



DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Quality Assurance Project Plan**

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# **Seasonal Water Quality Study of Vancouver Lake Tributaries for PCBs, Dioxin, and Chlorinated Pesticides**

January 2010

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WQP – Water Quality Program  
EAP - Environmental Assessment Program  
EIM - Environmental Information Management system

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## Abstract

Each study conducted by Ecology must have an approved Quality Assurance (QA) Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

A 1993 study conducted by the Washington State Department of Ecology (Davis, et al., 1995) first reported that fish in Vancouver Lake contained elevated levels of polychlorinated biphenyls (PCBs) and DDE (metabolite of DDT). Concentrations exceeded EPA National Toxics Rule for human health criteria. More recent studies by Ecology and others have also detected these pollutants in tissue and sediments, but with mixed results.

Past studies have focused primarily on fish and sediment because of the difficulty measuring these pollutants in whole water samples without special sampling methods. This study will determine if surface water inputs to Vancouver Lake from Burnt Bridge Creek, Flushing Channel, and Lake River are contributing significant amounts of PCBs, dioxins, or chlorinated pesticides. Inputs to Vancouver Lake will be evaluated and prioritized for any needed follow-up activities.

Between January and September 2010, seasonal water samples will be collected on three occasions, once in winter, spring, and summer at four locations. One site each in Burnt Bridge Creek and Flushing Channel will be sampled, while Lake River will have one site at both the northern and southern extent.

Semipermeable membrane devices (SPMDs) will be used to collect and concentrate target analytes from the surface waters. SPMDs are passive samplers that collect hydrophobic contaminants over time. Samplers will be deployed for one month at each site per season. Chemical analysis of SPMDs will include PCBs, dioxin/furans, and chlorinated pesticides. Total organic carbon and total suspended solids' samples will be collected as grabs. Temperature data will also be collected by an in-situ temperature probe.

# Background

## Site Description

Vancouver Lake covers 2,414 acres and is situated between the city of Vancouver, Washington to the east, Vancouver Lake Wildlife Area to the south, and Shillapoo Wildlife Area to the west (Figure 1). Burnt Bridge Creek is the only natural surface water drainage discharging directly to the lake, flowing into Vancouver Lake's southeast corner. In addition, a few other small discharges to the lake also exist but are generally insignificant. Outflow is to the north into Lake River, ultimately discharging to the Columbia River.

Vancouver Lake is very shallow and historically ranged from one to four feet deep. During the early 1980s, some areas of the lake were dredged to roughly between five and 10 feet. A large island in the north central area of the lake was developed for wildlife habitat from dredge spoils. During this same period, a Flushing Channel was cut connecting Vancouver Lake with the Columbia River.

This manmade Flushing Channel was intended to provide Vancouver Lake with higher quality water from the Columbia River. The approximately one-mile long channel is located near the lake's southwest extent (Figure 1). Due to tidal influences on the Columbia River, tide gates were installed to prevent backflow. During falling tides when the water level of the lake is higher than the Columbia River, the tide gates close.

Lake River is the outlet from Vancouver Lake. About 11 miles long, it connects Vancouver Lake to the Columbia River. Lake River is tidally influenced; but, unlike the Flushing Channel, does not have flow control devices. Flow direction in Lake River is controlled by the tidal stage of the Columbia River. During flood tides, Lake River can reverse its course and discharge back into Vancouver Lake. Ebb tides allow the lake to drain down Lake River into the Columbia River.

## 303(d) Listings

The 2008 Washington State 303(d) listings for toxic pollutants in Vancouver Lake are shown below on Table 1. Not all 303(d) listed parameters for Vancouver Lake are included. Fecal coliform and total phosphorus are also currently listed. This study addresses only toxic substances that have exceeded water quality standards in Vancouver Lake.

The fishery (ie, aquatic life) is the main beneficial use identified as being impaired by toxic substances in Vancouver Lake. The National Toxics Rule (NTR) human health criteria for edible fish tissue have been exceeded by concentrations of polychlorinated biphenyls (PCBs), 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD), and chlorinated pesticides. Fish tissue results responsible for 303(d) listings are presented in Table A1 in the Appendix.

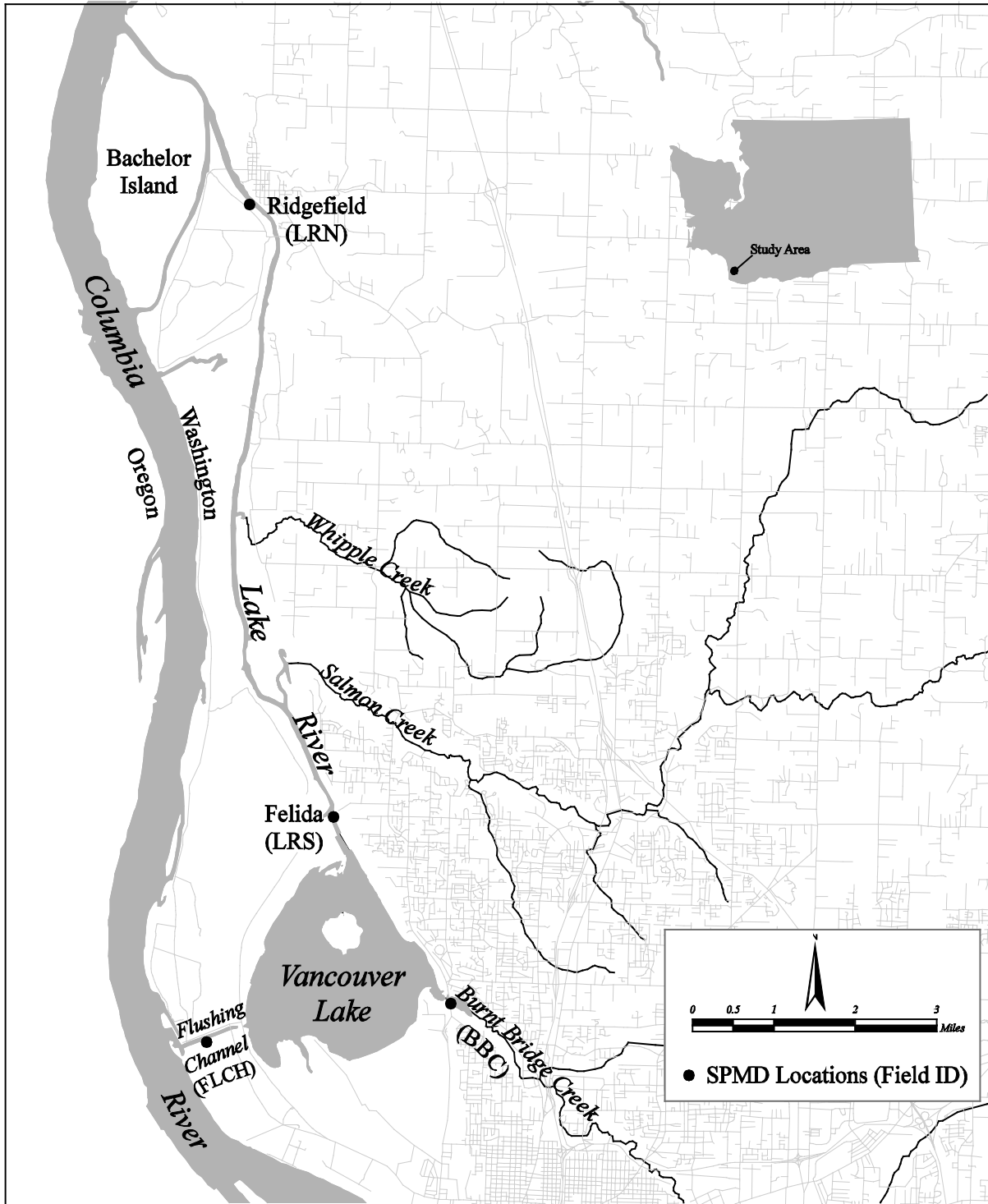


Figure 1. Study area showing SPMD sample sites.



Table 1. Vancouver Lake 2008 303(d) listings for total PCBs, TCDD, and chlorinated pesticides in fish tissue.

Waterbody	Parameter	Listing ID	Township	Range	Section
Vancouver Lake	Total PCBs	42172	T2N	R1W	5
	2,3,7,8-TCDD	53204	T2N	R1W	5
	4,4'-DDE	42187	T2N	R1W	5
	Dieldrin	53205	T2N	R1W	5
	Toxaphene	42282	T2N	R1W	5

## Historical Data

Inputs to Vancouver Lake have not been evaluated as sources of toxic pollutants. Water column data on PCBs, dioxins/furans, and chlorinated pesticides in Vancouver Lake do not exist. Earlier studies have focused on fish and sediment.

In 1993, Ecology first reported PCBs and DDE (a metabolite of DDT) in fish tissue from Vancouver Lake exceeding the EPA's NTR human health criteria (Davis, et al., 1995).

A more recent Ecology study, conducted in 2005-2006, sampled fish tissue and sediment reporting results for PCBs, dioxin/furans, and chlorinated pesticides (Coots, 2007). In this study the NTR criteria were exceeded in fish tissue collected from Vancouver Lake and Lake River for total PCBs, TCDD, DDE, dieldrin, and toxaphene. Results for sediment chemistry were low. This study recommended a surface water quality study for PCBs and chlorinated pesticides in Vancouver Lake.

A recent site assessment in 2009 by the United States Environmental Protection Agency (EPA) analyzed sediments in Vancouver Lake, Flushing Channel, Burnt Bridge Creek, Lake River, and the Columbia River (EPA, 2009; unpublished). Sediments were collected from 32 locations. Preliminary results showed screening levels were exceeded in three samples for metals and one sample for polyaromatic hydrocarbons (PAHs). No PCBs were detected, although concerns were raised about reporting limits not being low enough. The sediments are currently being re-analyzed for PCBs.

A study of Flushing Channel sediments was conducted in September and October 2003 by Hart Crowser under contract with the Port of Vancouver (Hart Crowser, 2003). The purpose of the work was to characterize Flushing Channel sediments for proposed dredging operations and the suitability for stockpiling and use as clean fill on upland properties. Ten sediment samples were collected and analyzed for PCBs, chlorinated pesticides, semivolatile organics, tributyltin, metals, total organic carbon (TOC), and grain size. All analytes were reported below screening level values.

Two water column studies have reported results for the Columbia River in the general vicinity of Flushing Channel and Lake River. Both studies collected samples by semipermeable membrane devices (SPMDs). SPMDs are passive samplers that are used to concentrate hydrophobic contaminants over time.

Ecology conducted the more recent study (Johnson and Norton, 2005) in the fall of 2003 through spring 2004 reporting data on toxic pollutants for one station located about 0.7 miles south of the mouth of Lake River. An additional station was located in the mainstem Columbia River about two miles south (upstream) of the Flushing Channel.

Three seasonal samples were collected from the two sites. Estimates of total PCBs exceeded NTR criteria in at least two of three sample periods, while DDT and metabolites were generally within, or slightly above, criteria. The May to June sample period tended to have the highest levels of these compounds.

The other SPMD study was conducted by the United States Geological Survey (USGS) from summer 1997 through spring 1998 (McCarthy and Gale, 1999). PCBs, dioxins/furans, organochlorine pesticides, and PAHs were analyzed. One study site was located near the mouth of Lake River and another near Hayden Island just upstream of the confluence with the Willamette River.

Results showed concentrations of organochlorine compounds and PAHs were highest during late summer to early fall. The study authors concluded, because of the overall low levels of contaminants reported for the Hayden Island site, that elevated concentrations of contaminants found in the Portland-Vancouver area are from local rather than upstream sources. The highest concentrations of PCBs were reported for tributaries in the Portland-Vancouver urban area, which included the Lake River site.

## Project Description

Sources of the toxic pollutants in Vancouver Lake fish are not well understood but could be associated with surface runoff, air deposition, and past handling practices as well as some fish move between Vancouver Lake, Lake River, and the Columbia River. The latter suggests the possibility that some of the pollutants measured in Vancouver Lake fish may be from other water bodies.

The Ecology Water Quality Program, Vancouver Field Office, has requested a study to determine if surface water inputs to Vancouver Lake are sources of 303(d) listed PCBs, dioxins/furans, and chlorinated pesticides found in fish and sediments. Surface water sources to the lake need to be evaluated and prioritized to determine the need for further investigation.

The goal of this study is to determine if inputs to Vancouver Lake from Burnt Bridge Creek, Flushing Channel, and Lake River contribute significant levels of PCBs, dioxin/furans, and chlorinated pesticides. These compounds will be monitored seasonally from winter through summer 2010. Results from this survey will determine what type of future work should be performed, whether a total maximum daily load (TMDL), watershed assessment, or other study or type of cleanup plan.

As previously noted, source assessment studies have not been conducted for Vancouver Lake for toxic pollutants. It is currently not known whether toxic pollutants are entering the lake in surface water. Target compounds will be collected from surface waters by passive sampling using semipermeable membrane devices (SPMDs). SPMDs are used to concentrate hydrophobic contaminants over time because of their low solubility in water. They mimic the biological uptake of organic compounds and have the ability to concentrate chemicals that have low concentrations in water. A total of three seasonal samples will be collected at each of the four sites (Figure 1).

The study will be conducted by Ecology's Environmental Assessment Program. Samples will be analyzed by the Manchester Environmental Laboratory (MEL) and their contractors. Extraction of SPMDs is a proprietary methodology. Environmental Sampling Technologies (EST) will provide the SPMDs and extract the membranes following deployment at the study site.

This QA Project Plan follows the Ecology guidance in Lombard and Kirchmer (2004).

## Organization and Schedule

The following people are involved in this project. All are employees of the Washington State Department of Ecology.

Table 2. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Tonnie Cummings Southwest Region – Vancouver Field Office Phone: (360) 690- 4664	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP. Reviews and approves the final report.
Randy Coots Toxic Studies Unit SCS Phone: (360) 407-6690	Project Manager/ Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Michael Friese Toxics Study Unit SCS Phone: (360) 407-6737	Field Assistant	Helps collect samples and records field information.
Kristin Carmack Toxics Study Unit Eastern Operations Section Phone: (509) 454-4243	EIM Data Engineer	Reviews laboratory results and uploads data into EIM.
Dale Norton Toxics Studies Unit SCS Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Toxic Studies Unit SCS Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

SCS – Statewide Coordination Section.

EAP – Environmental Assessment Program.

EIM – Environmental Information Management system.

QAPP – Quality Assurance Project Plan.

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	October 2010	Randy Coots
Laboratory analyses completed	December 2010	
Environmental Information System (EIM) database		
EIM user study ID	RCOO0011	
Product	Due date	Lead staff
EIM data loaded	March 2011	Kristin Carmack
EIM QA	April 2011	Kristin Carmack
EIM complete	May 2011	Kristin Carmack
Final report		
Author lead	Randy Coots	
Schedule		
Draft due to supervisor	February 2011	
Draft due to client/peer reviewer	March 2011	
Final (all reviews done) due to publications coordinator	April 2011	
Final report due on web	May 2011	

## Quality Objectives

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

Analytical precision and bias will be evaluated and controlled by use of laboratory check standards, duplicates, spikes, and blanks analyzed along with study samples.

*Precision* is a measure of the ability to consistently reproduce results. Precision will be evaluated by analysis of check standards, duplicates/replicates, spikes, and blanks. Results of duplicate (split) analyses will be used to estimate laboratory precision.

*Bias* is the systematic error due to contamination, sample preparation, calibration, or the analytical process. Most sources of bias are minimized by adherence to established protocols for the collection, preservation, transportation, storage, and analysis of samples. Check standards (also known as laboratory control standards) contain a known amount of an analyte and indicate bias due to sample preparation or calibration.

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

Labeled congeners or surrogates, as appropriate, will be added to all organic samples prior to extraction. Surrogates have similar characteristics to target compounds. The recovery is used to estimate the recovery of target compounds in samples.

The lowest concentrations of interest in Table 4 are the reporting limits MEL and their contractors have reported for analysis of SPMDs from previous studies.

Table 4. Measurement quality objectives.

Parameter	Lab Control Samples (% Recovery)	Duplicate Samples (RPD <sup>1</sup> )	Matrix Spike (% Recovery)	Matrix Spike Duplicates (RPD)	Surrogate Recoveries (% Recovery)	Lowest Concentration of Interest
PCB Congeners	50 – 150	≤50%	NA	NA	25 - 150 <sup>2</sup>	0.10 ng/Sample
Dioxins and Furans	25 – 150	≤50%	NA	NA	25 - 150	0.10 ng/Sample
Chlorinated Pesticides	50 – 150	≤50%	50 - 150%	40%	30 - 150 <sup>3</sup>	1 ng/Sample
TOC	80 – 120	≤20%	75 – 125%	NA	NA	1 mg/L
TSS	80 – 120	≤20%	NA	NA	NA	1 mg/L

1 = Relative percent difference.  
2 = Labeled congeners.

3 = Surrogate recoveries are compound specific.  
NA = Not applicable.

## Sampling Design

This study will generate baseline data on PCBs, dioxins/furans, and chlorinated pesticides in the water column of Burnt Bridge Creek, Flushing Channel, and Lake River. The data will be used to (1) determine if these contaminants are being discharged to Vancouver Lake from surface water inputs, (2) establish baseline conditions for these contaminants as inputs to the lake, and (3) prioritize these inputs and the need for follow-up activities.

Concentrations of target chemicals are anticipated to be below detection levels in whole water samples. As a result, SPMDs will be used as a means to concentrate and quantify the contaminants. SPMDs are passive samplers which concentrate hydrophobic organic chemicals. They provide a time-weighted average of the bioavailable fraction (dissolved) of the contaminants of concern and estimation of the biological exposure and bioconcentration potential. Total concentrations for target compounds will be estimated using the relationship with TOC developed by Meadows et al. (1998) based on organic carbon-water equilibrium partitioning.

Total suspended solids (TSS) samples will be collected along with the TOC samples to evaluate predictable relationships with organic analytes. TSS and TOC data will be compared to organics' results for correlations.

Sample locations will be positioned as close to discharge as possible within each surface water input, at the same time providing a secure location. The closer sampling occurs to the discharge point the more representative results are for the surface water input.

SPMDs will be deployed for roughly one month during each seasonal period. Seasonal sampling will occur three times: winter, spring, and summer 2010 at four locations. Sampling periods were selected to represent a range of seasonal levels of contaminants and discharge. Timing of sample collection was intended to represent the period during the winter wet weather, spring run-off, and at the end of the dry season. These seasonal deployments will capture both the low-flow and high-flow periods of the year (Figure 2).

The USGS reviewed Pacific Northwest data on pesticide occurrence in surface water and found that the type of runoff was the controlling factor. In Western Washington and urban areas pesticides were associated most with rainfall runoff during winter and spring, and on the eastside irrigation season during spring and summer (Anderson et al., 2005). The two SPMD studies in the lower Columbia River around the Vancouver and Portland area measured PCB concentrations highest during both high flow (Johnson and Norton, 2005) and low flow (McCarthy and Gale, 1999).

Discharge data for Burnt Bridge Creek will be obtained from the gaging station currently being operated by Ecology (28C080) at river mile 1.6. This is a former USGS gaging station (14211902) taken over by Ecology in May 2007. Due to recent budget constraints, Ecology is planning to discontinue operation of this station. The USGS has been funded and is planning to re-establish operation.

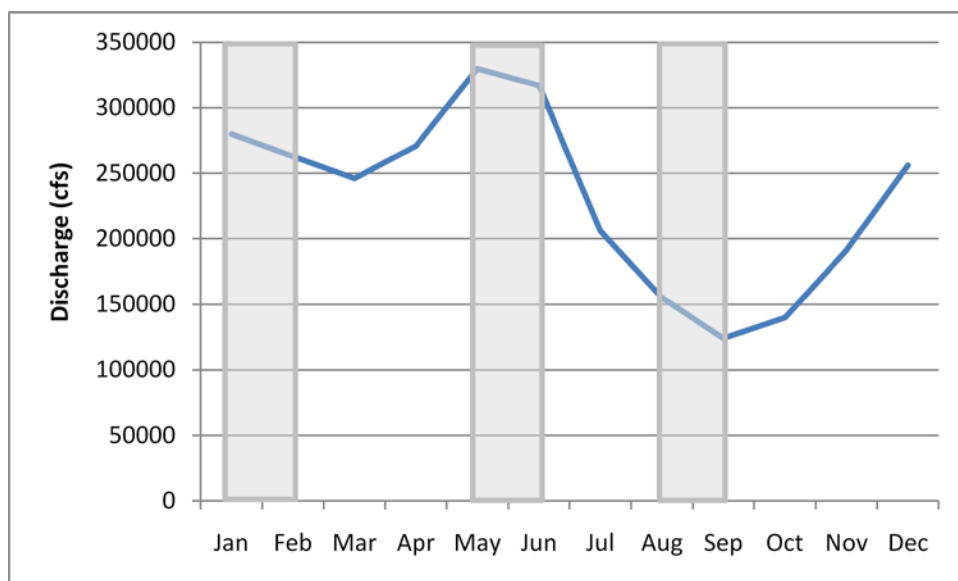


Figure 2. Annual flow for the Columbia River at Beaver Army Terminal and approximate periods of SPMD deployment. (USGS 14246900 – from mean daily flow; 1969 to 2009.)

The Ecology period of record for the Burnt Bridge Creek station starts late May 2007. To date, rating curves have not yet been developed but are expected to be available by this study’s conclusion. Loading rates will be calculated for target pollutants from SPMD results and average discharge from mean daily flow records over the sample period. There is no discharge information available for the Lake River or the intermittent flow from the Flushing Channel. Loading will not be calculated for these inputs.

Locations of sampling sites are shown on Figure 1. Table 5 presents information on SPMD site latitudes, longitudes, and the general description of SPMD locations.

Table 5. Sample stations, coordinates, and location.

Waterbody	Latitude	Longitude	Location
Burnt Bridge Creek (BBC)	45.67499	-122.69066	Just upstream of RR culvert
Flushing Channel (FLCH)	45.66708	-122.75222	Mid-point of Flushing Channel
Lake River North (LRN)	45.81360	-122.74811	Northern-most boathouse at the Ridgefield Marina
Lake River South (LRS)	45.70685	-122.72200	Southern-most boathouse at the Felida Moorage

Datum = NAD83 HARN.



## Sampling Procedures

The SPMD membranes and stainless steel canisters used to house the membranes will be purchased from Environmental Sampling Technologies (EST). SPMD membranes are preloaded onto spindles by EST in a clean room environment and shipped in solvent-rinsed metal cans filled with argon gas. Each SPMD canister deployed will have five membranes. The SPMD membranes will be kept frozen until deployed.

SPMDs will be deployed and retrieved following guidance in Huckins et al. (2000 and 2006) and Ecology SOP EAP001 (Johnson, 2007). Standard SPMDs (91 x 2.5 cm) containing 1 mL of triolein, spindle carriers that maintain the SPMDs while deployed, and stainless steel containers will be purchased through EST. SPMDs will be preloaded onto spindles by EST.

Rates of SPMD uptake of target contaminants and release of performance reference compounds (PRCs) are used to estimate ambient concentrations of pollutants. Prior to deployment, known concentrations of PRCs are spiked into SPMDs by EST. These compounds are not normally found in the environment at significant concentrations and slowly release over time. For this study, PCB 14, PCB 29, and PCB 50, will be used as PRCs.

The PRC release rate can be used to adjust uptake (sampling) rates of the target contaminants. Uptake of contaminants and release of PRCs are affected by the turbulence and velocity of water, temperature, and biofouling.

At the sample site, cans containing SPMD membranes will be carefully pried open. Five of the SPMD membrane spindles will be slid into each canister, and closed by screwing on the lid. Loading the SPMDs into the canisters will be done as quickly as possible because they are known to be potent air samplers. The SPMDs will be fixed to anchors and attached to a rigid structure by lanyard. The SPMDs will be situated off the bottom thus not allowing contact with substrate.

SPMDs will remain submerged until retrieved. Field personnel will wear nitrile gloves and avoid touching membranes. The sampling period will be approximately 30 days. Retrieval will follow reverse order of deployment.

Care must be taken with the cans holding the membranes. Can seals must not be damaged as membranes will need to be resealed in their original container following retrieval to prevent contamination. SPMDs must be maintained at or near freezing until they arrive at EST for dialysis and cleanup.

A Tidbit temperature logger will be attached to the SPMD canister to log water temperature on the half hour. At deployment, retrieval, and in the middle of the deployment cycle a TOC and TSS sample will be collected from each SPMD location.

TOC and TSS samples will be collected as wrist-depth grab samples at SPMD sites. Containers for the TOC and TSS grab samples will be obtained from MEL and cleaned to analyte-specific standards. Samples will be placed on ice in a cooler immediately following collection. Table 6 shows requirements for sample size, container type, preservative needed, and holding time for the TOC and TSS samples.

Table 6. TOC and TSS sample size, containers, preservatives, and holding time requirements.

Parameter	Sample Size	Container	Preservative	Holding Time
TOC	100 mL	2-60 mL poly	1:1 HCl to pH <2.0; cool to <4 °C	28 days
TSS	1000 mL	1 L poly	Cool to <4 °C	7 days

Sampling sites will be located by a Global Positioning System (GPS), which will be noted in field logs. Procedures for establishing GPS positions of SPMD sampling locations will follow SOP EAP013 – Determining Global Positioning System Coordinates (Janisch, 2006).

SPMD membranes will be shipped, under chain-of-custody, to EST by overnight Federal Express, in coolers packed in blue ice. Other water samples will be returned to Ecology Headquarters under chain-of-custody to be transported to MEL the following day.

## Measurement Procedures

Analytical parameters, sample numbers, methods, and reporting limits to be used for the study are presented below in Table 7. Method selection was based on the lowest detection limits available for the proposed analysis. A complete analyte list for chlorinated pesticides by EPA method 8081 can be found in Appendix C.

All samples will be placed in coolers on ice at or below 4°C following collection. Chain-of-custody procedures will be maintained throughout the sampling and analysis process.

All project samples will be analyzed at MEL or a laboratory contracted by MEL. Laboratories may use other appropriate methods as needed following consultation with the project manager.

Table 7. Laboratory parameters, number of samples, and analytical methods for sample analyses.

Parameter	Sample Number + QA	Expected Range of Results	Reporting Limits	Sample Cleanup Method	Analytical Method
TOC (mg/L)	39	1 – 10.0	1	-	SM5310B
TSS (mg/L)	39	1 – 10.0	1	-	SM2540SD
PCB Congeners <sup>1</sup> (pg/sample)	21	5 - 500	10	Dialysis/GPC <sup>2</sup>	EPA 1668A HRGC/HRMS
Dioxins and Furans <sup>1</sup> (pg/sample)	21	0.01-100	4.4	Dialysis/GPC <sup>2</sup>	EPA 1613B HRGC/HRMS
Chlorinated Pesticides <sup>1</sup> (ng/sample)	21	0.1 - 3.0	0.1 - 3.0	Dialysis/GPC <sup>2</sup>	EPA 8081

<sup>1</sup> = Reporting limits and expected ranges of results will vary for different compounds.

<sup>2</sup> = EST SOPs E14, E15, E19, E21, E33, E44, E48.

HRGC/HRMS = High Resolution Gas Chromatography / High Resolution Mass Spectrometry.

After retrieving SPMDs from sample canisters, they will be carefully sealed in their original containers, maintained at or near freezing, and sent overnight delivery to the EST lab for processing. EST will conduct dialysis and gel permeation chromatography (GPC) cleanup (also known as extraction) on SPMDs. This is a patented procedure as described in Huckins et al. (2000 and 2006). Following dialysis and GPC cleanup, extracts will be sealed in glass ampoules equally divided (50:50) for analysis at appropriate laboratories. One ampoule of the extract will be sent to MEL for chlorinated pesticide analysis, while the other will be sent to the contracted lab conducting PCB congeners and dioxin/furan analysis. Laboratories will report SPMD results as total ng/sample and be made aware the volume of extract is half the 5.0 mL total in each field sample.

Water concentrations of contaminants will be estimated by inputting results from SPMD analysis into a USGS Estimated Water Concentration spreadsheet calculator. Results, from analysis of the PRCs that were spiked into SPMDs prior to deployment, will be used to determine an exposure adjusted factor for calibration of the effects from temperature, water velocity, and biofouling. More information can be found at [www.aux.cerc.usgs.gov/SPMD/index.htm](http://www.aux.cerc.usgs.gov/SPMD/index.htm).

The total analytical cost for the project is estimated to be \$60,099 (Table 8). The estimate includes a 50% cost discount for analysis conducted at MEL. Also included is a 25% surcharge for MEL's contracting services and data quality review for results from contract laboratories. The cost estimate assumes analysis of samples collected on three occasions at four sites, plus quality assurance samples.

Table 8. Cost of water sample analyses.

	Number of Samples Per Event	Membranes Per Station	Total Membranes	Unit Cost	Subtotals
<b>SPMD Preparation and Extraction</b>					
Monitoring Stations	4+1 <sup>1</sup>	5	25	45	1125
Air Blank	1	5	5	45	225
Dialysis + GPC	6			310	1860
PRC and Surrogate Spikes	6	5	30	2	60
Estimated SPMD Preparation and Extraction Cost per 1 event					\$3,270

Parameter	Number of Samples	Number of QA Samples	Sample Total Per Event	Cost Per Sample	Subtotals
<b>Chemical Analysis</b>					
TOC	12	1	13	33	429
TSS	12	1	13	11	143
PCB Congeners	5	2 <sup>2</sup>	7	1063 <sup>3</sup>	7441
Dioxins and Furans	5	2 <sup>2</sup>	7	1000 <sup>3</sup>	7000
Chlorinated Pesticides	5	2 <sup>2</sup>	7	250	1750
Estimated Analytical Cost per 1 event					\$16,763
Estimated Total Laboratory Cost for 1 Event					\$20,033
Estimated Total Laboratory Cost for 3 Events					\$60,099

1 = Four monitoring stations plus one replicate.

2 = QA samples include 1 air blank and 1 day-zero dialysis blank per event.

3 = The estimate includes the cost of MEL contracting services.

# Quality Control Procedures

## Field

Table 9 lists the field quality control (QC) samples to be analyzed for the project. Field QC samples will provide an estimate of the total variability of the results (field plus laboratory) and will consist of collection and analysis of replicate samples.

Estimates of variability will be assessed from replicate samples consisting of two samples collected as close to the same time and location as possible and sent to the laboratory as two independent samples.

Contamination during deployment and retrieval will be assessed with air blanks. Air blanks will be shipped from EST in airtight cans like other SPMDs. Because SPMDs are known to be potent air samplers air blanks are used to correct SPMD data for exposure during deployment and retrieval.

The amount of time SPMDs are exposed to ambient air, during deployment and retrieval, is recorded in field logs. This generally takes between 60 and 90 seconds. Air blanks will be exposed for the average time this takes at all four sites. One air blank will be exposed at a different sample site for each seasonal period. After exposure of air blanks, they are sealed in their original can and returned to the EST laboratory the same as other samples for dialysis and cleanup. Following dialysis and cleanup, the extracts will be sent to MEL and their contract laboratory for analysis. Results of compounds detected in air blanks will be used to correct SPMD results.

Table 9. Field quality control samples.

Analysis	Replicates	Air Blanks
TOC	2/event	-
TSS	2/event	-
PCB Congeners	1/event	1/event
Dioxins and Furans	1/event	1/event
Chlorinated Pesticides	1/event	1/event

All efforts will be made to avoid cross-contamination. Field staff will wear non-talc nitrile gloves throughout the sample collection process. Immediately following collection, samples will be stored and shipped on ice to EST for dialysis and cleanup.

To help minimize field variability from sample collection, field samplers will be familiar with and follow methods for the collection and processing of SPMD samples. Guidance can be found in the Ecology SOPs *Standard Operating Procedure for Using Semipermeable Membrane Devices to Monitor Hydrophobic Organic Compounds in Surface Water* (Johnson, 2007) and *Manually Obtaining Surface Water Samples* (Joy, 2006).

Any equipment used in collection or processing samples will be decontaminated prior to going to the field. Sample equipment will be washed thoroughly with hot tap water and Liquinox detergent, followed by sequential rinses of 10% nitric acid, de-ionized water, and finally pesticide grade acetone. After decontamination, sampling equipment will be air dried under a fume hood, covered with aluminum foil, and placed in a new plastic bag until used.

## Laboratory

The PCB congener and dioxins/furan analysis will be conducted by a laboratory contracted by MEL. All other analysis will be completed by MEL.

Table 10 lists the laboratory QC samples to be analyzed for the project.

Table 10. Laboratory quality control samples.

Analysis	Method Blank	Check Standard	Duplicates	Surrogate Spikes	Labeled Compounds	MS/MSD <sup>1</sup>	ORP <sup>2</sup> Standards
TOC	1/batch	1/batch	1/batch	-	-	1/batch	-
TSS	1/batch	1/batch	1/batch	-	-	-	-
PCB Congeners	1/batch	1/batch	-	-	all samples	-	-
Dioxins and Furans	1/batch	1/batch	-	-	all samples	-	each batch
Chlorinated Pesticides	2/batch	1/batch	-	all samples	-	1/batch	each batch

<sup>1</sup> = Matrix spike/Matrix spike duplicate.

<sup>2</sup> = Ongoing precision and recovery.

SPMDs also require a special group of method blanks which will be prepared by EST for the dialysis and cleanup process. These blanks are in addition to method blanks typically run by labs during analysis (see Appendix C). In efforts to reduce cost, only the day-zero blank will be analyzed along with study samples. The others will be kept frozen at the analytical labs for analysis in the event that contamination or other problems occur.

Surrogates will be spiked at the EST laboratory into one of the five membranes per sample, prior to dialysis and cleanup, to calculate analytical recovery for each class of compounds. Surrogates will be provided by the laboratories conducting the analysis. MEL will provide EST surrogates for the chlorinated pesticides which will include tetrachloro-m-xylene and 4,4'-dibromo octafluoro biphenyl. Surrogates for the PCB congener and dioxin/furan analysis will include a suite of labeled PCBs and dioxin/furans represented by low, middle, and high molecular weight compounds.

In addition, MEL will make up and send to EST matrix spikes for the chlorinated pesticides analysis. EST will spike one new SPMD membrane in the laboratory with various chlorinated pesticides. A new SPMD will be used to avoid interference with target analytes.

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

## Data Management Procedures

All field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets after return from the field. Data entries will be independently verified for accuracy by another member of the project team.

Case narratives, included in the data package from MEL, will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory QC results will also be included in the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, and laboratory blanks. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Field and laboratory data for the project will be entered into Ecology's EIM system. Laboratory data will be downloaded directly into EIM from MEL's data management system. Data from contract laboratories will be submitted in electronic format for inclusion into the EIM system.

## Audits and Reports

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

A draft report of the study findings will be completed by the principal investigator in February 2011 and a final report in May 2011. The report will include, at a minimum, the following:

- Map showing all sampling locations and any other pertinent features of the study area.
- Coordinates of each sampling site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Summary tables of the chemical and physical data.
- Results of the toxic contaminants related to available standards and ranking of surface water inputs.
- Discussion of seasonal data on concentrations of toxic chemicals in the surface water inputs.
- Complete set of chemical and physical data and MEL quality assurance review in the Appendix.

Upon study completion, all project data will be entered into Ecology's EIM system. Public access to electronic data and the final report for the study will be available through Ecology's Internet homepage ([www.ecy.wa.gov](http://www.ecy.wa.gov)).



## **Data Verification**

Data verification is a process conducted by those producing data. Verification of laboratory data is normally performed by a MEL unit supervisor or an analyst experienced with the method. It involves a detailed examination of the data package using professional judgment to determine whether the measurement quality objectives (MQOs) have been met.

Final acceptance of the project data is the responsibility of the principal investigator. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

Data verification involves examining the data for errors, omissions, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages, including QC results for analyses conducted by MEL, will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review.

MEL staff will provide a written report of their data review which will include a discussion of whether (1) MQOs were met; (2) proper analytical methods and protocols were followed; (3) calibrations and controls were within limits; and (4) data were consistent, correct, and complete, without errors or omissions.

## **Data Quality (Usability) Assessment**

After the project data have been reviewed and verified, the principal investigator will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures, as well as results from field replicates, laboratory duplicates, and surrogate recoveries, will provide information to determine if MQOs have been met. A review of sample results will be performed following each seasonal sampling event to assess the need for modifications to the sampling or analysis program. Laboratory and quality assurance staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of field replicates, along with laboratory QC results. This will include assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and the success of laboratory QC samples meeting control limits.

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# Appendices

## Appendix A. 303(d) Fish Tissue Exceedances and NTR Criteria

Table A1. Vancouver Lake fish tissue summary of results causing 303(d) listing (Coots, 2007).

Sample Identification 06):	Largescale Sucker			Common Carp			Largemouth Bass	NTR Criteria <sup>1</sup>
	194210	194209	194208	194217	194215	194216	194211	
Lipid (%)	2.1	1.4	1.5	3.2	1.2	9.7	2.2	
PCB - 1242	4.8 U	4.8 U	5.0 U	9.6 UJ	4.7 U	4.9 U	<b>8.0</b>	<b>1.4</b>
PCB - 1254	<b>29 J</b>	<b>18 J</b>	<b>33 J</b>	<b>185 J</b>	<b>25 J</b>	<b>62 J</b>	<b>53</b>	<b>1.4</b>
PCB - 1260	<b>16 J</b>	<b>10 J</b>	<b>21 J</b>	77 UJ	<b>26 J</b>	<b>20 J</b>	<b>22 J</b>	<b>1.4</b>
Total PCBs	<b>45J</b>	<b>28J</b>	<b>54J</b>	<b>185J</b>	<b>51J</b>	<b>82J</b>	<b>83J</b>	<b>5.3</b>
4,4'-DDE	<b>24</b>	<b>10</b>	<b>23</b>	<b>96 J</b>	<b>27</b>	<b>37 J</b>	<b>34</b>	<b>31.6</b>
4,4'-DDD	<b>3.8</b>	<b>1.4</b>	<b>3.5</b>	<b>22 J</b>	<b>1.4</b>	<b>7.0 J</b>	<b>5.2</b>	<b>45.0</b>
4,4'-DDT	<b>1.4 J</b>	0.48 U	<b>1.7 J</b>	<b>3.3 J</b>	<b>1.1 J</b>	<b>1.4 J</b>	<b>2.6 J</b>	<b>31.6</b>
Dieldrin	0.48 UJ	0.48 UJ	0.50 UJ	0.48 UJ	0.94 UJ	0.49 UJ	<b>1.1 J</b>	<b>0.65</b>
Toxaphene	9.6 UJ	9.7 UJ	9.9 UJ	96 UJ	9.4 UJ	9.9 UJ	<b>28 J</b>	<b>9.82</b>
2,3,7,8-TCDD (ng/Kg)		<b>0.103</b>			<b>0.069</b>			<b>0.07</b>

1 = Units are  $\mu\text{g}/\text{Kg}$  except for 2,3,7,8-TCDD which is  $\text{ng}/\text{Kg}$ .

**Bold** = Visual aid for detected compounds.

## Appendix B. Analyte List for Chlorinated Pesticides

### List of analytes for chlorinated pesticides analysis by EPA Method 8081.

Aldrin	Dieldrin
<i>alpha</i> -BHC	Endosulfan I
<i>beta</i> -BHC	Endosulfan II
<i>delta</i> -BHC	Endosulfan Sulfate
<i>gamma</i> -BHC (Lindane)	Endrin
Chlorpyrifos	Endrin Aldehyde
<i>cis</i> -Chlordane ( <i>alpha</i> -Chlordane)	Endrin Ketone
<i>trans</i> -Chlordane ( <i>gamma</i> )	Heptachlor
Chlordane (Tech)	Heptachlor Epoxide
Dacthal (DCPA) <sup>1</sup>	Hexachlorobenzene
2,4'-DDD	Methoxychlor
4,4'-DDD	Mirex
2,4'-DDE	<i>cis</i> -Nonachlor
4,4'-DDE	<i>trans</i> -Nonachlor
4,4'-DDMU <sup>1</sup>	Oxychlordane
2,4'-DDT	Pentachloroanisole <sup>1</sup>
4,4'-DDT	Toxaphene

<sup>1</sup> These compounds have inconsistent and poor recoveries.

### Surrogates

Tetrachloro-m-xylene (TCMX)  
4,4'-dibromo octafluoro biphenyl (DBOB)

## Appendix C. List of Dialysis and Cleanup Method Blanks

Below is a summary of possible dialysis and cleanup method blanks for dialysis and GPC cleanup of SPMD samples (from Sandvik, 2009).

SPMD method blanks:

- Day-zero dialysis blank to serve as a reference point for chemical compound loss and to represent background during dialysis and cleanup. This blank will contain 5 membranes, as in the field samples, and will be manufactured at the same time as field samples.
- Fresh day-zero blank, prepared just prior to dialysis, contains one membrane for MEL analysis and one membrane for PCB and dioxin/furan analysis to serve as a control.
- Dialysis with no spikes, containing the same amount of membranes as the field samples (5), but having no spiked compound injected into them such as PRCs, surrogates, or matrix spikes.
- Spiking blank, a spiked single membrane, to assess contamination of membranes exposed while spiking the SPMDs at EST after field sampling but before dialysis and cleanup.
- Solvent blank, (same as reagent blank), to assess contamination independent of the SPMDs. This blank does not go through any SPMD process.
- Solvent-GPC blank to assess contamination of the GPC process. This blank is run through GPC.