

PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter from Washington State Rivers and Lakes, 2009 Results



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### PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter from Washington State Rivers and Lakes, 2009 Results

by Callie Meredith and Chad Furl

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Waterbody Numbers:

Duwamish River	WA-09-1010
Hylebos Creek	WA-10-1011
Lake Washington	WA-08-9340
Lower Columbia River	WA-CR-1010
McNary Dam	WA-CR-1026
Okanogan River	WA-49-1010
Queets River	WA-21-1030
Rock Island Dam	WA-CR-1040
Snohomish River	WA-07-1020
Spokane River at Idaho border	WA-57-1010
Spokane River at Ninemile	WA-54-1020
Upper Columbia River	WA-CR-1060
Walla Walla River	WA-32-1010
Wenatchee River	WA-45-1010
Yakima River	WA-37-1010

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## Abstract

This report summarizes results from the second year (2009) of trend monitoring for lead in suspended particulate matter (SPM) by the Washington State Department of Ecology (Ecology). Lead sampling began in 2008 as a component of Ecology's persistent, bioaccumulative, and toxic chemical (PBT) monitoring program. Primary objectives of the program were to establish baseline lead concentrations and to evaluate spatial and temporal trends for lead in Washington State rivers and lakes.

A total of 60 SPM samples were collected from 15 sites statewide during the spring and fall of 2009. Two samples were collected per season at each site and analyzed for total lead.

Lead was detected in 95% of the samples. Concentrations ranged from 7 - 1,214 mg/Kg in the spring and from non-detect - 809 mg/Kg in the fall. The highest concentrations were from the Spokane River at the Idaho border in both seasons. Median values measured across the 15 monitoring sites were 20 and 25 mg/Kg during the spring and fall, respectively.

Lead concentrations at the Spokane River and Upper Columbia River in 2009 were lower than values measured in 2008. Higher concentrations were found in 2009 at the Duwamish, Snohomish, and Queets Rivers compared to 2008.

With the exception of the Spokane, Upper Columbia, and Duwamish Rivers, lead concentrations in SPM were near or slightly above background bottom-sediment levels measured at nine freshwater reference sites in Washington State.

Ten percent of the samples exceeded Ecology's proposed freshwater sediment lowest apparent effects threshold (LAET) of 335 mg/Kg. No guidelines are currently available for lead in SPM.

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## Introduction

### Background

Lead is a naturally occurring element that is ubiquitous and persistent in the environment, bioaccumulative, and highly toxic to humans and wildlife. Because of these properties, lead was classified as a metal of concern under Ecology's PBT (Persistent, Bioaccumulative, Toxics) Rule (WAC 173-333-110).

Re-distribution of lead by humans has greatly increased its prevalence in the environment. The physical properties of lead – malleability, low-melting point, and corrosion resistance – have contributed to extensive anthropogenic use throughout history. Use of alkyl-lead additives in gasoline in the 20<sup>th</sup> century resulted in widespread lead pollution to the environment until U.S. restrictions phased out use in the 1980s and 1990s (Davies, 2009).

Currently, major sources of lead in Washington State's freshwater systems include releases from sewage treatment plants and industrial facilities such as mining operations, the Hanford nuclear reservation, military bases, and large energy users (Davies, 2009). Historical soil contamination from smelting activities and lead-arsenate insecticide use also contribute lead to the aquatic environment (Glass, 2003; Peryea and Creger, 1994).

Lead is highly toxic to humans and wildlife, with particular concern for developing nervous systems in infants and young children. Lead exposure can also harm the cardiovascular, gastrointestinal, immune and reproductive systems, as well as kidneys and blood (Davies, 2009). Exposure in humans and wildlife primarily occurs through ingestion and inhalation of lead-containing materials, such as contaminated water or dust (ATSDR, 2009). Once exposed, lead is stored in bones and accumulates over the organism's lifetime.

The Washington State Departments of Ecology (Ecology) and Health (DOH) prepared a Chemical Action Plan for lead in response to concern over these health risks (Davies, 2009). The lead Chemical Action Plan (1) describes the toxic effects of lead, (2) identifies where the substance is found in the environment, and (3) recommends ways to reduce or prevent its harm. The recommendations in the Chemical Action Plan were intended to reduce or phase out current uses of lead where possible and prevent future exposures (Davies, 2009).

Ecology began a PBT monitoring program in 2007 to assess levels of PBTs in rivers and lakes of Washington State (Johnson, 2007). Lead in suspended particulate matter (SPM) was added to the program in 2008 (Meredith and Furl, 2008). The primary objectives of the lead monitoring component are to:

- 1. Establish baseline levels of SPM-associated lead in the environment.
- 2. Measure spatial and temporal trends in lead over time as Chemical Action Plan reduction strategies are implemented.

#### Previous Ecology Studies on Lead in Freshwater Sediments and Suspended Particulate Matter

Several Ecology studies have assessed lead levels in bottom sediments and SPM in Washington State freshwaters. Studies conducted at waterbodies included in the lead monitoring program, as well as studies that examined background freshwater sediments, are described below.

#### Spokane River and Upper Columbia River

Ecology conducted studies on the Spokane River to examine metals contamination in bottom sediments from Long Lake through the Idaho border (Johnson et al., 1994; Batts and Johnson, 1995; Johnson, 1999; Johnson, 2000; Johnson and Norton, 2001). Elevated lead levels were consistently found throughout the river from Upriver Dam to the Idaho border. Average concentrations ranged from 195 - 659 mg/Kg. Lead concentrations in the sediment of Nine Mile Reservoir were much lower, from 22 - 54 mg/Kg.

Lead concentrations at the Upper Columbia River in both SPM (Serdar et al., 1994) and bottom sediments (Era and Serdar, 2001) have been characterized. Elevated lead levels were found in both studies, with ranges of 498 – 554 mg/Kg and 182 – 344 mg/Kg, respectively.

#### Sediment Reference Waterbodies

Sloan and Blakley (2009) analyzed metals in bottom sediments from nine proposed freshwater reference waterbodies in 2008. Lead concentrations ranged from 3.2 - 55 mg/Kg, and the mean value was 14 mg/Kg (n = 27). This was a statewide study designed to provide baseline values for waterbodies not impacted by lead contamination.

# **Study Design**

During 2009, SPM was collected from 15 monitoring sites across Washington State for the second year as part of a long-term lead monitoring study. SPM samples were collected via in-line filtration during the spring and fall. Sampling events were scheduled during spring high-flow and fall low-flow conditions to assess seasonal differences in lead concentrations. Two samples were collected at each site per season. No changes were made to the study design in 2009. Sampling was conducted in accordance with a Quality Assurance Project Plan (Meredith and Furl, 2008).

Samples were collected from monitoring sites established in 2008 (Figure 1). Three of the locations were selected based on increased potential for lead contamination: Hylebos Creek, Spokane River at the Idaho border, and the Upper Columbia River. These sites have known metals problems and are undergoing cleanup actions (Ecology, 2007; Butkus and Merrill, 1999; Ecology, 2009; EPA, 2008). The Queets River, located in an undeveloped drainage area, serves as a reference waterbody for the study. Other sites are distributed across the state and have varying land uses and contamination potential.

Monitoring sites are described in detail in Johnson (2007) and Meredith and Furl (2008). Brief monitoring site descriptions can be found in Appendix B.



Figure 1. Lead Monitoring Sites, 2009.

## **Methods**

### **Field Procedures**

SPM samples were collected using in-line filtration of river or lake water. Water was pumped and filtered through pre-weighed, 0.45-µm pore-size (47-mm membrane) nitrocellulose filters using in-line, 47-mm membrane Teflon filter holders. The intake of the tubing was placed 0.5-3 feet below the water surface, suspended above the river or lake bottom, for the duration of sampling. Once filters had accumulated enough SPM to restrict water flow, they were carefully removed from the filter holder and stored in pre-acid-washed aluminum sample containers. The volume of water that passed through each filter was recorded after sampling.

One filter was collected per sample. Sample containers were bagged and stored upright on blue ice for transport to Ecology headquarters. Samples were stored at Ecology headquarters at 4° C until shipment to Manchester Environmental Laboratory (MEL) for analysis. Samples were collected following Ecology's Environmental Assessment (EA) Program's *Standard Operating Procedure for Collecting Freshwater Suspended Particulate Matter Samples using In-Line Filtration* (Meredith, 2008).

Temperature, pH, and conductivity were measured at each site. pH was measured following a modification of *Standard Operating Procedures for the Collection and Analysis of pH Samples* (Ward, 2007).

### **Laboratory Procedures**

MEL analyzed lead (in  $\mu$ g per filter) following EPA Method 200.8 (ICP-MS). Prior to analysis, filter samples were dried at 103-105 °C, weighed to determine dry SPM weight, and digested following EPA Method 3050B.

Dry SPM weight was used to determine lead results in mg/Kg. Results are presented throughout this report as lead by weight in mg/Kg (dry weight) and as lead by volume in  $\mu$ g/L, using the volume of water passed through each filter.

Total suspended solids (TSS) values used throughout this report were calculated as the dried SPM weight on sample filters divided by volume passed through the filter. This is not a standard TSS value due to the filter size used in this study (0.45- $\mu$ m). The standard filter pore-size used by MEL in TSS analyses is 1.5- $\mu$ m.

# **Data Quality**

MEL did not encounter any problems during the analyses of lead in SPM, and all results were reported to the project manager without qualification. MEL received SPM samples in good condition and within the proper holding times. MEL provided case narratives documenting instrument calibration, calibration checks, method blanks, matrix spikes, laboratory control samples, and internal standards. Copies of case narratives are available upon request.

All instrument calibration checks and internal standard recoveries were within acceptance limits. No significant levels of lead were detected in the method blanks.

Laboratory data quality was assessed by comparing matrix spikes and laboratory control samples to measurement quality objectives (MQOs) outlined in the project plan (Meredith and Furl, 2008). MQOs are listed in Appendix C. Matrix spike recoveries ranged from 99 - 105%. Recoveries of laboratory control samples were in the range of 97-107%. Recoveries from both quality control tests met MQOs.

Quality control of field technique was assessed by comparing the relative percent difference (RPD) of field samples and field replicate samples to MQOs. Three of the four field replicate samples were within the MQO guideline for RPD ( $\pm 50\%$ ). One replicate sample was a non-detect for lead while the field sample was quantified as 28 mg/Kg, resulting in an RPD outside of MQOs. The field sample was assigned a data qualifier, J, indicating the value was an estimation.

MEL analyzed seven field blanks over the spring and fall sampling periods. Lead was not detected at the 0.05  $\mu$ g/filter level in six of the samples. One field blank sample taken at the Walla Walla River site measured 0.33  $\mu$ g lead/filter. The field sample collected at this site on the same date was qualified J. A relatively low lead concentration was found in the field sample, within the range measured previously at this site.

Complete results of laboratory and field quality control tests can be found in Appendix C.

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# **Results**

A total of 60 SPM samples were analyzed for lead during the spring and fall of 2009. Table 1 displays the spring and fall lead concentrations measured at each waterbody. A statistical summary of the data is presented in Table 2.

		Spring		Fall		
Waterbody	Collection Date	Lead (mg/kg)	TSS (mg/L)	Collection Date	Lead (mg/kg)	TSS (mg/L)
Columbia Diver Lower	4/29/09	25	16	8/31/09	18	2
Columbia River, Lower	5/27/09	18	21	9/28/09	21	3
Columbia Diver et MeNery Dem	4/30/09	23	8	9/1/09	14	2
	5/28/09	32	9	9/29/09	23	4
Columbia River at Rook Jaland Dom	4/28/09	25	10	9/1/09	44	2
Columbia River at Rock Island Dam	5/26/09	34	5	9/28/09	56	1
Columbia Diver Llaner	4/29/09	21	9	9/2/09	120	1
	5/27/09	98	6	9/29/09	111	1
Duwomich Bivor	4/28/09	15	12	9/3/09	101	1
Duwamish River	5/26/09	13	9	10/1/09	17	6
Hulphan Crack	4/28/09	41	5	9/3/09	32	2
Hylebos Creek	5/26/09	33	5	10/1/09	35	4
	4/28/09	35	4	9/3/09	ND	1
Lake washington	5/26/09	53	5	10/1/09	39	1
Okanagan Divar	4/29/09	13	17	9/2/09	19	2
Okanogan River	5/27/09	12	68	9/28/09	ND	1
Questa Diver	5/4/09	16	18	8/31/09	34	3
Queets River	6/1/09	18	19	10/5/09	27 J	2
Crahemiah Diver	4/28/09	15	7	9/3/09	26	4
Shonomish River	5/26/09	12	18	10/1/09	24	4
Spakene Diver at the Idaha harder	4/30/09	348	7	9/3/09	653	1
Spokane River at the idano border	5/28/09	1214	3	9/30/09	809	1
Spakene Diver et Nine Mile Dem	4/30/09	354	10	9/3/09	135	1
Spokane River at Nine Mile Dam	5/28/09	454	7	9/30/09	143	2
	4/30/09	17 J	59	9/1/09	13	2
vvalla vvalla River	5/28/09	10	40	9/29/09	21	2
Wanatahaa Diyar	4/28/09	14	7	9/1/09	14	2
	5/26/09	7	22	9/28/09	ND	1
Vakima Divar	4/30/09	19	20	9/1/09	17	3
	5/28/09	14	42	9/29/09	12	3

Table 1. Lead Concentrations and TSS Measured at Monitoring Sites, 2009.

 $J=Value \ is \ an \ estimate. \quad ND=Analyte \ not \ detected. \quad TSS=Total \ Suspended \ Solids.$ 

Summary	Spri	ng	Fall		
Statistics	Lead (mg/Kg)	TSS (mg/L)	Lead (mg/Kg)	TSS (mg/L)	
Minimum	7	3	ND	1	
Maximum	1214	68	809	6	
Mean	100	16	86	2	
SD	238	16	181	1	
Median	20	10	25	2	

Table 2. Statistical Summary of Lead-SPM Concentrations and TSS Measured at Monitoring Stations during Spring and Fall, 2009.

SD = Standard Deviation. TSS = Total Suspended Solids.

ND = Non-detect.

Lead was detected in 95% of the samples. Lead concentrations ranged from 7 - 1,214 mg/Kg in the spring and non-detect - 809 mg/Kg in the fall. Statewide median values were 20 and 25 mg/Kg during the spring and fall sampling periods, respectively.

Spring TSS values ranged from 3 - 68 mg/L, with a median of 10 mg/L. Fall TSS levels were 1 - 6 mg/L, with a median value of 2 mg/L. Complete lead, TSS, pH, conductivity, and temperature results are available in Appendix D.

### **Discussion**

### Ranking

Lead levels at the Spokane River sites remained highly elevated compared to other monitoring sites in 2009. Concentrations were highest at the Spokane River Idaho border site. Values greater than 100 mg/Kg were also found at the Spokane River (Nine Mile) in both seasons and at the Upper Columbia and Duwamish Rivers in the fall. Figure 2 displays the average spring and fall values at the monitoring sites and ranks them in order of average 2009 lead concentrations.



Figure 2. Lead Concentration Ranking at Monitoring Sites, 2009.

Light orange bars display mean spring values (n = 2); dark grey bars display mean fall values (n = 2). Error bars represent one standard error.

#### **Seasonal Variation**

Seasonal variation was assessed by non-parametric Wilcoxon Signed Ranks tests using average spring and fall lead values at the 15 monitoring sites. Lead concentrations (mg/Kg) did not differ significantly between spring and fall at the sites (mean difference = 14 mg/Kg, p = 0.909). Mean lead levels were slightly higher in the fall at the 12 low-contamination sites than in the spring (mean difference = 4 mg/Kg), and levels were lower in the fall for the Upper Columbia and Spokane Rivers sites (mean difference = 86 mg/Kg). However, these differences were not significant (p = 0.694 and p = 0.593, respectively).

Lead concentrations were also calculated on a volume basis by dividing the amount of lead on each filter by filtrate volume. Seasonal differences were encountered when examining lead on a volume basis ( $\mu$ g/L). Concentrations per volume ( $\mu$ g/L) were significantly higher in the spring than in the fall (mean difference = 0.581  $\mu$ g/L, p = 0.001). All sites had higher  $\mu$ g/L levels in the spring with the exception of the Snohomish River. This difference in lead volumes between seasons is likely driven by significantly greater TSS levels in the spring (mean difference = 14.1 mg/L, p = 0.001).

### Loading

SPM-associated lead loadings at each monitoring site were estimated using lead concentrations by volume ( $\mu$ g/L) and river streamflow (cfs) (Figure 3). Seasonal differences in loadings were assessed using non-parametric Wilcoxon Signed Ranks tests. Particulate lead loads were significantly higher in the spring than in the fall (mean difference = 86.4 Kg/day, *p* < 0.001). Flow was also significantly greater in the spring at the monitoring sites (mean difference = 51,243 cfs, *p* = 0.001). The greatest loadings were found at the Columbia River and Spokane River sites. Lead loadings at the 2009 monitoring sites are presented in Figure 3. The two sites for which no flow data were available are omitted.



Figure 3. Estimated Particulate-Bound Lead Loads (Kg/day) at 13 River Monitoring Sites, 2009.

Spatial differences in lead loadings were assessed through independent samples t-tests. Lead loads at eastern Washington sites were greater than at western Washington sites in the spring by an average of 103 Kg/day (p = 0.015). In contrast, lead loads at eastern Washington sites were only 5.53 Kg/day higher, on average, than at western Washington sites in the fall (p = 0.042).

Sampling captured annual high-flow periods in eastern Washington during the spring snowmelt. However, flow patterns at western Washington sites were considerably different than at eastern Washington sites and thus spring sampling did not capture peak flows at the western sites.

Hydrographs of western Washington sites showed peak flows appeared in pulses during the winter, likely from storm event run-off (see Appendix F for hydrographs of monitoring sites). These hydrological differences during sampling events likely contributed to the higher lead loads

in eastern Washington than in western Washington during the spring. This is due to measuring a pulse of particulates during high flow in eastern Washington, whereas western Washington loads more likely reflect baseline conditions.

Monitoring sites were not selected randomly for assessment of spatial differences between eastern and western Washington. Other variables, such as river size and drainage land use, were not included in this analysis, but may also be influencing lead loadings.

### Correlations

Pearson's correlations were performed on combined 2008 and 2009 data from individual monitoring sites to examine relationships between lead concentrations and environmental variables. Correlation coefficients of lead levels by weight (mg/Kg) and by volume ( $\mu$ g/L) correlated with TSS and flow are presented in Appendix E.

Lead concentrations by volume ( $\mu$ g/L) were strongly correlated with TSS and flow at most sites. These relationships were positive across all sites, indicating that with greater flows and increased TSS levels, lead concentrations by volume ( $\mu$ g/L) also increased.

For the majority of monitoring sites, the relationships between lead by weight (mg/Kg) and lead ( $\mu$ g/L), TSS, and flow were negative. Lead concentrations by weight (mg/Kg) at higher contamination sites, however, correlated positively with lead ( $\mu$ g/L), TSS, and flow. This conflicting pattern may be explained by a dilution of SPM-associated lead in the low-contamination sites and resuspension of lead-containing sediments in high-contamination sites.

With greater flows and higher TSS levels, dilution of lead-containing particulate matter by relatively clean sediment inputs may occur at sites with near-background lead levels, resulting in lower lead concentrations. This dilution effect has been hypothesized as the result of increased coarse particle loads, which have lower surface areas and thus lesser capacities for metal binding (Benoit and Rozan, 1999; Dawson and Macklin, 1998).

Sites with high lead contamination, on the other hand, experience an increase in lead concentrations as TSS levels and flows increase, likely indicating that lead-contaminated sediments are being redistributed in the river system. This occurs from lead-contaminated banks and flood-plain sediments washing into the water column or contaminated bed sediments resuspending into the water column during higher flows (Shafer et al., 1997; Alkhatib and Castor, 2000).

### **Temporal Trends**

Ecology completed the first year of sampling lead in SPM for the current trend monitoring study in 2008 (Meredith and Furl, 2009). A total of 46 SPM samples were collected from 15 monitoring sites across Washington State during spring and fall. Lead levels ranged from non-detect (ND) to 3,121 mg/Kg, with a median value of 26 mg/Kg.

Lead concentrations measured in 2009 were compared to 2008 values reported by Meredith and Furl (2009). Comparisons were made between seasonal averages at each monitoring site. Figure 4 displays the percent change between 2008 and 2009 lead levels.



Figure 4. Percent Change in Mean Spring and Fall Lead Values (mg/Kg) between 2009 and 2008.

Lead concentrations were lower in the 2009 samples collected at the three highest-contamination sites, Spokane River (ID border and Nine Mile) and Upper Columbia River, than in samples collected at those sites during both spring and fall of 2008. Lead concentrations were higher in the 2009 samples at the Duwamish, Snohomish, and Queets Rivers in both seasons compared to 2008. At the remaining sites, higher levels were found in the spring and lower levels in the fall of 2009 when compared to 2008.

Spring flows in 2009 were, on average, 25% lower than flows during 2008 spring sampling at the monitoring sites. Fall flows were also lower during 2009, by an average of 34%. As mentioned earlier, lead levels (mg/Kg) were positively correlated with flow at the Spokane and Upper Columbia River sites, which may be contributing to the lower 2009 levels at these sites compared to 2008. In the past, higher particulate-bound lead loadings in the Spokane River have been found in years with greater peak flows (USGS, 2005). 2009 flow data for monitoring sites are presented in Appendix F.

Temporal trends are difficult to assess when limited to two years of data. Changes in lead values may not be representative of increasing or decreasing trends, and are likely reflecting differences in other variables, such as flow. Long-term monitoring over several years would allow for greater detection of increasing or declining patterns in lead levels across the monitoring sites.

#### **Comparison to Background Levels and Guidelines**

Lead concentrations were generally near background bottom-sediment levels measured in Washington State reference waterbodies (Sloan and Blakley, 2009). Exceptions to this include the Spokane River Idaho border and Nine Mile mean lead values, which were 56 and 20 times greater than the average lead background value, respectively. The average Upper Columbia River concentration was six times above reference values, while Columbia River (Rock Island Dam), Duwamish River, Hylebos Creek, and Lake Washington were two to three times greater.

Figure 5 displays 2009 lead in SPM values in relation to the mean lead value in bottom sediments calculated from nine freshwater reference sites (Sloan and Blakley, 2009). Ecology's proposed lowest apparent effects threshold (LAET) for lead in freshwater sediments is also displayed in Figure 5. The LAET guideline of 335 mg/Kg was developed for freshwater sediments to identify contaminant levels at which possible biological effects may occur (Cubbage et al., 1997; Betts, 2003).

Six of the 60 SPM samples collected in 2009 had lead levels higher than the LAET for lead in freshwater sediments. All four samples collected from the Spokane River (border) site exceeded this guideline. The two spring samples at Spokane (Nine Mile) also exceeded the 335 mg/Kg guideline. There are currently no guidelines or criteria for lead in SPM.

Ecology's Freshwater Monitoring Unit conducts bimonthly sampling at locations across the state. Water samples for analysis of dissolved metals are collected near four of this study's monitoring stations: Spokane River (ID border), Upper Columbia River, Snohomish River, and Yakima River. Two water samples collected in February and June, 2009, from the Spokane River at the Idaho border exceeded water quality criteria for dissolved lead (River and Stream Water Quality Monitoring website, accessed on 03/18/2010 from: <a href="https://www.ecy.wa.gov/programs/eap/fw\_riv/rv\_main.html">www.ecy.wa.gov/programs/eap/fw\_riv/rv\_main.html</a>). No dissolved lead exceedances were found at any other station. Sampling was not conducted in the same months as the current study's spring and fall SPM sampling events.

![](_page_23_Figure_0.jpeg)

Figure 5. Lead Concentrations in SPM in Relation to Mean Lead Reference Waterbody Sediment Value, 2009.

Diamonds represent individual 2009 lead in SPM samples. LAET = Lowest Apparent Affects Threshold.

# Conclusions

A total of 60 suspended particulate matter (SPM) samples were collected from 15 statewide monitoring sites during the spring and fall of 2009 and analyzed for total lead. Lead sampling was carried out as part of the second year of a long-term trend monitoring study.

- SPM-associated lead was detected in 95% of the samples analyzed. Lead concentrations ranged from 7 1,214 mg/Kg in the spring and from non-detect 809 mg/Kg in the fall. Median values measured were 20 and 25 mg/Kg during the spring and fall, respectively.
- Lead levels measured in the Spokane River (Idaho border and Nine Mile) remained highly elevated compared to the other monitoring sites in 2009. Other values greater than 100 mg/Kg were found at the Upper Columbia and Duwamish River sites in the fall.
- With the exception of the Spokane, Upper Columbia, and Duwamish River sites, SPMassociated lead concentrations were low and generally at or slightly above Washington State reference waterbody bottom-sediment levels.
- The Spokane and Upper Columbia River sites had lower lead values in SPM samples in 2009 compared to 2008. Higher values were found at the Duwamish, Snohomish, and Queets Rivers in 2009. Among the other sites, 2009 values were higher in spring and lower in fall.
- Lead by weight (mg/Kg) values did not differ significantly between seasons. Lead by volume (μg/L) concentrations, however, were significantly higher in the spring than during the fall low-flow sampling period. Flow and total suspended solids (TSS) levels were also significantly higher in the spring.
- Estimated SPM-lead loadings were higher in the spring than in the fall, and loadings were much greater at the Columbia and Spokane River sites.
- Ten percent of SPM samples exceeded Ecology's proposed lowest apparent effects threshold (LAET) for lead in freshwater sediments guideline of 335 mg/kg. Four of these samples were collected from the Spokane River at the Idaho border and two were from the Spokane River at Nine Mile.

# Recommendations

Based on sampling for lead in SPM during 2009, the following recommendations are made:

- 1. Continue SPM sampling at the same 15 monitoring sites, at the same frequency, to assess temporal trends in future years.
- 2. Continue to conduct field blank sampling at three sites per season, rotating sites.
- 3. Consider sampling for dissolved lead at the Spokane River and Upper Columbia River sites.
- 4. Add streamflow measurements to Hylebos Creek sampling.

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#### Appendix A. Glossary, Acronyms, and Abbreviations

#### Glossary

Anthropogenic: Human-caused.

**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.

**Hydrograph:** A graph showing the discharge of a river over a period of time.

**Parameter:** Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

**Persistent, bioaccumulative, toxic substance (PBT):** A distinct group of chemicals that threaten the health of people and the environment. They (1) remain in the environment for a long time without breaking down (persist), (2) are accumulated by animals and humans and increase in concentration up the food chain (bioaccumulate), and (3) are linked to toxic effects in fish, wildlife, and humans (toxic).

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Suspended particulate matter: Solids suspended in freshwater captured by filtration through a  $0.45 \ \mu m$  filter membrane.

**Total suspended solids (TSS):** The suspended particulate matter in a water sample as retained by a filter.

#### Acronyms and Abbreviations

The following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
LAET	Lowest apparent effects threshold
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
ND	Non-detect
Pb	Lead
PBT	(See Glossary above)
RPD	Relative percent difference
SPM	Suspended particulate matter
SOP	Standard operating procedures

SRM	Standard reference materials
TSS	(See Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area
WSTMP	Washington State Toxics Monitoring Program

#### Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
dw	dry weight
ft	feet
g	gram, a unit of mass
m	meter
mg	milligrams
mg/Kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliters
mm	millimeters
μg/L	micrograms per liter (parts per billion)
μm	micrometer
μs	microsiemens per centimeter
μS/cm	microsiemens per centimeter, a unit of conductivity

### Appendix B. Monitoring Site Descriptions

Monitoring Site	County	WBID <sup>1</sup>	WRIA <sup>2</sup> Number	Latitude <sup>3</sup>	Longitude <sup>3</sup>	Description
Columbia River, Lower	Wahkiakum	WA-CR-1010	25	46.18490	-123.18760	Columbia River near Clatskanie, OR, RM 54.
Columbia River at McNary Dam	Benton	WA-CR-1026	31	45.93940	-119.29720	Columbia River at McNary Dam near Umatilla, OR, RM 292.0.
Columbia River at Rock Island Dam	Chelan- Douglas	WA-CR-1040	44	47.34390	-120.09390	Columbia River at Rock Island Dam, 10 miles south of Wenatchee, RM 453.5.
Columbia River, Upper	Stevens	WA-CR-1060	61	48.92161	-117.77445	Upper Columbia River at Northport, RM 735.
Duwamish River	King	WA-09-1010	9	47.48525	-122.26140	Duwamish River at Foster Golf Links in Tukwila, RM 10.
Hylebos Creek	Pierce	WA-10-1011	10	47.25335	-122.35013	Hylebos Creek in Fife, at 4th St. bridge.
Lake Washington	King	WA-08-9340	8	47.64750	-122.30190	Lake Washington in Seattle at Montlake Cut, East of University of Washington Marina.
Okanogan River	Okanogan	WA-49-1010	49	48.28060	-119.70500	Okanogan River at Malott, RM 17, private property.

Table B-1.2009 Lead in SPM Trend Monitoring Site Descriptions.

Monitoring Site	County	WBID <sup>1</sup>	WRIA <sup>2</sup> Number	Latitude <sup>3</sup>	Longitude <sup>3</sup>	Description
Queets River	Jefferson	WA-21-1030	21	47.55220	-124.19780	Queets River in Olympic National Forest, 2 miles up Queets River Rd, RM 11.5.
Snohomish River	Snohomish	WA-07-1020	7	47.91080	-122.09920	Snohomish River at Snohomish, behind visitor's center, RM 12.5.
Spokane River at ID Border	Spokane	WA-57-1010	54	47.69483	-117.05133	Spokane River near the Idaho border, RM 96.
Spokane River at Nine Mile	Spokane	WA-54-1020	57	47.77470	-117.54440	Upstream side of Spokane River's Nine Mile Dam, RM 58.1.
Walla Walla River	Walla Walla	WA-32-1010	32	46.07090	-118.82680	Walla Walla River, about 5 miles east of Wallula Junction, RM 9, private property.
Wenatchee River	Chelan	WA-45-1010	45	47.50070	-120.42570	Wenatchee River, about 5 miles NW of Wenatchee, RM 7.1, near Old Monitor Rd. Bridge.
Yakima River	Benton	WA-37-1010	37	46.37830	-119.41810	Yakima River, 12 miles NW of Richland, RM 18.0. Diversion structure at Wanawish Dam (Horn Rapids Dam).

<sup>1</sup>WBID - Waterbody Identification Number. <sup>2</sup>WRIA - Water Resource Inventory Area. <sup>3</sup>NAD83 HARN. RM - River Mile.

#### Appendix C. Quality Assurance Data

Manchester Environmental Laboratory (MEL) received all samples in good condition and within the proper temperature range. MEL conducted the lead analyses on June 10, June 26, September 24, and October 26 of 2009. All analyses were conducted within established EPA holding times. Data quality was assessed by comparing the results to the MQOs outlined the Quality Assurance Project Plan (Meredith and Furl, 2008). Table C-1 displays the MQOs for lead analysis.

Analysis	Check Standards	Matrix Spikes (%recovery)	Field Replicates (RPD)	Lowest Concentration of Interest
Lead	± 15% LCS	70-130%	50%	1 mg/Kg dw

Table C-1.	Measurement	Quality	Objectives.
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dw - dry weight.

MEL assessed laboratory quality control by analyzing matrix spikes, control samples, and blanks (Tables C-2 through C-4). All laboratory quality control were within MQOs.

Table C-2. Laboratory Matrix Spikes.

Sample Number	Analysis Date	Recovery (%)
0906028-07	6/10/2009	105
0906028-36	6/26/2009	103
0909042-16	9/24/2009	99
0910019-12	10/26/2009	99

Table C-3. Laboratory Control Samples.

Sample Number	Analysis Date	Recovery (%)
B09F056-BS1	6/10/2009	107
B09F208-BS1	6/26/2009	102
B09I222-BS1	9/24/2009	97
B09J199-BS1	10/26/2009	101

Table C-4. Laboratory Blanks.

Sample Number	Analysis Date	Result (µg)
B09F056-BLK1	6/10/2009	0.05 U
B09F056-BLK2	6/10/2009	0.05 U
B09F208-BLK1	6/26/2009	0.05 U
B09I222-BLK1	9/24/2009	0.05 U
B09J199-BLK1	10/26/2009	0.05 U

U – Analyte not detected at or above the reported value.

Tables C-5 and C-6 display field quality control tests. One field replicate and one field blank were outside of MQO limits. This is addressed in the "Data Quality" section of the report.

Sample Number	Collection Date	Result (mg/Kg)	RPD (%)
0906028-05 Rep 1	4/29/2009	13	247
0906028-06 Rep 2	4/29/2009	17	24.7
0906028-32 Rep 1	5/28/2009	454	22.2
0906028-35 Rep 2	5/28/2009	568	22.3
0909042-14 Rep 1	9/2/2009	120	19.5
0909042-15 Rep 2	9/2/2009	100	10.0
0910019-10 Rep 1	10/5/2009	28	*
0910019-11 Rep 2	10/5/2009	ND	

Table C-5. Field Replicates.

\*RPD calculation includes one detected and one undetected value.

Table C-6. Field Blanks.

Sample Number	Collection Date	Result (µg/filter)
0906028-14	4/30/2009	0.33
0906028-16	5/28/2009	0.05 U
0906028-26	5/27/2009	0.05 U
0909042-12	9/1/2009	0.05 U
0909042-19	9/3/2009	0.05 U
0910019-07	10/26/2009	0.05 U
0910019-17	9/29/2009	0.05 U

U = Analyte not detected at or above the reported result.

### Appendix D. Lead in SPM Data

MEL ID	Station	Date	Pb (mg/kg)	Pb (µg/L)	TSS (mg/L)	Temperature (°C)	рН	Conductivity (µS/cm)
0906028-08	Columbia Diver Lower	4/29/09	25	0.388	16	10.1	8.0	133
0906028-25	Columbia River, Lower	5/27/09	18	0.377	21	14.4	8.2	126
0906028-11	Columbia River et McNery Dem	4/30/09	23	0.172	8	10.5	8.3	159
0906028-29	Columbia River at Michary Dam	5/28/09	32	0.291	9	15.3	8.3	121
0906028-10	Columbia Diver at Deak Jaland Dam	4/28/09	25	0.257	10	10	n/a	132
0906028-28		5/26/09	34	0.183	5	11.8	7.8	72
0906028-18	Columbia Divor Llopor	4/29/09	21	0.195	9	9	7.9	146
0906028-34		5/27/09	98	0.633	6	12	8.2	126
0906028-02		4/28/09	15	0.173	12	9.2	7.1	76
0906028-21	Duwarnish River	5/26/09	13	0.119	9	10.5	7.1	50
0906028-04	Hylobos Crook	4/28/09	41	0.215	5	11.6	7.2	218
0906028-23	Hylebos Creek	5/26/09	33	0.175	5	14.9	7.6	270
0906028-01	Laka Washington	4/28/09	35	0.125	4	11.9	8.7	91
0906028-20		5/26/09	53	0.267	5	16.4	8.1	98
0906028-05	Okonogan Biyar	4/29/09	13	0.226	17	11.2	6.8	170
0906028-24	Okanogan River	5/27/09	12	0.826	68	12.8	7.4	83
0906028-19	Questa Biyer	5/4/09	16	0.297	18	9.1	6.9	64
0906028-37		6/1/09	18	0.340	19	12.2	7.4	61
0906028-03	Snahamiah Divar	4/28/09	15	0.110	7	8.4	6.3	33
0906028-22	Shohomish Kiver	5/26/09	12	0.218	18	9.4	7.2	17
0906028-17	Spokano River at border	4/30/09	348	2.500	7	9.2	7.3	79
0906028-33		5/28/09	1214	3.317	3	13.5	7.2	43

Table D-1. Lead in SPM and Ancillary Data Collected in Spring, 2009.

MEL ID	Station	Date	Pb (mg/kg)	Pb (µg/L)	TSS (mg/L)	Temperature (°C)	рН	Conductivity (µS/cm)
0906028-15	Spokona Divar at Nina Mila Dam	4/30/09	354	3.594	10	7.7	7.1	62
0906028-32	Spokane River at Nine Mile Dam	5/28/09	454	3.105	7	12.9	7.4	51
0906028-38		4/30/09	17 J	1.000	59	11.1	7.8	115
0906028-31		5/28/09	10	0.404	40	17.9	8.0	107
0906028-09	Wanatahaa Biyar	4/28/09	14	0.099	7	8	6.7	56
0906028-27		5/26/09	7	0.149	22	10.2	8.3	29
0906028-12	Vakima Biyar	4/30/09	19	0.375	20	104	8.0	178
0906028-30	fakilla River	5/28/09	14	0.603	42	15.6	7.9	99

J = Value is an estimation.

MEL ID	Station	Date	Pb (mg/kg)	Pb (µg/L)	TSS (mg/L)	Temperature (°C)	pН	Conductivity (µS/cm)
0909042-01	Columbia River Lower	8/31/09	18	0.034	2	20.9	6.8	148
0910019-01		9/28/09	21	0.073	3	18.3	8.1	142
0909042-02	Columbia River at McNary Dam	9/1/09	14	0.034	2	23.1	8.7	155
0910019-02		9/29/09	23	0.088	4	19	8.3	173
0909042-11	Columbia Divor at Book Island Dam	9/1/09	44	0.066	2	22	7.9	328
0910019-14	Columbia River at Rock Island Dam	9/28/09	56	0.056	1	20.1	7.8	129
0909042-14	Columbia River Hoper	9/2/09	120	0.172	1	20.1	8.4	128
0910019-16		9/29/09	111	0.073	1	16.6	8.3	120
0909042-06	Duwomich Bivor	9/3/09	101	0.074	1	16.7	7.1	166
0910019-06	Duwamish River	10/1/09	17	0.112	6	13.1	7.0	114
0909042-08	Hulahaa Craak	9/3/09	32	0.053	2	14.4	7.5	293
0910019-09	Hylebos Creek	10/1/09	35	0.122	4	10.4	7.7	284
0909042-05	Lake Washington	9/3/09	ND	0.039	1	21.2	8.0	103
0910019-05		10/1/09	39	0.048	1	17.5	7.7	100
0909042-13	Okanagan Biyar	9/2/09	19	0.044	2	24	8.4	283
0910019-15	Okanogan Kiver	9/28/09	ND	0.032	1	16.8	8.5	279
0909042-09	Queste Biver	8/31/09	35	0.101	3	17.1	7.8	85
0910019-10	Queets River	10/5/09	28 J	0.053	2	11.3	7.8	80
0909042-07	Snahomiah Biyor	9/3/09	26	0.111	4	19	7.1	67
0910019-08	Shohomish River	10/1/09	24	0.090	4	13	7.1	55
0909042-18	Spekene Biver et herder	9/3/09	653	0.548	1	22	7.8	51
0910019-19	Spokalle River at border	9/30/09	809	0.686	1	17.5	8.1	46
0909042-17	Spokono Divor et Nino Milo Dom	9/3/09	135	0.150	1	16.8	8.4	276
0910019-18		9/30/09	143	0.231	2	13.1	8.2	215
0909042-04		9/1/09	13	0.032	2	25.8	8.5	414
0910019-04		9/29/09	21	0.034	2	15.2	8.9	354

Table D-2. Lead in SPM and	Ancillary Data Collected in Fall, 20	009.
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MEL ID	Station	Date	Pb (mg/kg)	Pb (µg/L)	TSS (mg/L)	Temperature (°C)	pН	Conductivity (µS/cm)
0909042-10	Wanatahaa Diwar	9/1/09	14	0.028	2	22.8	9.3	74
0910019-13	Wenalchee River	9/28/09	ND	0.043	1	12.2	8.6	70
0909042-03	Vokima Biyar	9/1/09	17	0.053	3	22.8	8.2	270
0910019-03	fakilla River	9/29/09	12	0.038	3	15.6	8.3	271

ND = Analyte not detected in sample.

### Appendix E. Pearson Correlation Results

Table E-1. Pearson Correlation Coefficients for Relationships between Lead (mg/Kg), Lead ( $\mu$ g/L), and Variables.

Monitoring sites are displayed in descending order of mean lead (mg/Kg) concentration. Bolded values indicate a significant relationship at the 0.05 confidence level. Negative values are shaded in grey.

Monitoring Sito	L	ead (mg/Ko Coefficient	Lead (µg/L) Coefficient		
Monitoring Site	Lead Lead TSS Flow		Flow	TSS	Flow
Spokane River at ID Border	0.943	0.147	0.686	0.451	0.849
Spokane River at Nine Mile	0.965	0.432	0.834	0.634	0.934
Columbia River, Upper	0.454	-0.565	0.448	0.397	0.965
Columbia River at Rock Island	-0.916	-0.932	-0.876	0.922	0.962
Duwamish River	-0.727	-0.743	-0.531	0.809	0.340
Hylebos Creek	0.722	0.562		0.912	
Lake Washington	0.353	0.187		0.928	
Queets River	-0.604	-0.622	-0.746	0.996	0.872
Columbia River at McNary	0.528	0.166	0.061	0.875	0.823
Columbia River, Lower	-0.126	-0.862	-0.503	0.560	0.884
Snohomish River	-0.722	-0.791	-0.787	0.977	0.850
Yakima River	-0.356	-0.501	-0.554	0.956	0.851
Walla Walla River	-0.394	-0.529	-0.541	0.941	0.915
Okanogan River	-0.162	-0.171	-0.161	1.000	0.999
Wenatchee River	-0.393	-0.380	-0.401	0.989	0.986

#### Appendix F. Flow Data and Sampling Dates

Figure F-1. Flow Data and Sampling Dates for the 2009 Lead in SPM Monitoring Sites.

Flow data were compiled from the USGS National Water Information System (retrieved from <u>http://waterdata.usgs.gov/nwis</u> on 1/26/2010) and the University of Washington's Columbia River Data Access in Real Time (retrieved from <u>www.cbr.washington.edu/dart</u> on 1/27/2010). Flow data were provisional at the time of data retrieval and are subject to change.

![](_page_41_Figure_3.jpeg)

![](_page_42_Figure_0.jpeg)

![](_page_43_Figure_0.jpeg)

![](_page_44_Figure_0.jpeg)

![](_page_45_Figure_0.jpeg)