590 U	
Total PBDEs	380 J	370 J	4	180 J	180 J	3

U = not detected at or above reported result.
J = estimated concentration.

Performance/Permeability Reference Compound (percent recovered)			
PRC	Spokane River	RepSpok	RPD %
PCB-004	25	28	11
PCB-029	54	50	8
PCB-050	42	42	0

Appendix H. Mean Water Temperatures and Exposure Times

Table H-1. Mean Temperatures and Exposure Times for the SPMDs, 2007.

Site	April-June		Aug.-Sept.	
	Temp (ºC)	Time (days)	Temp (ºC)	Time (days)
Lower Columbia River	13.6	28.1	19.8	27.9
Duwamish River	**11.9**	**28.0**	**16.5**	**28.0**
Lake Washington	13.1	28.1	20.4	27.8
Snohomish River	10.3	28.0	16.7	27.9
Wenatchee River	8.9	28.0	16.8	27.9
Upper Columbia River at Rock Island Dam	10.3	28.0	19.5	27.9
Okanogan River	11.5	28.0	19.2	27.9
Yakima River at Wanawish Dam	16	27.9	19.7	27.9
Middle Columbia River at McNary Dam	12.6	28.0	20.5	28.0
Walla Walla River	18.3	27.9	19.8	28.0
Spokane River at Nine Mile Dam	13.2	28.3	14.6	28.1
Spokane Replicate	13.3	28.3	14.5	28.1
Queets River	10.8	31.0	14.6	28.0

Appendix I. Performance Reference Compounds (PRC) Recovery in SPMDs

Table I-1. PRC Recovery in 5-SPMDs for the 2007 PBT Trends Study.

Site	Sample No.	PCB #4	PCB #29	PCB #50
April – June				
Lower Columbia River	7284800	18%	54%	57%
Duwamish River	7284801	33%	67%	64%
Lake Washington	7284802	40%	61%	59%
Snohomish River†	7284803	49%	76%	74%
Wenatchee River	7284804	35%	72%	73%
Upper Columbia River at Rock Island Dam	7284805	20%	47%	46%
Okanogan River	7284806	*	*	*
Yakima River at Wanawish Dam	7284807	18%	51%	56%
Middle Columbia River at McNary Dam	7284808	37%	66%	69%
Walla Walla River	7284809	23%	58%	61%
Spokane River at Nine Mile Dam†**	7284810	5%	18%	18%
Spokane Replicate	7284811	*	*	*
Queets River	7284812	41%	66%	63%
August - September				
Lower Columbia River	7284800	4%	23%	21%
Duwamish River	7284801	22%	50%	41%
Lake Washington	7284802	21%	51%	42%
Snohomish River	7284803	35%	60%	51%
Wenatchee River	7284804	35%	59%	48%
Upper Columbia River at Rock Island Dam	7284805	17%	54%	48%
Okanogan River	7284806	31%	61%	52%
Yakima River at Wanawish Dam	7284807	10%	44%	39%
Middle Columbia River at McNary Dam	7284808	27%	62%	52%
Walla Walla River	7284809	8%	41%	38%
Spokane River at Nine Mile Dam	7284810	25%	54%	42%
Spokane Replicate	7284811	28%	50%	42%
Queets River	7284812	23%	61%	53%

† Four SPMD membranes per composite.
* SPMD field compromised by sedimentation or water drawdown.
** Lab accident lost >60% extract.

Appendix J. Streamflow Data

Table J-1. Flow Data for the 2007 PBT Trends Study, Spring.

Flow Data Site Name	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River near Clatskanie	54	USGS	14246900	Columbia R @ Beaver Army Terminal near Quincy, OR	4/30/2007 - 5/28/2007	278,000-338,000	311,015.5
Duwamish River	10[1]	USGS	12113000	Green River near Auburn, WA	5/1/2007 - 5/29/2007	883-1,460	1,126.3
Lake Washington near outlet	na	King Co.	(King County, 2005)	(water level is controlled: fluctuation ~ 2 ft)	5/1/2007 - 5/29/2007	Flushing Rate 0.43 / year	-
Snohomish River	12.5[2]	USGS	12150800 & 12155300	Snohomish River near Monroe, WA Pilchuck River near Snohomish, WA	5/7/2007 - 6/4/2007	8,327-18,670	12,117.6
Wenatchee River	7.1	USGS	12462500	Wenatchee River at Monitor, WA	5/3/2007 - 5/31/2007	5,390-10,700	8,312.6
Upper Columbia River at Rock Island Dam	453.5	USGS	12462600	Columbia River below Rock Island Dam, WA	5/2/2007 - 5/30/2007	148,000-211,000	167,682.3
Okanogan River	17	USGS	12447200	Okanogan River at Malott, WA	5/2/2007 - 5/30/2007	6,410-12,700	9,164.8

Flow Data Site Name	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Yakima River at Wanawish Dam	18	USGS	12510500	Yakima River at Kiona, WA	5/3/2007 - 5/31/2007	3,470-7,150	5,069.3
Middle Columbia River at McNary Dam	292.0[3]	USACE/ USGS	McNary/14019200	Columbia River at McNary Dam near Umatilla, OR	5/3/2007 - 5/31/2007	465,700-578,600	527,885.0
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	5/3/2007 - 5/31/2007	85-672	226.4
Spokane River at Nine Mile Dam	58.1[4]	USGS & Spokane	12422500, 12424000, & (City of Spokane 2008)	Spokane River at Spokane, WA Hangman Creek at Spokane, WA RPWRF Spokane WWTP	5/4/2007 - 6/1/2007	5095-13450	9232.8
Queets River	11.5[5]	USGS	12040500	Queets River near Clearwater, WA	5/4/2007 - 6/4/2007	1,332-2,957	1,786.6

1. Mill and Spring Creeks discharge below the USGS station upstream of the sampling station. Mill and Spring Creeks' historical averaged monthly high discharge is not significant at 34 and 19 cfs respectively.
2. Flow for the Snohomish station was the sum discharge from Snohomish and Pilchuck Rivers.
3. Flow for the McNary site was the sum discharge; Outflow Discharge, Outflow Discharge from Power Generation, and Spillway Outflow Discharge.
4. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Waste Water Treatment Plant. Historical (1995-2007) WWTP contribution ranged from .44-5.27%.
5. Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.

Table J-2. Flow Data for the 2007 PBT Trends Study, Fall.

Flow Data Site Name	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Lower Columbia River near Clatskanie	54	USGS	14246900	Columbia R @ Beaver Army Terminal near Quincy, OR	8/28/2007 - 9/25/2007	87,400-157,000	109,356.2
Duwamish River	10[1]	USGS	12113000	Green River near Auburn, WA	8/27/2007 - 9/24/2007	312-526	367.5
Lake Washington near outlet	-	King Co.	(King County, 2005)	(water level is controlled: fluctuation ~ 2 ft)	8/27/2007 - 9/24/2007	Flushing Rate 0.43 / year	-
Snohomish River	12.5[2]	USGS	12150800 & 12155300	Snohomish River near Monroe, WA Pilchuck River near Snohomish, WA	8/27/2007 - 9/24/2007	1,499-2,650	1,860.5
Wenatchee River	7.1	USGS	12462500	Wenatchee River at Monitor, WA	8/27/2007 - 9/24/2007	371-673	482.0
Upper Columbia River at Rock Island Dam	453.5	USGS	12462600	Columbia River below Rock Island Dam, WA	8/28/2007 - 9/25/2007	37,500-128,000	65,870.9
Okanogan River	17	USGS	12447200	Okanogan River at Malott, WA	8/28/2007 - 9/25/2007	595-1,050	793.7
Yakima River at Wanawish Dam	18	USGS	12510500	Yakima River at Kiona, WA	8/29/2007 - 9/26/2007	1,340-1,880	1,649.1

Flow Data Site Name	River Mile	Source of Flow Data	Station Identifier	Station Identifier Name	Date	Flow Range (cfs)	Geometric Mean (cfs)
Middle Columbia River at McNary Dam	292.0[3]	USACE/USGS	McNary/14019200	Columbia River at McNary Dam near Umatilla, OR	8/29/2007 - 9/26/2007	115,900-349,900	173,636.0
Walla Walla River	9	USGS	14018500	Walla Walla River near Touchet, WA	8/29/2007 - 9/26/2007	8.9-67	22.4
Spokane River at Nine Mile Dam	58.1[4]	USGS & Spokane	12422500, 12424000, & (City of Spokane 2008)	Spokane River at Spokane, WA, Hangman Creek at Spokane, WA, & RPWRF Spokane WWTP	8/30/2007 - 9/27/2007	603-1261	904.6
Queets River	11.5[5]	USGS	12040500	Queets River near Clearwater, WA	8/30/2007 - 9/27/2007	324-568	410.5

1. Mill and Spring Creeks discharge below the USGS station upstream of the sampling station. Mill and Spring Creeks' historical averaged monthly high discharge is not significant at 34 and 19 cfs respectively.
2. Flow for the Snohomish station was the sum discharge from Snohomish and Pilchuck Rivers.
3. Flow for the McNary site was the sum discharge; Outflow Discharge, Outflow Discharge from Power Generation, and Spillway Outflow Discharge.
4. Flow for the Spokane site was the sum discharge from Spokane River, Hangman Creek, and the Spokane Waste Water Treatment Plant. Historical (1995-2007) WWTP contribution ranged from .44-5.27%.
5. Flow for the Queets site was calculated by subtracting the Clearwater River percent contribution (23%) from the Queets River flow data based on available historical data for the Queets River above Clearwater.

Appendix K. Ancillary Water Quality Data

Table K-1. Ancillary Water Quality Data, Spring.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)	TOC (mg/L)	Salinity (g/Kg)
Lower Columbia River	LCR	7184800	4/30/2007	167	18	2	NA
	LCR	7204800	5/14/2007	157	19	1.9	NA
	LCR	7224800	5/28/2007	144	15	5.3	NA
Duwamish River	DUWAM	7184801	5/1/2007	101	6	1.2	2 U
	DUWAM	7204801	5/15/2007	110	5	1.2	2 U
	DUWAM	7224801	5/29/2007	105	6	1.1	2 U
Lake Washington	WASH	7184802	5/1/2007	121	3	2.5	NA
	WASH	7204802	5/15/2007	110	2	2.7	NA
	WASH	7224802	5/29/2007	122	3	3.4	NA
Snohomish River	SNOHO	7184803	5/1/2007	40	7	1	2 U
	SNOHO	7204803	5/15/2007	40	8	1	2 U
	SNOHO	7224803	5/29/2007	35	6	1 U	2 U
Wenatchee River	WEN	7184804	5/3/2007	10.5	6	1.9	NA
	WEN	7204804	5/16/2007	47	11	1.7	NA
	WEN	7224804	5/31/2007	39	9	1.3	NA
Upper Columbia River at Rock Island Dam	ROCK	7184805	5/2/2007	125	3	2.6	NA
	ROCK	7204805	5/16/2007	163	4	2.2	NA
	ROCK	7224805	5/30/2007	133	3	1.7	NA
Okanogan River	OKAN	7184806	5/2/2007	152	27	5.3	NA
	OKAN	7204806	5/16/2007	145	49	5.3	NA
	OKAN	7224806	5/30/2007	*	41	3.8	NA
Yakima River at Wanawish Dam	YAK	7184807	5/3/2007	186	19	2.3	NA
	YAK	7204807	5/17/2007	180	41	2.3	NA
	YAK	7224807	5/31/2007	154	35	2.6	NA
Middle Columbia River at McNary Dam	MCNARY	7184808	5/3/2007	174	4	2.3	NA
	MCNARY	7204808	5/17/2007	156	4	2.3	NA
	MCNARY	7224808	5/31/2007	149	3	2.1	NA
Walla Walla River	WALLA	7184809	5/3/2007	171	44	2.4	NA
	WALLA	7204809	5/17/2007	262	18	3	NA
	WALLA	7224809	5/31/2007	357	6	3	NA
Spokane River at Nine Mile Dam	SPOK	7184810	5/4/2007	91	6	1.6	NA
	SPOK	7214810	5/21/2007	75	3	1.9	NA
	SPOK	7224810	6/1/2007	119	2	1.4	NA
Queets River	QUEETS	7184812	5/4/2007	50	13	1.3	NA
	QUEETS	7204812	5/18/2007	89	8	1 U	NA
	QUEETS	7224812	6/1/2007	80	32	1 U	NA

U = Not detected at or above reported quantitation limit.
*Equipment failure.

Table K-2. Ancillary Water Quality Data, Fall.

Site	Field ID	Sample Number	Collection Date	Conduct. (us/cm)	TSS (mg/L)	TOC (mg/L)	Salinity (g/Kg)
Lower Columbia River	LCR	7354800	8/28/2007	137	6	1.9	NA
	LCR	7374800	9/11/2007	142	6	1.7	NA
	LCR	7394800	9/25/2007	76	11	1.8	NA
Duwamish River	DUWAM	7354801	8/27/2007	160	7	2.2	2 U
	DUWAM	7374801	9/10/2007	132	7	1.7	2 U
	DUWAM	7394801	9/24/2007	96	10	1.6	2 U
Lake Washington	WASH	7354802	8/27/2007	96	2	3.2	NA
	WASH	7374802	9/10/2007	102	2	2.7	NA
	WASH	7394802	9/24/2007	50	1	3	NA
Snohomish River	SNOHO	7354803	8/27/2007	46	16	1.1	2 U
	SNOHO	7374803	9/10/2007	56	10	1 U	2 U
	SNOHO	7394803	9/24/2007	31	8	1.1	2 U
Wenatchee River	WEN	7354804	8/27/2007	76	2	1.1	NA
	WEN	7374804	9/10/2007	76	1	1 U	NA
	WEN	7394804	9/24/2007	93	1 U	1.1	NA
Upper Columbia River at Rock Island Dam	ROCK	7354805	8/28/2007	145	2	1.7	NA
	ROCK	7374805	9/11/2007	124	2	1.4	NA
	ROCK	7394805	9/25/2007	126	1	1.5	NA
Okanogan River	OKAN	7354806	8/28/2007	245	11	2.9	NA
	OKAN	7374806	9/11/2007	316	1	2.8	NA
	OKAN	7394806	9/25/2007	308	3	3.6	NA
Yakima River at Wanawish Dam	YAK	7354807	8/29/2007	255	4	2.5	NA
	YAK	7374807	9/12/2007	128	4	2.2	NA
	YAK	7394807	9/26/2007	131	4	2.1	NA
Middle Columbia River at McNary Dam	MCNARY	7354808	8/29/2007	138	5	1.9	NA
	MCNARY	7374808	9/12/2007	150	2	2.5	NA
	MCNARY	7394808	9/26/2007	75	2	2	NA
Walla Walla River	WALLA	7354809	8/29/2007	271	1	3.1	NA
	WALLA	7374809	9/12/2007	170	1	3	NA
	WALLA	7394809	9/26/2007	175	1 U	2.8	NA
Spokane River at Nine Mile Dam	SPOK	7354810	8/30/2007	259	2	1.3	NA
	SPOK	7374810	9/13/2007	*	3	1.4	NA
	SPOK	7394810	9/27/2007	225	2	1.2	NA
Queets River	QUEETS	7354812	8/30/2007	90	3	1 U	NA
	QUEETS	7374812	9/13/2007	74	3	1 U	NA
	QUEETS	7394812	9/27/2007	38	2	1 U	NA

U = Not detected at or above reported quantitation limit.
*No data available.

Appendix L. Estimated Dissolved Concentrations of Pesticides and T-PCBs Detected in SPMDs

Table L-1. Estimated Concentrations of Pesticides and T-PCBs Detected in SPMDs April – May 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12	58
Sample No.	#7284800	#7284801	#7284802	#7284803	#7284804	#7284805	#7284806	7284807	#7284808	#7284809	#7284810	#7284811	#7284812
p,p'-DDT	**5.8**	<6.4	<6.7	<8.3	**21**	**5.3**	no data	**17**	<6.9	**17**	no data	<6.7	no data
p,p'-DDE	**37**	<6.8	<7.2	<8.9	**50**	**33**	"	**160**	**36**	**78**	"	<7.2	"
p,p'-DDD	**29**	<6.3	<6.7	<8.2	**18**	**30**	"	**36**	**26**	**2.4**	"	<6.7	"
o,p'-DDT	<4.7	<6.3	<6.6	<8.2	**8.3**	<4.3	"	<4.6	<6.8	<5.2	"	<6.6	"
o,p'-DDE	<4.8	<6.3	<6.6	<8.2	<7.5	<4.3	"	<4.6	<6.8	<5.3	"	<6.6	"
o,p'-DDD	**11**	<6.7	<7.1	<8.7	<8.1	<4.3	"	<4.7	**11**	**10**	"	<7.1	"
Total DDT[1]	**82**	<6.8	<7.2	<8.9	**97**	**68**	"	**220**	**73**	**110**	"	<7.2	"
DDMU[2]	**10**	<6.4	<6.7	<8.2	<7.5	**11**	no data	**14**	**8.9**	**13**	no data	<6.7	no data
Dieldrin	**20**	<11	**36**	<15	<13	<9.8	"	**50**	<12	**40**	"	<18	"
Chlorpyrifos	**110**	<21	<21	<27	<22	<21	"	**1200**	**85**	**3800**	"	<21	"
Endosulfan I	**730**	**310**	<220	<280	**2000**	**600**	"	**2700**	**950**	**730**	"	<220	"
Endosulfan-II	<460	<460	<460	<580	**920**	<460	"	**740**	<460	**1200**	"	<460	"
Endosulfan Sulfate	<320	<320	<320	<400	<320	<320	"	**510**	<320	**540**	"	<320	"
Hexachlorobenzene (HCB)	**17**	**8.2**	<6.6	<8.2	**11**	**5.9**	"	**8.7**	**10**	**34**	"	<6.6	"
Pentachloroanisole (PCA)	**15**	**29**	**18**	**21**	**17**	**7.9**	"	**14**	**13**	**10**	"	**7.4**	"
Toxaphene	**91**	<98	<100	<120	<110	<81	"	**190**	<102	**1200**	"	<100	"
Total Chlordane[3]	<6.0	<7.4	<7.8	<9.6	<8.9	<4.7	"	**4.9**	<8.0	**23**	"	<7.8	"
Dacthal	<19	<20	<20	<25	<21	<19	"	<19	**30**	<19	"	<20	"
Heptachlor Epoxide	<12	<13	<13	<16	<14	<12	"	<12	<13	**19**	"	<13	"
Lindane	<68	ND	<68	<85	ND	<68	"	<68	<68	**760**	"	ND	"
Total PCB	**91**	**72**	**42**	**38**	**54**	**9.8**	no data	**40**	**58**	**42**	no data	**25**	no data

1-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT. DDD = p,p'-dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.

2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.

3-The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total Chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

ND = less than field blank.

Table L-2. Estimated Concentrations of Pesticides and T-PCBs Detected in SPMDs, August – September 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12	58
Sample No.	#7404800	#7404801	#7404802	#7404803	#7404804	#7404805	#7404806	#7404807	#7404808	7404809	#7404810	#7404811	#7404812
p,p'-DDT	**3.0**	**4.4**	<4.4	<5.5	**20**	**11**	**7.1**	**4.6**	<5.3	**4.8**	<4.6	<5.2	<4.6
p,p'-DDE	**20**	<4.4	**8.8**	<5.8	**51**	**120**	**37**	**63**	**39**	**63**	<4.7	<5.4	<4.6
p,p'-DDD	**16**	<4.2	**14**	<5.4	**14**	**160**	**15**	**18**	**28**	**11**	<4.4	<5.0	<4.4
o,p'-DDT	<2.8	<4.3	<4.3	<5.4	<5.2	<4.4	<5.3	<3.7	<5.2	<3.5	<4.5	<5.1	<4.5
o,p'-DDE	<2.8	<4.3	<4.3	<5.4	<5.2	**6.7**	<5.4	<3.7	<5.2	<3.6	<4.5	<5.1	<4.5
o,p'-DDD	**3.8**	<4.3	<4.3	<5.7	<5.4	**42**	<5.6	<3.6	**7.6**	**4.5**	<4.6	<5.3	<4.6
Total DDT[1]	**43**	**4.4**	**23**	<5.8	**85**	**340**	**60**	**86**	**74**	**84**	<4.7	<5.4	<4.6
DDMU[2]	<6.4	<6.1	<17	<5.5	<9.5	**33**	<5.9	**9.8**	<11	<10.9	<5.0	<5.2	<4.6
Dieldrin	**14**	**12**	**32**	<11	**12**	<9.9	<11	**71**	**11**	**21**	**14**	<10	**13.0**
Chlorpyrifos	<21	<21	<21	<21	<21	<21	<21	**730**	**36**	**150**	<21	<21	<21
Endosulfan I	<220	**710**	<220	<220	**1100**	**350**	<220	**420**	**270**	**510**	<220	<220	<220
Endosulfan-II	<880	<460	<460	<460	**1100**	<460	<460	<460	<790	<460	<460	<460	<460
Endosulfan Sulfate	<320	<320	<320	<320	**760**	<320	<320	**790**	<320	**2700**	<320	<320	<320
Hexachlorobenzene (HCB)	**4.0**	**5.0**	<4.2	<5.4	<5.2	**4.8**	<5.3	<3.6	**5.2**	**30**	**7.1**	<5.0	**6.6**
Pentachloroanisole (PCA)	**6.2**	**17**	**9.6**	**11**	<5.3	<4.5	<5.4	**5.7**	<5.3	<3.7	**31**	<5.2	**27**
Toxaphene	<88	<81	<81	<90	<88	<82	<89	**180**	<88	**510**	<82	<87	<82
Total Chlordane[3]	<3.2	<4.7	**15**	<6.2	<5.9	<4.9	<6.1	<4.0	<5.9	**13**	**11**	<5.7	**5.2**
Dacthal	<18	<19	<19	<19	<19	<19	<19	<19	<19	<18.5	<19	<19	<19
Heptachlor Epoxide	<11	<11	<12	<12	<12	<12	<12	<11	<12	**12**	<12	<12	<12
Lindane	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68
Total PCBs	**16**	**24**	**31**	**21**	**45**	**27**	**15**	**17**	**59**	**6.2**	**99**	**22**	**61**

1-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT. DDD = p,p'-dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.

2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.

3-The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total Chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

ND = less than field blank.

Table L-3. Estimated Concentrations of PBDEs Detected in SPMDs, April – May and August – September, 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12
Sample No.*	#...4800	#...4801	#...4802	#...4803	#...4804	#...4805	#...4806	#...4807	#...4808	#...4809	#...4810	#...4811
April - May 2007												
PBDE-47	**16**	**3.5**	**13**	**13**	**10**	**7.2**	no data	**22**	**12**	**19**	no data	**10**
PBDE-49	<2.0	<2.8	<3.0	<3.7	<3.4	<1.8	"	**3.0**	<3.1	<2.3	"	<3.0
PBDE-66	<2.0	<2.8	<3.0	<3.7	<3.4	<1.8	"	<2.0	<3.1	<2.3	"	<3.0
PBDE-99	**7.6**	ND	**9.5**	**12**	**9.8**	**7.3**	"	**11**	**8.8**	**12**	"	**11**
PBDE-100	**2.1**	<4.3	**2.1**	**3.0**	**2.3**	**2.2**	"	**2.6**	**2.1**	**3.3**	"	**2.4**
PBDE-138	<8.7	<12	<13	<16	<15	<7.6	"	**8.4**	<14	<9.9	"	<13
PBDE-153	ND	<9.3	**0.1**	**0.2**	ND	ND	"	**0.3**	ND	**0.2**	"	ND
PBDE-154	**1.3**	<11	**1.3**	**1.4**	**1.8**	**0.4**	"	<7.4	**1.5**	**1.4**	"	**1.0**
PBDE-183	**1.0**	<14	<14	**1.6**	**2.1**	<8.5	"	**2.8**	ND	**4.7**	"	**1.3**
PBDE-184	<15	<21	<22	<28	<26	<13	"	**14**	<23	<17	"	<22
Total PBDEs	**28**	**3.5**	**25**	**31**	**26**	**17**	no data	**64**	**24**	**40**	no data	**26**
August - September 2007												
PBDE-47	**10**	**9.1**	**13**	**6.8**	ND	**2.9**	**5.3**	**4.2**	**5.1**	**0.6**	**101**	**11**
PBDE-49	<1.0	<1.8	<1.8	<2.4	<2.3	<1.9	<2.3	<1.5	<2.3	<1.4	**5.3**	<2.2
PBDE-66	<1.0	<1.8	<1.8	<2.4	<2.3	<1.9	<2.3	<1.5	<2.3	<1.4	**2.4**	<2.2
PBDE-99	**3.4**	**6.4**	**20**	**4.0**	ND	ND	**2.5**	**0.1**	**0.6**	ND	**54**	**4.5**
PBDE-100	**1.8**	**1.5**	**2.7**	**1.1**	<2.7	**0.6**	**1.1**	**0.5**	<2.7	**0.3**	**12**	**1.0**
PBDE-138	<4.0	<7.6	<7.6	<10	<9.8	<8.0	<10	<6.1	<9.8	<5.8	<8.1	<9.5
PBDE-153	<3.0	<5.7	**3.2**	<7.7	<7.4	<6.0	<7.6	<4.7	<7.4	<4.4	**4.3**	<7.2
PBDE-154	<3.5	<6.7	<6.7	<9.0	<8.6	<7.0	<8.9	<5.4	<8.6	<5.1	**4.7**	<8.3
PBDE-183	<4.4	<8.4	<8.4	<11	<11	<8.8	<11	<6.8	<11	<6.4	<9.0	<11
PBDE-184	<6.7	<13	<13	<18	<17	<14	<17	<10	<17	<9.9	<14	<16
Total PBDEs	**15**	**17**	**39**	**12**	ND	**3.5**	**8.9**	**4.8**	**5.7**	**0.9**	**184**	**16**

*Sample numbers begin with 0728... for spring and 0740... for fall.

ND = less than field blank.

Appendix M. Estimated Total Concentrations of Pesticides and T-PCBs Detected in SPMDs

Table M-1. Estimated Total Concentrations of Pesticides and PCBs, April – May 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12	58
Sample No.	#7284800	#7284801	#7284802	#7284803	#7284804	7284805	#7284806	7284807	#7284808	#7284809	#7284810	7284811	#7284812
p,p'-DDT	**8.0**	<7.3	<9.1	<9.3	**25**	**6.7**	no data	**22**	<8.7	**22**	no data	<7.6	no data
p,p'-DDE	**100**	<11	<19	<14	**95**	**74**	"	**380**	**82**	**200**	"	<12	"
p,p'-DDD	**49**	<8.0	<11	<10	**25**	**45**	"	**57**	**39**	**4.0**	"	<8.4	"
o,p'-DDT	<7.0	<7.5	<9.7	<9.5	**10**	<5.8	"	<6.4	<9.2	<7.5	"	<7.8	"
o,p'-DDE	<7.0	<7.4	<9.5	<9.4	<9.3	<5.7	"	<6.2	<9.0	<7.5	"	<7.7	"
o,p'-DDD	**28**	<11	<17	<13	<15	<9.0	"	<10	**23**	**25**	"	<11	"
Total DDT[1]	**180**	<11	<19	<14	**160**	**120**	no data	**460**	**140**	**250**	no data	<12	no data
DDMU[2]	**14**	<7.4	<9.2	<9.3	<9.1	**15**	no data	**18**	**12**	**17**	no data	<7.7	no data
Dieldrin	**21**	<12	**38**	<15	<13	<10	"	**52**	<12	**42**	"	<12	"
Chlorpyrifos	**120**	<22	<23	<28	<23	<22	"	**1400**	**92**	**4100**	"	<22	"
Endosulfan I	**740**	**310**	<220	<280	**2100**	**600**	"	**2700**	**960**	**740**	"	<220	"
Endosulfan-II	<460	<460	<460	<580	**930**	<460	"	**740**	<460	**1200**	"	<460	"
Endosulfan Sulfate	<320	<320	<320	<400	<320	<320	"	**510**	<320	**540**	"	<320	"
Hexachlorobenzene (HCB)	**28**	**10**	<11	<9.9	**14**	**8.6**	"	**13**	**15**	**55**	"	<8.1	"
Pentachloroanisole (PCA)	**21**	**33**	**25**	**24**	**20**	**10**	"	**18**	**17**	**14**	"	**8.4**	"
Toxaphene	**97**	<100	<110	<130	<110	<85	"	**200**	<107	**1200**	"	<103	"
Total Chlordane[3]	<20	<16	<29	<18	<22	<14	"	**6.0**	<24	**46**	"	<16	"
Dacthal	<19	<20	<20	<25	<21	<19	"	<19	**30**	<19	"	<20	"
Heptachlor Epoxide	<14	<14	<16	<17	<15	<13	"	<13	<15	**23**	"	<14	"
Lindane	<68	ND	<69	<85	ND	<68	"	<68	<68	**760**	"	ND	"
Total PCB	**370**	**160**	**160**	**75**	**140**	**31**	no data	**140**	**180**	**160**	no data	**52**	no data

1-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT. DDD = p,p'-dichlorodiphenyldichloroethane. DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.

2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.

3-The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total Chlordane is the sum of cis- and trans-chlordane, cis- and trans- nonachlor, and oxychlordane.

ND = less than field blank.

Table M-2. Estimated Total Concentrations of Pesticides and PCBs, August – September 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12	58
Sample No.	#7404800	#7404801	#7404802	#7404803	#7404804	#7404805	#7404806	7404807	#7404808	#7404809	#7404810	7404811	#7404812
p,p'-DDT	**3.6**	**5.4**	<6.0	<6.2	**23**	**14**	**9.7**	**5.8**	<6.7	**6.5**	<5.3	<5.8	<5.3
p,p'-DDE	**40**	<8.9	**24**	<9.4	**83**	**220**	**100**	**140**	**85**	**170**	<8.2	<8.5	<8.0
p,p'-DDD	**23**	<5.9	**24**	<6.8	**18**	**210**	**26**	**28**	**42**	**19**	<5.7	<6.2	<5.7
o,p'-DDT	<3.6	<5.5	<6.4	<6.3	<6.1	<5.5	<7.9	<5.1	<6.9	<5.2	<5.4	<5.9	<5.4
o,p'-DDE	<3.6	<5.5	<6.2	<6.3	<6.1	**8**	<7.9	<5.0	<6.8	<5.2	<5.4	<5.9	<5.4
o,p'-DDD	**7.1**	<8.1	<11	<8.8	<8.3	**74**	<14	<7.7	**16**	**11**	<7.6	<7.9	<7.6
Total DDT[1]	**74**	**5.4**	**48**	<9.4	**120**	**530**	**140**	**180**	**140**	**210**	<8.2	<8.5	<8.0
DDMU[2]	<7.9	<7.5	<24	<6.3	<11	**39**	<8.3	**13**	<13	<15	<5.8	<5.9	<5.4
Dieldrin	**14**	**12**	**33**	<11	**12**	<10	<11	**74**	**11**	**22**	**14**	<11	**13**
Chlorpyrifos	<22	<22	<23	<22	<22	<22	<23	**780**	**38**	**170**	<22	<22	<22
Endosulfan I	<220	**710**	<220	<220	**1100**	**360**	<220	**420**	**270**	**500**	<220	<220	<220
Endosulfan-II	<880	<460	<460	<460	**1100**	<460	<460	<460	<790	<460	<460	<460	<460
Endosulfan Sulfate	<320	<320	<320	<320	**760**	<320	<320	**800**	<320	**2700**	<320	<320	<320
Hexachlorobenzene (HCB)	**5.5**	**6.9**	<6.9	<6.7	<6.4	**6.3**	<8.8	<5.3	**7.5**	**49**	**9.0**	<6.1	**8.4**
Pentachloroanisole (PCA)	**7.6**	**21**	**13**	**13**	<6.0	<5.3	<7.5	**7**	<6.7	<5.1	**36**	<5.8	**31**
Toxaphene	<91	<84	<86	<92	<90	<85	<95	**190**	<92	**550**	<85	<89	<85
Total Chlordane[3]	<6.9	<13	**32**	<13	<12	<12	<24	<12	<17	**30**	**13**	<11	**5.9**
Dacthal	<19	<19	<19	<19	<19	<19	<19	<19	<19	<19	<19	<19	<19
Heptachlor Epoxide	<12	<13	<14	<13	<13	<13	<15	<13	<14	**15**	<13	<13	<13
Lindane	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68	<68
Total PCBs	**45**	**65**	**120**	**44**	**93**	**66**	**61**	**57**	**180**	**24**	**230**	**43**	**140**

1-Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT. DDD = p,p'-dichlorodiphenyldichloroethane.
DDE = p,p'-dichlorodiphenyldichloroethylene. DDT = p,p'-dichlorodiphenyltrichloroethane.
2-DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethene) is a breakdown product of DDE.
3-The NTR criterion for chlordane is interpreted as the sum of five chlordane components: Total Chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane.

Table M-3. Estimated Total Concentrations of PBDEs, April – May and August – September 2007 (pg/L).

Site	Lower Columbia River	Duwamish River	Lake Washington	Snohomish River	Wenatchee River	Upper Columbia River	Okanogan River	Yakima River	Middle Columbia River	Walla Walla River	Spokane River	Queets River	RepSpok
River Mile	54	10	outlet	13	7	454	17	18	292	9	58	12	58
Sample No.*	#...4800	#...4801	#...4802	#...4803	#...4804	#...4805	#...4806	#...4807	#...4808	#...4809	#...4810	#...4811	#...4812
April - May 2007													
PBDE-47	**50**	**6.4**	**38**	**22**	**21**	**18**	no data	**58**	**31**	**55**	no data	**18**	no data
PBDE-49	<6.2	<5.1	<8.9	<6.2	<7.1	<4.5	"	**8.0**	<7.8	<6.7	"	<5.3	"
PBDE-66	<6.5	<5.3	<9.4	<6.4	<7.4	<4.7	"	<5.5	<8.1	<7.0	"	<5.4	"
PBDE-99	**62**	<65	**73**	**39**	**46**	**44**	"	**73**	**54**	**86**	"	**40**	"
PBDE-100	**14**	<14	**13**	**8.3**	**8.8**	**11**	"	**14**	**11**	**20**	"	**7.2**	"
PBDE-138	<420	<240	<590	<260	<380	<260	"	**320**	<470	<430	"	<230	"
PBDE-153	ND	<77	**2.3**	**1.1**	ND	ND	"	**5.0**	ND	**3.4**	"	ND	"
PBDE-154	**43**	<140	**39**	**16**	**31**	**9.7**	"	<190	**34**	**41**	"	**12**	"
PBDE-183	**64**	<360	<900	**35**	**73**	<400	"	**140**	ND	**280**	"	**31**	"
PBDE-184	<3500	<2000	<5000	<2100	<3200	<2200	"	**2600**	<3900	<3600	"	<1900	"
Total PBDEs	**230**	**6.4**	**170**	**120**	**180**	**83**	no data	**3300**	**130**	**490**	no data	**110**	no data
August - September 2007													
PBDE-47	**22**	**20**	**40**	**12**	ND	**6.0**	**17**	**11**	**12**	**1.7**	**190**	**18**	**170**
PBDE-49	<2.2	<4.0	<5.5	<4.2	<4.0	<3.8	<7.2	<3.9	<5.6	<4.3	**10**	<3.7	**8.8**
PBDE-66	<2.3	<4.2	<5.7	<4.3	<4.1	<4.0	<7.5	<4.0	<5.8	<4.5	**4.7**	<3.8	**5.8**
PBDE-99	**18**	**33**	**160**	**14**	ND	ND	**21**	**0.9**	**3.8**	ND	**220**	**15**	**210**
PBDE-100	**7.4**	**6.3**	**17**	**3.4**	<8.1	**2.0**	**7.3**	**2.4**	<13	**1.8**	**41**	**2.9**	**40**
PBDE-138	<110	<220	<360	<180	<170	<190	<490	<220	<320	<270	<170	<160	<170
PBDE-153	<36	<68	**61**	<59	<57	<61	<150	<70	<100	<85	**38**	<51	**41**
PBDE-154	<67	<130	<210	<110	<100	<110	<290	<130	<190	<160	**67**	<92	**61**
PBDE-183	<170	<330	<540	<280	<260	<290	<740	<340	<490	<410	<260	<230	**230**
PBDE-184	<930	<1800	<3000	<1500	<1400	<1600	<4100	<1800	<2700	<2300	<1400	<1200	<1400
Total PBDEs	**48**	**60**	**270**	**30**	ND	**8.0**	**44**	**14**	**16**	**3.6**	**570**	**36**	**770**

*Sample numbers begin with 0728... for spring and 0740... for fall.
ND = less than field blank.

Appendix N. Water Quality Criteria for Chemicals Analyzed

Table N-1. Water Quality Criteria for Chemicals Analyzed in the 2007 PBT Chemical Trends Study Using SPMDs (pg/L).

Chemical	Washington State				EPA (2006) Recommended Criteria[c]			
	Aquatic Life		Human Health (NTR)[b]		Aquatic Life		Human Health	
	Freshwater Acute	Freshwater Chronic	Water + fish Consumption	Fish Consumption	Freshwater Acute	Freshwater Chronic	Water + fish Consumption	Fish Consumption
p,p'-DDT	-	-	590	590	-	-	220	220
p,p'-DDE	-	-	590	590	-	-	220	220
p,p'-DDD	-	-	830	840	-	-	310	310
o,p'-DDT	-	-	-	-	-	-	-	-
o,p'-DDE	-	-	-	-	-	-	-	-
o,p'-DDD	-	-	-	-	-	-	-	-
DDT and metabolites[d]	1,100,000	1,000	-	-	1,100,000	1,000	-	-
DDMU[e]	-	-	-	-	-	-	-	-
Dieldrin	-	-	140	140	240,000	56,000	52	54
Aldrin	-	-	130	140	3,000,000	-	49	50
Dieldrin and aldrin[f]	2,500,000	1,900	-	-	-	-	-	-
Chlorpyrifos	83,000	41,000	-	-	83,000	41,000	-	-
Endosulfan[g]	220,000	56,000	-	-	220,000[h]	56,000[h]		
Endosulfan I (alpha)	-	-	930,000	2,000,000	220,000[h]	56,000[h]	62,000,000	89,000,000
Endosulfan-II (beta)	-	-	930,000	2,000,000	220,000[h]	56,000[h]	62,000,000	89,000,000
Endosulfan Sulfate	-	-	930,000	2,000,000	-	-	62,000,000	89,000,000
Hexachlorobenzene (HCB)	-	-	750	770	-	-	280	290
Pentachloroanisole (PCA)	-	-	-	-	-	-	-	-
Toxaphene	730,000	200	730	750	730,000	2,000	280	280
Total Chlordane[i]	2,400,000	4,300	570	590	2,400,000	4,300	800	810
Dacthal	-	-	-	-	-	-	-	-
Heptachlor	520,000	3,800	210	210	520,000	3,800	79	79
Heptachlor Epoxide	-	-	100	110	520,000	3,800	39	39
alpha-Benzenehexachloride (a-BHC)	-	-	3,900	13,000	-	-	2,600	4,900

Chemical	Washington State				EPA (2006) Recommended Criteria[c]			
	Aquatic Life		Human Health (NTR)[b]		Aquatic Life		Human Health	
	Freshwater Acute	Freshwater Chronic	Water + fish Consumption	Fish Consumption	Freshwater Acute	Freshwater Chronic	Water + fish Consumption	Fish Consumption
beta-Benzenehexachloride (b-BHC)	-	-	14,000	46,000	-	-	9,100	17,000
delta-Benzenehexachloride (d-BHC)	-	-	-	-	-	-	-	-
gamma - Benzenehexachloride (g-BHC) (Lindane)	2,000,000	80,000	19,000	63,000	950,000	-	980,000	1,800,000
Endrin	180,000	2,300	760,000	810,000	86,000	36,000	59,000	60,000
Endrin ketone	-	-	-	-	-	-	-	-
Endrin Aldehyde	-	-	760,000	810,000	-	-	290,000	300,000
Mirex	-	-	-	-	-	1,000	-	-
p,p'-Methoxychlor	-	-	-	-	-	-	-	-
Total PCBs[j]	2,000,000	14,000	170	170	-	14,000	64	64
Total PBDEs[k]	-	-	-	-	-	-	-	-

a - Water Quality Standards for Surface Waters of the State of Washington Chapter 173-201A WAC (Ecology 2006a).

b - EPA 1992 National Toxics Rule.

c - National Recommended Water Quality Criteria (EPA 2006).

d - Total DDT is the sum of 2,4'- and 4,4'- isomers of DDD, DDE, and DDT as defined by Ecology, 2006b.

e - DDMU is a breakdown product of DDE.

f - Aldrin is metabolically converted to Dieldrin. Therefore, the sum of the Aldrin and Dieldrin concentrations are compared with the Dieldrin criteria.

g - Endosulfan is the sum of alpha and beta endosulfan.

h - Value derived from endosulfan and is appropriately applied to the sum of alpha- and beta-endosulfan (EPA 2006).

i - Total chlordane is the sum of cis- and trans- chlordane, cis- and trans- nonachlor, and oxychlordane as defined by Ecology, 2006b.

j - Total PCBs is the sum of Aroclors or congeners.

k - Total PBDEs is the sum of the congeners.