

THE DEPARTMENT OF ECOLOGY
Environmental Assessment Program

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**SUBJECT: Baseline Summary of a Long-term Monitoring Effort in the Spokane River
for PCBs, PBDEs, and Metals**

Background

The Spokane River in eastern Washington contains elevated levels of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans, and metals. These contaminants are prevalent in water, sediment, and fish tissue. There are numerous studies and clean-up activities addressing contamination in the Spokane River. Information about the Spokane River, water quality, research studies, clean-up efforts, and resources can be found on Washington State Department of Ecology's (Ecology) website for the Spokane River Basin at www.ecy.wa.gov/geographic/spokane/spokane_river_basin.htm.

The Spokane River has been part of several statewide monitoring efforts for some years. These statewide efforts increased sampling in the Spokane River in 2009 and 2010 in order to help develop a long-term effectiveness monitoring program (Era-Miller, 2009) for the Spokane River Urban Waters Initiative (www.ecy.wa.gov/urbanwaters/spokaneriver.html). This initiative focuses on urban waterbodies and aims to prevent contamination or re-contamination of waterways by identifying and eliminating toxic chemicals at their source.

The goal of the 2009 and 2010 supplemental monitoring was to help establish a baseline characterization of PCBs, PBDEs, arsenic, cadmium, lead, and zinc as part of the beginning efforts of the Urban Water Initiative. The supplemental monitoring was conducted as part of three long-term statewide efforts, with extra sites and analytes added for the Spokane River sites:

- The River and Stream Water Quality Monitoring program samples for metals and conventional parameters (Hallock and Ehinger, 2003; Hallock, 2007; Hopkins, 1995).
- Monitoring for PBTs using Suspended Particulate Material (SPM). Lead is the main target analyte; arsenic, cadmium, and zinc were added for the Spokane River sites (Meredith and Furl, 2008).
- Monitoring for Persistent, Bioaccumulative and Toxic (PBT) chemicals using semi-permeable membrane devices (SPMDs). Target chemicals included pesticides, PCBs, PBDEs, and PAHs (Johnson, 2007a; Sandvik, 2010a).

A description of the long-term monitoring programs, access to historical data and previous annual reports can be found on Ecology's Internet web site at www.ecy.wa.gov under the "Environmental Assessment" program. Water quality monitoring information is listed under "River and Stream Water Quality Monitoring" at www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html and the PBT Trends can be found listed under "Toxics Monitoring by Ecology" in the "Washington State Toxics Monitoring Program" (WSTMP) at www.ecy.wa.gov/programs/eap/toxics/wstmp.htm.

Methods and results are summarized below.

Monitoring Design

Sites and Timeframes

Two locations were sampled for the baseline characterization effort (Figure 1). These sites are currently being used in the PBT studies and in the River and Stream Water Quality Monitoring program although additional sampling and analytes were added for the baseline project. Descriptions of the monitoring sites are in Appendix A.

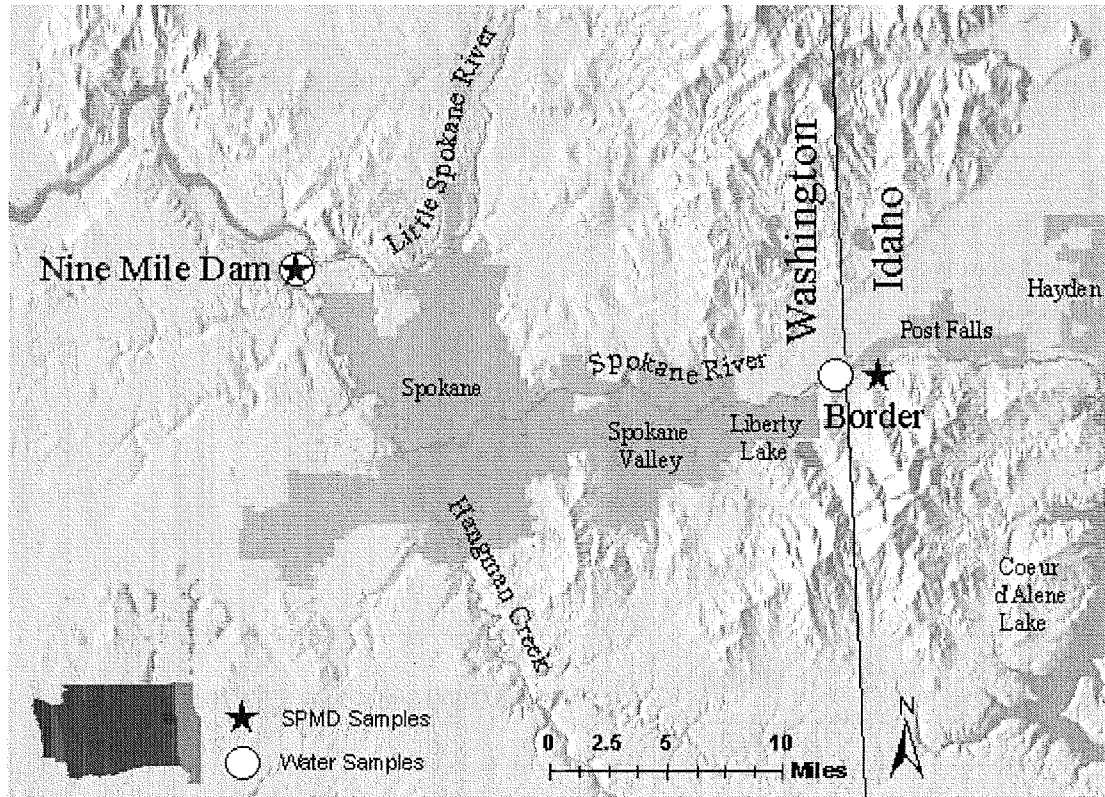


Figure 1. Site Locations in the Spokane River.

Sampling took place in fall 2009 (September) and spring 2010 (May and June). Sampling during these periods captured typical seasonal low-flow (fall) and high-flow (spring) conditions for the river. Sample collection by the various methods usually overlapped in time. SPM collection was taken twice during each of the SPMD deployments. Water samples were taken during one SPMD deployment, and after one SPMD deployment.

Methods

Chemicals Monitored

Table 1 shows analytes monitored by collection method for each sampling period.

Table 1. Chemical, Metal, and Ancillary Parameters Analyzed.

Parameters	Collection Method	Sampling Timeframe		
Water				
Lead, total and dissolved	Grab	9/22/2009 and 6/14/2010		
Arsenic, total and dissolved				
Cadmium, total and dissolved				
Zinc, total and dissolved				
Hardness				
TOC				
TSS				
Flow				
Conductivity	Field measurement			
Water temperature				
pH				
PBDEs	SPMDs ¹	9/3-30/2009 and 4/28 - 5/27/2010		
PCB congeners				
Water temperature	TidbiTs ^{1,2}			
TOC	Grab	9/3/2009 and 4/28/2010	9/21/2009 and 5/14/2010	9/30/2009 and 5/27/2010
TSS				
Water temperature	Field measurement			
Conductivity				
Particulates				
Lead, particulates	SPM	9/3/2009 and 4/28/2010	-	9/30/2009 and 5/27/2010
Arsenic, particulates				
Cadmium, particulates				
Zinc, particulates				
TSS, particulate fraction				
pH	Field measurement			

1. Passive monitoring: continuous or near continuous sample collection.

2. TidbiTs: Onset Computer Corporation Hoboware temperature loggers.

SPM: suspended particulate matter.

SPMD: semipermeable membrane devices.

TOC: total organic carbon.

TSS: total suspended solids.

Whole water samples for metals were collected once during each sampling period. SPM and SPMD samples were collected near each other and during the same sampling time period.

Conventional parameters such as TOC, TSS, water temperature, pH, and conductivity were collected during all sampling efforts (i.e. metals, SPM, and SPMDs), which may have varying sampling timeframes.

Field Procedures

Sample collection and field measurements followed Ecology's standard operating procedures (SOPs). SOPs followed for this study are listed in Appendix B.

Brief descriptions of field procedures referenced to each project's Quality Assurance Project Plans (QAPPs) are:

- Water sample collections were single, near-surface grab samples from highway bridges (Hallock and Ehinger, 2003; Hallock, 2007; and Hopkins, 1995).
- SPM were collected using in-line filtration of river water taken from 0.5 - 3 feet below the surface (Meredith and Furl, 2008).
- Sample collection with SPMDs used a composite of 5 standard SPMD membranes and then deployed into the water for a one-month period. The SPMDs were deployed for approximately 28 days each sampling period (Johnson 2007a; Sandvik, 2010a).

Laboratory Procedures

Chemicals analyzed in the samples collected at each site are shown in Table 1 above.

Water and SPM samples were analyzed by Ecology's Manchester Environmental Laboratory (MEL). The SPMDs were prepared and processed by their manufacturer, Environmental Sampling Technology Laboratory (EST). The SPMD extracts were then analyzed by other laboratories: MEL performed PBDEs analyses while Analytical Perspectives Laboratory conducted PCB congener analyses.

Analytical methods, reporting limits, and a brief discussion on how final results are reported in this document can be found in Appendix C.

Detailed information regarding extraction, clean-up, analysis, and data reduction can be found in the QAPPs (referenced above). Annual reports with the Spokane River results discussed here include:

- River and Stream Water Quality Monitoring Report Water Year 2009 (Hallock, 2010b).
- River and Stream Water Quality Monitoring Report Water Year 2010 (Hallock, 2011).
- PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter from Washington State Rivers and Lakes, 2009 Results (Meredith and Furl, 2010).

- PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter from Washington State Rivers and Lakes, 2010 Results (Meredith and Roberts, 2011).
- Washington State Toxics Monitoring Program: Monitoring with SPMDs for PBTs in Washington Waters in 2009 (Sandvik and Seiders, 2011).
- Washington State Toxics Monitoring Program: Monitoring with SPMDs for PBTs in Washington Waters in 2010 (in draft).

Data Quality

The QAPP developed for each study established data quality requirements for accuracy, bias, and reporting limits with measurement quality objectives (MQOs). The project lead for each study compared results from field and laboratory QC samples to the MQOs to determine if the MQOs were met. Based on these assessments and reviews of laboratory data verification reports, the data were accepted, accepted with appropriate qualifications, or rejected. Results presented here were accepted and any qualifiers were retained. A summary of field and laboratory data quality are presented in Appendix D. For more discussion of specific data quality, refer to each project's annual report.

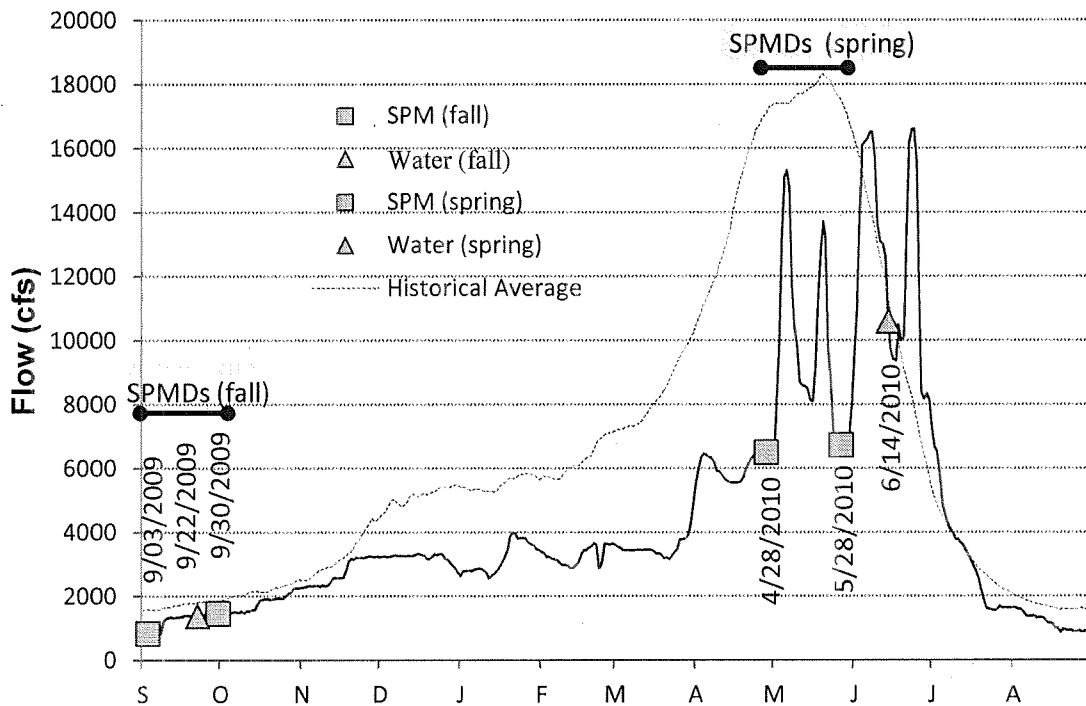
Results and Discussion

Data for this study is available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm or by contacting Ecology. At the website, search EIM User Study ID, AMS001 (water results) or PbTrends09 and PbTrends10 (SPM results). Data for SPMDs are not stored in Ecology's EIM system. SPMD data can be obtained by contacting the Ecology project officer: Patti Sandvik at patti.sandvik@ecy.wa.gov.

Discussions of the chemistry results follow a description of the flow in the Spokane River during the sampling events.

Flow

The Spokane River flow was below historical average for both sampling periods (2009 fall and 2010 spring) (Hopkins, 2009; Hopkins, 2010) during SPMD, SPM, and metal (2009 fall only) collection. Flow was above historical average for the metals sampling event in spring of 2010 (Hopkins, 2010). Figure 2 shows sample collections in relation to flow.



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

Figure 2. Stream Flow Pattern and Sampling Events in 2009 (fall) and 2010 (spring).

In the summer of 2009, low precipitation events coupled with above normal temperatures during July and August kept the majority of statewide in-stream flow levels (including Spokane River) towards the lower end of their normal historical ranges. Although precipitation and temperatures returned to normal in September, river levels remained below normal during the sampling period for this project.

In May of 2010, a majority of Washington State rivers had above normal flows, but not the Spokane River. Below normal precipitation was experienced most of the winter months (December through March) resulting in below normal river levels in most rivers statewide. Increased precipitation near the end of April increased river levels.

When SPMD and SPM sampling began at the end of April 2010, the Spokane River was below its 20th percentile: only 20 percent of historical stream flow for this time period fell below this level. The flow increased to between the 20th and 50th percentile (median historical stream flow) by the end of May when sampling ended. Above normal precipitation in June increased flow in the Spokane River (as well as the majority of rivers statewide) to above historical levels. Metals were sampled in the middle of June and, therefore, they sampled at or above historical river levels.

Chemistry Results

Chemistry results are shown in Table 2 (fall 2009) and Table 3 (spring 2010). Results reported in bold are above the Washington State Water Quality chronic criteria for dissolved metals or the Lowest Apparent Effects Threshold (LAET) for particulates. Results are discussed further for each sampling type (water, SPM, and SPMDs) below.

Table 2. Results of Chemical and Metal Tests of Spokane River Collected Fall 2009.

2009 Fall	Spokane R. at Nine Mile Dam			Spokane R. near Idaho Border		
	SPM 9/3/2009	Water 9/22/2009	SPM 9/30/2009	SPM 9/3/2009	Water 9/22/2009	SPM 9/30/2009
Metals						
Parameter	particulates (mg/Kg)	dissolved (ug/L)	particulates (mg/Kg)	particulates (mg/Kg)	dissolved (ug/L)	total (ug/L)
Lead	135	0.083	143	653	0.142	1.49
Arsenic	20.7	2.98	17.2 U	29.4 U	0.48	0.46
Cadmium	16.7 U	0.053	17.2 U	29.4 U	0.065	0.12
Zinc	1090	8.9	2800	3547	22.9	27.8
Organics						
Parameter	SPMD 9/3-30/2009					
Total PCBs	dissolved (pg/L)					
Total PBDEs	46					
	33					
Conventionals	SPM, SPMD 9/3/2009	SPMD 9/21/2009	Water 9/22/2009	SPM, SPMD 9/30/2009	SPMD 9/21/2009	Water 9/22/2009
Flow (cfs)	-	-	1195	1300 ^a	-	742
Water Temperature (C°)	16.8	-	13.3	13.1, 14.8 ^b	22	19.2
Conductivity (us/cm)	276	218	290	215	51, 49	52
pH	8.4	-	8.38	8.2	7.8	7.6
TSS (mg/L)	1, 2	2	2	2, 2	1, 1 U	2
TOC (mg/L)	1.0 U	1.2	1.1	1.3	1.5	1.4
Hardness (mg/Kg)	-	-	131	-	-	20.6

SPM: suspended particulate matter.

SPMD: semipermeable membrane device.

Water: Water grab samples.

TSS: total suspended solids.

TOC: total organic carbon.

U = not detected above reporting limit.

a. geometric mean for sampling period 9/3-30/2009.

b. average temperature for sampling period 9/3-30/2009.

-No individual result. May be part of an average or not analyzed.

Table 3. Results of Chemical and Metal Tests of Spokane River Collected Spring 2010.

2010 Spring	Spokane R. at Nine Mile Dam			Spokane R. near Idaho Border		
	SPM 4/28/2010	Water 6/14/2010	SPM 5/27/2010	SPM 4/29/2010	Water 6/14/2010	SPM 5/27/2010
Metals						
Parameter	particulates (mg/Kg)	total (ug/L)	particulates (mg/Kg)	particulates (mg/Kg)	total (ug/L)	particulates (mg/Kg)
Lead	338	1.40	212	1091	1.28	471
Arsenic	23.7	0.68	22.7 U	62.5 U	0.33	41.7 U
Cadmium	20.8 U	0.158	22.7 U	62.5 U	0.22	41.7 U
Zinc	2333	40.6	1391	4088	46.8	2942
Organics						
Parameter		SPMD 4/27 - 5/27/2010		SPMD 4/27 - 5/27/2010		
Total PCBs		dissolved (pg/L)		dissolved (pg/L)		
Total PBDEs		85 JK		140 JK		
		30 JK		41 JK		
Conventionals						
Flow (cfs)	SPM, SPMD 4/28/2010	SPMD 5/14/2010	SPM, SPMD 5/27/2010	SPM, SPMD 4/29/2010	Water 6/14/2010	SPM, SPMD 5/27/2010
Water Temperature (C°)	-	-	9696 ^a	-	10300	9722 ^a
Conductivity (us/cm)	8.8	-	12.6, 10.9 ^b	7.8	14.8	12.4, 10.4 ^b
pH	92	84	109	50, 50	52	50, 48
TSS (mg/L)	7.5	-	7.7	7.4	7.71	7.4
TOC (mg/L)	3, 3	4	4, 2	1, 2	2	2, 1
Hardness (mg/Kg)	1.5	1.6	1.6	1.6	1.5	1.9
	-	-	-	-	20.8	-

SPM: suspended particulate matter.
 SPMD: semipermeable membrane device.
 Water: Water grab samples.
 TSS: total suspended solids.
 TOC: total organic carbon.

U = not detected above reporting limit.
 JK: the analyte was positively identified. Reported results are an estimate with unknown bias.
 a. Geometric mean for sampling period 4/27 - 5/27/2010.
 b. Average temperature for sampling period 4/27 - 5/27/2010.
 - No individual result. May be part of an average or not analyzed.

Water

Results from fall 2009 and spring 2010 whole water samples ranged from 0.083 – 0.145 ug/L for lead (dissolved) and 8.9 - 46.8 ug/L for zinc (dissolved) at the Nine Mile Dam and Stateline sites. The Stateline dissolved zinc result (46.8 ug/L) exceeded the Washington State Water Quality chronic criteria for dissolved metals (27.63 ug/L based on hardness) by 69% in 2010. Furthermore, dissolved zinc at the Stateline site exceeded the criterion in all months for water year 2009 except August and September (Hallock, 2010b).

Dissolved cadmium was also higher in the Spokane River than typical for these two sampling periods (ranged 0.053 – 0.183 ug/L), but below the criteria for dissolved concentration based on hardness (ranged 0.32 – 1.36 ug/L). Many dissolved arsenic results were also elevated above the statewide median 0.55 ug/L, ranging from 0.35 to 2.98 ug/L, but lower than other sites statewide and considerably lower than the chronic water quality criteria (190 ug/L).

Overall, results for metals in water samples showed concentrations higher in the Spokane River when compared to other waterbodies (Hallock, 2010b; Hallock, 2011). In a statewide evaluation of concentrations of arsenic, cadmium, chromium, copper, lead, nickel, silver, and zinc in water samples, Hallock (2010b) found dissolved metals higher in eastern Washington than in western Washington. The Stateline Bridge samples from the Spokane River located at the Idaho border had dissolved metal concentrations, (all metals combined, median-normalized), above the 75th percentile of the body of ambient metals data and more than 75% of results were greater than reporting limits. Dissolved lead and zinc were much higher in the Spokane River than elsewhere making the comparison of metal concentrations more pronounced in the eastern Washington Rivers. The evaluation also found dissolved zinc appears to have a baseline concentration around 30 ug/L at the lowest flows.

Suspended Particulate Matter Samples

Results from fall 2009 and spring 2010 samples ranged from 135 – 1,091 mg/kg for lead and 1,090 – 4,088 mg/kg for zinc in the Nine Mile Dam and Stateline sites. Highest concentrations of lead and zinc were found at the Spokane River Idaho border site overall, which agreed with the water sample metal results above.

Concentrations of lead were high compared to other waterbodies (Meredith and Furl, 2010; Meredith and Roberts, 2011) and much higher than background levels found during a freshwater sediment reference study in Washington State. Zinc concentrations appear high also. The sediment reference study sampled bottom-sediments from nine lakes resulting in lead and zinc concentrations ranging from 3.18 – 55.4 mg/kg (average 13.6 mg/kg) and 23 – 110 (average 62.2 mg/kg), respectively (Sloan and Blakely, 2009).

Ecology developed guidelines to identify contaminant levels in sediments at which possible biological effects might occur by using the Lowest Apparent Effects Threshold (LAET) (Cubbage et al., 1997; Betts, 2003). The 2003 LAETs are 335 mg/kg for lead and 683 mg/kg for zinc. Comparing the results from the fall 2009 and spring 2010 sampling, one sample from the

Nine Mile Dam site and all samples from the Stateline site were above this threshold for lead and all samples for both sites were above the threshold for zinc.

Other SPM results (arsenic and cadmium) ranged from not detected to 23.7 mg/kg for arsenic and not detected in either sampling period for cadmium, falling near or below background levels. Two arsenic results, one from spring 2009 and one from spring 2010 sampled at the Nine Mile Dam site were above background bottom-sediment levels for Washington waterbodies (16.9 mg/kg). No cadmium results were above the 1.01 mg/kg background level. All arsenic and cadmium results fell below LAETs thresholds for arsenic (31.4 mg/kg) and cadmium (2.39 mg/kg).

Relationships

Previous monitoring efforts suggest existence of strong relationships among flow, metals concentrations, and TSS. During high flows, the dominant water in the Spokane River coming from the Coeur d'Alene system upstream of the Washington border is likely carrying re-suspended bank and bed sediment that are contaminated by historical mining (Hallock, 2010b). At low flow, the river contains a higher percent of groundwater (MacInnis et al., 2009). Seasonality, loading potential, and trends using these correlations have been reported where sufficient data is available (Hallock, 2010b; Meredith and Furl, 2010; Meredith and Roberts, 2011).

Meredith et al. (2010 and 2011) found lead concentrations by volume (particulate results divided by volume of filtered water (ug/L)) were significantly higher in the spring than in the fall ($p \leq 0.005$), likely driven by higher flows, which brought higher TSS (Table 4). Zinc was found higher in the spring than in the fall also. Arsenic and cadmium results were not detected in the spring but were found at low levels in the fall in some samples.

Table 4. Averaged Particulate Fraction Seasonal Comparison.

SPM by Volume (ug/L)	Spokane R. at Nine Mile Dam		Spokane R. near Idaho Border	
	2009 Fall	2010 Spring	2009 Fall	2010 Spring
Lead	0.1905	0.899	0.6	1.3605
Arsenic	0.0255 J	0.0795 J	0.0 U	0.0955 U
Cadmium	0.0235 U	0.076 U	0.0 U	0.0955 U
Zinc	2.865	6.05	3.4	6.495

Average results were qualified same as original results, except where one site had a mix of nondetects (U) and detected results, averaged results were qualified "J".

There appear to be strong indications that concentrations of total and dissolved cadmium, lead, and zinc are decreasing in the Spokane River. This observation is based on a review by Hallock (2010b) and a larger dataset than presented in this document, of which the 2009 water sample results are a part of. This decrease may be partially a result of declining trends in flow, though the trend in flow is not statistically significant. Variability in flow data and metal data as it relates to flow makes trend detection difficult.

Semipermeable Membrane Devices

PBDEs

Total PBDE results (dissolved) from SPMDs in the Spokane River ranged from 33 – 240 pg/L for 2009 fall and 2010 spring. Highest concentrations (240 pg/L) were found at the Nine Mile Dam site in the fall of 2009. Other waterbodies sampled for the PBT Trends Study generally had results below 50 pg/L. PBDE concentrations in the Spokane River at Nine Mile Dam have been consistently 5 to >10 times higher than other waterbodies statewide (Johnson et al., 2006; Sandvik, 2009; Sandvik, 2010b; Sandvik and Seiders, 2011). These elevated concentrations at this site are typically found in the fall samples. Statewide, seasonal patterns are not apparent at any of the other monitoring sites (Johnson et al., 2006; Sandvik, 2009; Sandvik, 2010b). There is insufficient data available to compare the seasonal observation with the Spokane River Idaho border sampling location, although concentrations remained lower (< 50 pg/L) for both fall (2009) and spring (2010) than at Nine Mile Dam.

PCBs

Results for total PCBs (dissolved) ranged from 46 – 140 pg/L for fall 2009 and spring 2010 SPMD samples in the Spokane River. Higher PCB concentrations were found in the spring 2010 samples for both Spokane River sampling sites. Previous PBT trend results from SPMDs (2007 – 2009), found total PCB concentrations in statewide waterbodies ranged from 5.4 – 130 pg/L (dissolved). The Spokane River and the Lower Columbia River generally had higher PCB levels than other sites.

Certain PCB congeners were identified as common contributors to field-trip blanks. Field samples also contained these same congeners at similar concentrations except for PCB-011. Several field samples showed levels of PCB-011 contributing greater than 20% to total PCBs (Sandvik and Seiders, 2011). Recent studies are reporting PCB-011 to be a global inadvertent pollutant from production of pigments or dyes (Dingfei and Hornbuckle, 2010; Muñoz, 2007; Rodenburg et al., 2010). In the Spokane River samples discussed here, PCB-011 contributed 6% and 32% in the Spokane River Nine Mile Dam samples and 2% and 3% in the Idaho border samples for 2009 and 2010 respectively for each site. All blanks had <2% contribution of PCB-011. The high contributions of PCB-011 found in field samples compared to the low contributions in field-trip blanks suggests PCB-011 may be from a current local source rather than part of the background PCBs.

Whole water concentration (sum of dissolved and particulate) PCB results ranged from 120 – 410 pg/L. For comparative purposes only since no SPMD data are used for regulatory action, whole water concentrations were compared to the Washington State and national human health criterion for PCBs. All total concentration results for both Spokane River sites in 2009 and 2010 except one (the 2009 fall Spokane River border site) did not meet the Washington human health criterion of 170 pg/L. All total concentration results from fall 2009 and spring 2010 samples for the Spokane River were above the EPA national recommended human health criterion of 64

pg/L. Like dissolved results, higher total concentrations were found in the spring 2010 samples likely as a result of higher TOC in the spring associated with higher TSS and flows.

Caution should be taken when comparing SPMD results among different studies or determining trends because of high variability found in the sampling system (Sandvik and Seiders, 2011).

Conventional Parameters

Table 5 shows result ranges for conventional parameters, which include temperature, conductivity, TSS, TOC, flow, and pH.

Table 5. Ranges of Ancillary Results Collected During Fall 2009 and Spring 2010 Sampling in the Spokane River.

Site	Sample Event	Parameter	Range
Spokane R. at Nine Mile Dam	2009 fall	Temperature (C°)	13.1 - 16.8
		Conductivity (us/cm)	215 - 290
		TSS (mg/L)	1 - 2
		TOC (mg/L)	nd - 1.3
		Flow (geometric mean cfs)	1,300
		pH	8.2 - 8.4
Spokane R. near Idaho Border	2009 fall	Temperature (C°)	17.5 - 22
		Conductivity (us/cm)	46 - 52
		TSS (mg/L)	nd - 2
		TOC (mg/L)	1.3 - 1.7
		Flow (geometric mean cfs)	1,036
		pH	7.6 - 8.1
Spokane R. at Nine Mile Dam	2010 spring	Temperature (C°)	8.8 - 15
		Conductivity (us/cm)	84 - 109
		TSS (mg/L)	2 - 4
		TOC (mg/L)	1.5 - 1.6
		Flow (geometric mean cfs)	9,696
		pH	7.5 - 7.88
Spokane R. near Idaho Border	2010 spring	Temperature (mean C°)	7.8 - 14.8
		Conductivity (us/cm)	48 - 52
		TSS (mg/L)	1 - 2
		TOC (mg/L)	1.5 - 1.9
		Flow (cfs)	9,722
		pH	7.4 - 7.71

TSS: total suspended solids.
 TOC: total organic carbon.
 nd: not detected.

Recommendations

- Monitoring for metals (lead, cadmium, and zinc), PBDEs, and PCBs in the Spokane River should be continued in water, SPM, and SPMDs.
- Sampling locations should include Nine Mile Dam and near the Idaho border. An additional sampling site(s) should be considered in-between these two locations for some parameters such as PBDEs and PCBs. The Spokane River aquifer interchange should be considered when selecting a site(s).
- Address potential use of PCB congener pattern matching techniques to help identify current local sources in the Spokane River. For example, a reduction of PCB-011 may have a favorable reduction to total PCBs.
- Use information from this monitoring to help design an effectiveness monitoring program for toxics in the Spokane River.

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Appendix A. Monitoring Site Descriptions

Table A-1. Monitoring Site Descriptions, Fall 2009 and Spring 2010.

Site Description	Sample	River Mile (RM)	Latitude ¹	Longitude ¹	WBID ² WA-	Field ID ³
			Decimal Degrees	Decimal Degrees		
Spokane River at Nine Mile Dam	SPMDs	RM 58.1	47.7747	-117.5444	WA- 54-1020	SPOK and REPSPOK
Spokane River at Nine Mile Dam	SPM	RM 58.1	47.7747	-117.5444	WA- 54-1020	SPOKNM-PB
Spokane River at Nine Mile Dam	Water	RM 58	47.7767	-117.5448	WA- 54-1020	54A090
Spokane River near Idaho Border	SPMDs	RM 98.3	47.6942	-117.0094	WA- 57-1010	SPOKBD
Spokane near Idaho Border	SPM	RM 96	47.6948	-117.0513	WA- 57-1010	SPOKBD-PB
Spokane River near Idaho Border	Water	RM 96.35	47.6985	-117.0446	WA- 57-1010	57A150

1 - North American Datum 1983 is horizontal datum for coordinates.

2 - Ecology's Water Body Identification Number (WBID).

3 - Site identification as used in Ecology's Environmental Information Management system.

SPM = suspended particulate matter.

SPMDs = semipermeable membrane devices.

Appendix B. Ecology SOPs

Table B-1. Ecology SOPs for Sample Collecting and Processing.

Collection Method	Parameters	Reference to Ecology's SOPs
Whole Water Grab Sample	total and dissolved metals: lead, arsenic, cadmium, zinc, hardness	Ward 2007a, Ward 2007b
SPM	lead, arsenic, cadmium, zinc	Meredith 2008
SPMDs	PBDEs, PCB congeners	Johnson 2007b
Whole Water Grab Sample	TOC, TSS	Ward 2007b
TidbiTs	water temperature	Bilhimer and Stohr 2008
Field Measurement	water temperature	Nipp 2006
Field Measurement	pH	Ward 2007b
Field Measurement	conductivity	Ward 2007b

Flow information and data were obtained from Ecology's Environmental Assessment Program Freshwater Monitoring Unit, USGS, and other sources.

Appendix C. Analytical Methods, Reporting Limits, and Final Results Reported.

Table C-1. Laboratory and Measurement Procedures.

Analysis	Sample Matrix	Sample Prep Method	Analytical Method	Reporting Limit
PBDEs	SPMD extract	dialysis/GPC ¹	EPA 8270 ²	2 ng/Sample
PCB congeners	SPMD extract	dialysis/GPC ¹	EPA 1668A ³	0.1 ng/Sample
Lead	SPM	EPA 3050B	ICP/MS EPA 200.8	1 mg/Kg dw ⁴
Arsenic	SPM	EPA 3050B	"	1 mg/Kg dw ⁴
Cadmium	SPM	EPA 3050B	"	1 mg/Kg dw ⁴
Zinc	SPM	EPA 3050B	"	1 mg/Kg dw ⁴
Lead, dissolved	whole water	field filter	"	0.02 µg/L
Arsenic, dissolved	whole water	field filter	"	0.1 µg/L
Cadmium, dissolved	whole water	field filter	"	0.02 µg/L
Zinc, dissolved	whole water	field filter	"	1 µg/L
Lead, total	whole water	acid digest	"	0.1 µg/L
Arsenic, total	whole water	acid digest	"	0.1 µg/L
Cadmium, total	whole water	acid digest	"	0.1 µg/L
Zinc, total	whole water	acid digest	"	5 µg/L
Hardness	whole water	-	SM 2340B	0.3 µg/L
TOC	whole water	-	SM5310B	1 mg/L
TSS	whole water	-	SM2540D	1 mg/L

1. EST SOPs E14, E15, E19, E21, E32, E33, E44, E48.

2. GC/MS SIM = gas chromatography / mass spectrometry applying selective ion monitoring.

3. HRGC/HRMS = high resolution gas chromatography / high resolution mass spectrometry.

4. Assuming 0.5 g of field sample.

GPC = gel permeation chromatography.

dw = dry weight.

Results are reported as follows:

- Metal concentration results from water samples are reported in ug/L and hardness as mg/L. Water quality monitoring results are not considered finalized until the annual report is published, which is generally June of the following year. The 2009 fall and the 2010 spring results are finalized as of the printing of this report. These reports compare results to Washington Water Quality Criteria and are mentioned in this report.
- SPM laboratory results are reported in ug/filter. Final results are reported as mg/Kg dry weight. SPM results are also calculated based on volume as ug/L by dividing the laboratory-reported ug/filter value by the volume of water passed through the filter. SPM results (mg/Kg) were compared to the Lowest Apparent Effects Threshold (LAET) in freshwater sediments.

- The SPMD results are reported as total ng/sample as found in the entire extract; a 5-membrane composite. Residues are blank-corrected for background contamination as described in Appendix D before estimating water concentrations. Estimates of average water column concentrations are reported by using a USGS Estimated Water Concentration spreadsheet and PRCs. PRC loss rates are used to derive an exposure adjustment factor (EAF) to calibrate for the effects of temperature, water velocity, and biofouling. More information can be found through Huckins et al., 2006 and at www.waux.cerc.cr.usgs.gov/SPMD/index.htm. Water concentration is reported as pg/L (dissolved).
- Total PCB is the sum of the individual congeners. Total PBDE is the sum of the 13 congeners analyzed in this study. Non-detect results were treated as zero when summing compounds. Summed compounds were calculated from water concentration values (as opposed to the residue concentration).
- Currently, SPMD and SPM data are not used for 303(d) listing purposes or other direct regulatory actions. Comparison with water quality standards and other threshold levels in this report are for comparative purposes only. SPMD total water concentrations results (dissolved plus particulate fractions) were compared to the Washington human health criterion and EPA national recommended human health criterion for PCBs. Total concentrations for SPMD results were estimated using the relationship from TOC developed by Meadows et al., 1998 and Karickhoff's (1981) estimation for K_{oc} . There are no criteria for PBDEs.

Appendix D. Data Quality Summary

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. A QAPP developed for each study establishes a data quality guideline for accuracy, bias, and reporting limits with measurement quality objectives (MQOs) (See QAPP references listed in the Methods section).

Manchester's (MEL) quality assurance (QA) program includes the use of quality control (QC) charts, check standards, laboratory surrogates, in-house matrix spikes, laboratory replicates, and laboratory blanks, along with performance evaluation samples. For a more complete discussion of laboratory QA, see MEL's *Quality Assurance Manual* (MEL, 2006) and their *Lab Users Manual* (MEL, 2008).

To determine if MQOs were met, the project lead compared results on field and laboratory QC samples to the MQOs. Based on these assessments, a review of the laboratory data packages, and Manchester Laboratory's data verification reports, the data were either accepted, accepted with appropriate qualifications, or rejected. A summary of field and laboratory data quality are presented below. For more discussion of specific data quality, refer to each projects' annual report as mentioned above.

Field

Field Blanks

Field filter blanks were taken during each sampling period at one of the sample locations: one for SPMs and one for water samples. In the fall of 2009, a SPM field blank was taken at the Idaho border site and a whole water field blank at the Nine Mile Dam site. In the spring of 2010, a SPM field blank was taken at the Nine Mile Dam site and a whole water field blank at the Stateline border site. All results were below reporting limits except one water sample blank result. Dissolved zinc reported 1 ug/L in the water sample field blank taken during the 2010 spring sampling event. Since all results for this report are > 5ug/L, no qualifiers were applied (Hallock, personal communication, 2010a; Hallock, 2011).

A SPMD field trip blank was taken at the Nine Mile site during both sampling events. The field trip blank consisted of five membranes manufactured identically as for field samples. The blank was exposed to the site's ambient air for two minutes during deployment and again during retrieval of the field samples. Low levels of contaminants were found in both fall 2009 and spring 2010 field trip blanks. Sample results were evaluated and a blank-correction procedure used, where possible, before residue results were used for estimating water column concentrations (see below).

Field Replicates

There were no field replicates taken for SPM or water samples from the Spokane River. Field replicates for lead were taken from other sites during the routine sampling for SPM. High

variability was indicated by half the lead replicate results outside the MQOs ($\pm 50\%$ RPD) during the fall 2009 and spring 2010 sampling events.

A SPMD field replicate was deployed at the Nine Mile Dam location in the spring of 2010, but not during the fall of 2009. Results from the replicate were rejected due to a lab accident. Historical field replicates generally showed good precision having RPDs less than 20% for over 80% of the residue results (Sandvik 2009 and 2010b). Replicates deployed specifically at the Nine Mile Dam location in the spring of 2009 and fall of 2010 had good precision with over 90% of PBDE and PCB residue results having RPDs of 20% or less (Sandvik and Seiders 2011).

TidbiTs

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

Laboratory

All samples were prepared and analyzed within the methods holding times for the various parameters. Most QC procedures and corresponding samples fell within the acceptable limits. Exceptions were qualified as estimates when necessary and are briefly discussed below. One 2010 spring SPMD sample was rejected due to a laboratory accident; sample 1006021-15. Laboratory case narratives are available upon request for the project officers.

Metals

Matrix Spikes

The matrix spike and matrix spike duplicate recoveries for hardness analysis in the 2009 fall samples were below the acceptable criteria. Since the spike was insufficient for the elevated concentration of analyte in the field sample, no action was taken. All other associated matrix spike recoveries were within the acceptable limits.

SPM

All QC results were within acceptable limits. No additional qualitative action was needed.

SPMDs

Laboratory Blanks

Analytical laboratory method blanks showed no significant contamination for any of the chemicals analyzed. Individual PCB and PBDE compounds were detected in processing blanks. Concentrations of individual target chemicals in the blanks were inconsistent. Some of these same compounds were found at similar levels in the field trip blanks, suggesting a combination

of laboratory and field sources. Although the contamination source is unclear, a certain background level appears to exist and has been documented in previous reports (Sandvik, 2009; Sandvik, 2010b, Sandvik and Seiders 2011). Blank correction for background contamination is briefly described below. WSTMP annual reports for monitoring PBTs with SPMDs describe the blank correction procedure used for each sampling period in more detail.

TSS and TOC

All results for TOC and TSS met QA limits except for two TSS samples. TSS results were qualified as estimates because the samples had fast settling sand.

PCBs

All calibration standards were within the QC limits with a few exceptions. However, as the OPR recoveries were acceptable, no action was taken.

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

A number of congeners were qualified as estimates (J) because the concentration was below the lowest calibration standard. Also, low levels of certain target compounds were detected in the laboratory blanks. All corresponding concentrations were qualified as nondetects with an estimated reporting limit (UJ) because the values were below the reporting limit (0.02 ng/sample) and less than 10 times that of the corresponding method blank.

Target analyte recoveries were within method QC of 50% to 150% with several exceptions. Also, certain unlabeled analytes that were not deliberately spiked into an on-going precision and recovery (OPR) or laboratory control sample (LCS) were detected. These results and analytes were also found in field and laboratory blanks indicating certain background contamination of PCBs.

PBDEs

Sampling periods, (2009 fall and 2010 spring), had excellent QA results for PBDEs. Only one QA result for PBDE-138 in the 2010 spring samples required qualification (J) because of slightly low surrogate responses; sample 1006021-19.

Correction for Background Contamination (or Blank-Correction)

The sample results were screened to determine if they could be blank-corrected. Results that were greater than the mean plus two standard deviations of the field trip blank were deemed correctable. Correctable results were adjusted by subtracting the mean of the field trip blanks from the result; the adjusted results were then qualified as an estimate with an unknown bias (JK). For detected compounds that did not meet the blank-correction criteria, the original result

was used as an estimated reporting limit and qualified as being below the method detection limit with an unknown bias (UJK). The detection limit was used where a compound was not detected.

The fall sampling event in 2009 provided only one field trip blank. This result was assumed to represent the mean background contamination for that period because the samples were in the same waterbody (the Spokane River) and reasonably close in proximity (approximately 26 miles apart). The standard deviation of the fall field trip blank was estimated using the proportion of the standard deviation to the mean of the 2009 spring field trip blanks, which consisted of seven blanks. The assumption was made that the proportion of standard deviation to mean for one sampling period is similar to another sampling period. Even though this approach limits representativeness, the assumption seems fair, based on the review of the spring and fall field trip blank results.

The impact of the correction process varied among the chemical groups. For the combined 2009 fall and 2010 spring PBDE results, 42% were detected, and of those detected, 59% were correctable. For 2009 fall and 2010 spring PCBs, 84% were detected with 67% of those correctable.

Some results fell below the original reporting limit after they were blank-corrected. These results were considered detected at the "new" corrected level in the remainder of this report.