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# Spokane River PCBs Total Maximum Daily Load

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## Water Quality Improvement Report



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# Spokane River PCBs Total Maximum Daily Load

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## Water Quality Improvement Report

by

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Waterbody Numbers:

WA-57-1010 - Middle Spokane River  
WA-54-1010, WA-54-1020 - Lower Spokane River  
WA-54-9040 – Long Lake (Spokane River)  
WA-55-1010 - Little Spokane River

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# Glossary of Acronyms, Symbols, and Units

## Acronyms

303(d)	Section 303(d) of the federal Clean Water Act
BAF	bioaccumulation factor
BCF	bioconcentration factor
BSAF	biota-sediment accumulation factor
BW	body weight
CFR	Code of Federal Regulations
CSO	combined sewer overflow
CWA	Clean Water Act
DOC	dissolved organic carbon
dw	dry weight
EIM	Environmental Information Management (Ecology database accessible through internet)
EPA	U.S. Environmental Protection Agency
FC	fish consumption
FS	feasibility study
HHC	human health criteria
LA	load allocation
MEL	Manchester Environmental Laboratory
MTCA	Model Toxics Control Act
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NTR	National Toxics Rule
OC	organic carbon
PCB	polychlorinated biphenyl
RF	risk factor
RI	remedial investigation
RM	river mile
RPD	relative percent difference
SPMD	semi-permeable membrane device
SRHD	Spokane Regional Health District
SRM	standard reference material
SV	screening value
TMDL	Total Maximum Daily Load
t-PCB	total PCB (the sum of PCB congeners or Aroclors)

TOC	total organic carbon
TSS	total suspended solids
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WC	water consumption
WDFW	Washington Department of Fish and Wildlife
WDOH	Washington State Department of Health
WLA	wasteload allocation
WQS	water quality standard(s)
WRIA	Water Resource Inventory Area
ww	wet weight
WWTP	wastewater treatment plant

### **Symbols**

$C_d$	concentration in the dissolved phase
$C_s$	concentration in sediment or solids
$C_t$	concentration in tissue
$C_w$	concentration in whole water
$f_{oc}$	fraction of organic carbon
$f_s$	fraction of solid in water
$K_{oc}$	sediment-water partition coefficient normalized for organic carbon
$K_{ow}$	octanol-water partitioning coefficient
$Q$	discharge
$q1^*$	cancer slope factor
Pb	lead

### **Units**

cm	centimeter
l/kg	liters per kilogram
mg/d	milligrams per day
mg/l	milligrams per liter (parts per million)
Ml	megaliter (one million liters)
mm	millimeter
ng/g	nanograms per gram (parts per billion)
ng/l	nanograms per liter (parts per trillion)
pg/g	picograms per gram (parts per trillion)
pg/l	picograms per liter (parts per quadrillion)
$\mu\text{g/l}$	microgram per liter (parts per billion)

## Abstract

The Washington State Department of Ecology conducted a Total Maximum Daily Load (TMDL) assessment for PCBs in the Spokane River, during 2003-2004. Sampling included analysis of PCBs in river water, industrial and municipal effluents, stormwater, suspended particulate matter, bottom sediments, sediment cores, and fish tissue. The study area covered the Spokane River from the Idaho border (RM 96.1) to the mouth at the Columbia River, and the Little Spokane River.

Total PCB concentrations in water increase with successive reaches moving downstream from the Idaho border (106 pg/l) to lower Long Lake (399 pg/l), with a corresponding eight-fold increase in loads (477 – 3,664 mg/d), on average. Point source PCB loads from industrial and sewage treatment facilities are responsible for approximately 20% of instream loads. Stormwater from the City of Spokane may occasionally deliver large PCB loads to the river (1,100 mg/d, on average). Current PCB concentrations in some fish samples were found to be up to an order of magnitude lower than historical levels.

A PCB loading scenario was proposed based on meeting the Spokane Tribe water criterion for PCBs (3.37 pg/l). The scenario requires a 95% PCB load reduction at the Idaho border, a 97% load reduction in the Little Spokane River, and ≥99% reductions in municipal, industrial, and stormwater discharges. A food-web bioaccumulation model indicated that PCB loads in water and PCB concentrations in sediment would require reductions of ≥99% in order to meet the Spokane Tribes tissue criterion.

A Preliminary Implementation Strategy is presented which describes a general framework for reducing PCBs discharged to the Spokane River. It is intended to provide the starting point for developing the Water Quality Implementation Plan. This Plan will describe and prioritize specific actions planned to improve water quality and achieve water quality standards in the Spokane River.

# Acknowledgements

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  - Ken Merrill and John Roland of Ecology's Eastern Regional Office provided valuable advice from the project's inception through its completion.
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# Introduction

## Problem Statement

The Spokane River in eastern Washington contains elevated levels of polychlorinated biphenyls (PCBs) in surface water, sediments, and fish tissue, and in effluents being discharged to the river. The Washington State Department of Ecology (Ecology) first documented PCB contamination in fish tissue two decades ago (Hopkins et al., 1985), and numerous investigations by Ecology and others have been conducted to evaluate the extent of the contamination (e.g., Ecology, 1995; Johnson, 1997; Johnson, 2001; Anchor Environmental, 2004). One Spokane River location requires clean-up of PCBs in bottom sediments under the Model Toxics Control Act (MTCA, WAC 173-340). In addition, fish consumption advisories have been issued for parts of the river due to elevated PCB levels in tissue (Spokane Regional Health District and Washington State Department of Health, 2003).

Most of the Spokane River fish analyzed for PCBs fail to meet state surface water quality standards that have been established to protect beneficial uses of surface waters, such as fish consumption. Section 303(d) of the federal Clean Water Act (CWA) requires Washington to periodically prepare a list of all surface waters in the state for which beneficial uses are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that are not expected to improve within the next two years.

Waters placed on the 303(d) list require the preparation of Total Maximum Daily Loads (TMDLs), a key tool in the work to clean up polluted waters. TMDLs identify the maximum amount of a pollutant allowed to be released into a waterbody so as not to impair uses of the water.

There are fourteen separate entries for PCBs in the Spokane River and one for the Little Spokane River on the candidate 2004 303(d) list (Table 1). A TMDL has been determined to be the action needed to address these listings, triggering a technical assessment which is the subject of the present report. This TMDL technical assessment will be the basis for a plan to cleanup PCBs in the Spokane River, with the exception of the MTCA cleanup previously mentioned.

Table 1. Entries for Total PCBs in Tissue on the Candidate 2004 CWA Section 303(d) List.

Waterbody	Segment	Watercourse Number	Township-Range-Section	Listing ID	1998 List?	1996 List?
Spokane River	WA-57-1010 <sup>a</sup>	QZ45UE	25N-45E-01	14397	No	No
			25N-44E-03	14398	No	No
			25N-44E-04	8201	Yes	Yes
			25N-44E-05	8207	Yes	Yes
			25N-43E-09	8202	Yes	Yes
			25N-43E-16	14402	No	No
	WA-54-1010 <sup>b</sup>	QZ45UE	26N-42E-28	14400	No	No
			26N-42E-17	14385	No	No
26N-42E-07			9033	Yes	Yes	
Long Lake (Spok. R.)	WA-54-9040	QZ45UE	26N-42E-05	9021	Yes	Yes
			27N-41E-22	36441	No	No
			27N-40E-22	9015	Yes	Yes
			27N-39E-24	36440	No	No
Spokane River	WA-54-1020 <sup>c</sup>	QZ45UE	28N-37E-33	9027	Yes	Yes
Little Spokane River	WA-55-1010	JZ70CP	26N-42E-04	9051	Yes	Yes

<sup>a</sup> Hangman Creek to Idaho border

<sup>b</sup> Ninemile Bridge to Hangman Creek

<sup>c</sup> From mouth at Columbia River to Long Lake Dam



## Watershed Description

### Hydrology

The Spokane River begins in northern Idaho at the outlet of Lake Coeur d'Alene and flows west 112 statute miles to the Columbia River (Figure 1). The River basin encompasses over 6,000 square miles (15,500 km<sup>2</sup>) in Washington and Idaho. The river flows through large urban areas of Spokane and Spokane Valley, and the smaller cities of Post Falls and Coeur d'Alene in Idaho. Other cities in the basin include Liberty Lake, Deer Park, and Medical Lake as well as Wallace and Kellogg upstream from Lake Coeur d'Alene.

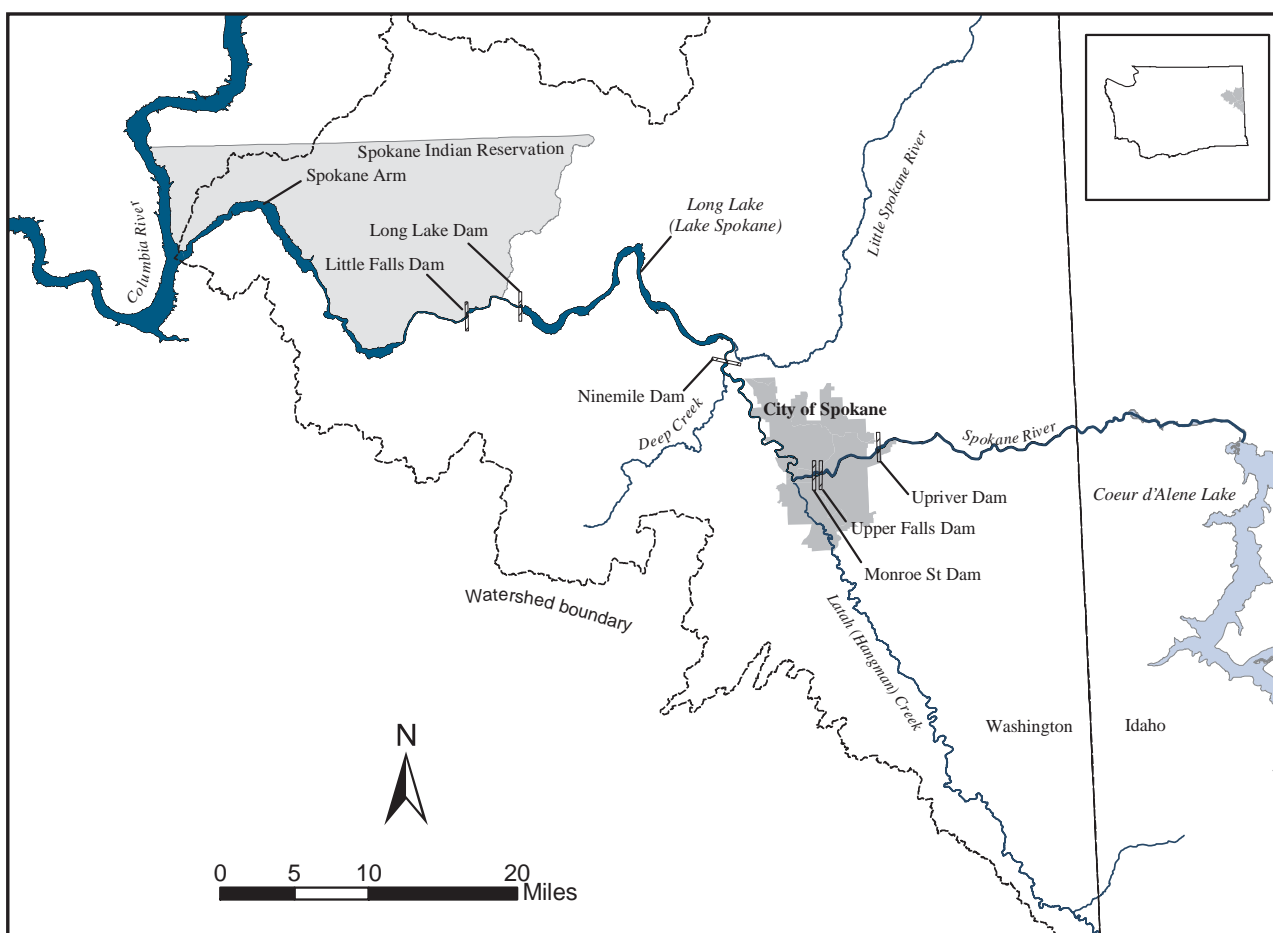


Figure 1. Middle and Lower Spokane River Basin.

There are seven dams along the Spokane River: Post Falls at river mile (RM) 100.8, Upriver Dam (RM 80.2), Upper Falls Dam (RM 74.5), Monroe Street Dam (RM 74.0), Nine Mile Dam (RM 58.1), Long Lake Dam (RM 33.9), and Little Falls Dam (RM 29.3). The dams create a series of pools which vary in length, the largest being Long Lake (also referred to as Lake Spokane) at 23 miles. Downstream from Long Lake the Spokane River forms the southern boundary of the Spokane Indian Reservation from Chamokane Creek (RM 32.5) to the Columbia River at RM 639.0.

The flow regime for the Spokane River is dictated largely by freezing temperatures in the winter followed by summer snowmelt (Figure 2). The annual harmonic mean flow is approximately 61,000 l/s as the river crosses the Idaho border. Flow increases to 82,000 l/s downstream of Spokane, reflecting the influx of groundwater through this river reach. Prior to 1969 there were unquantified agricultural diversions from the Spokane River in the vicinity of Post Falls.

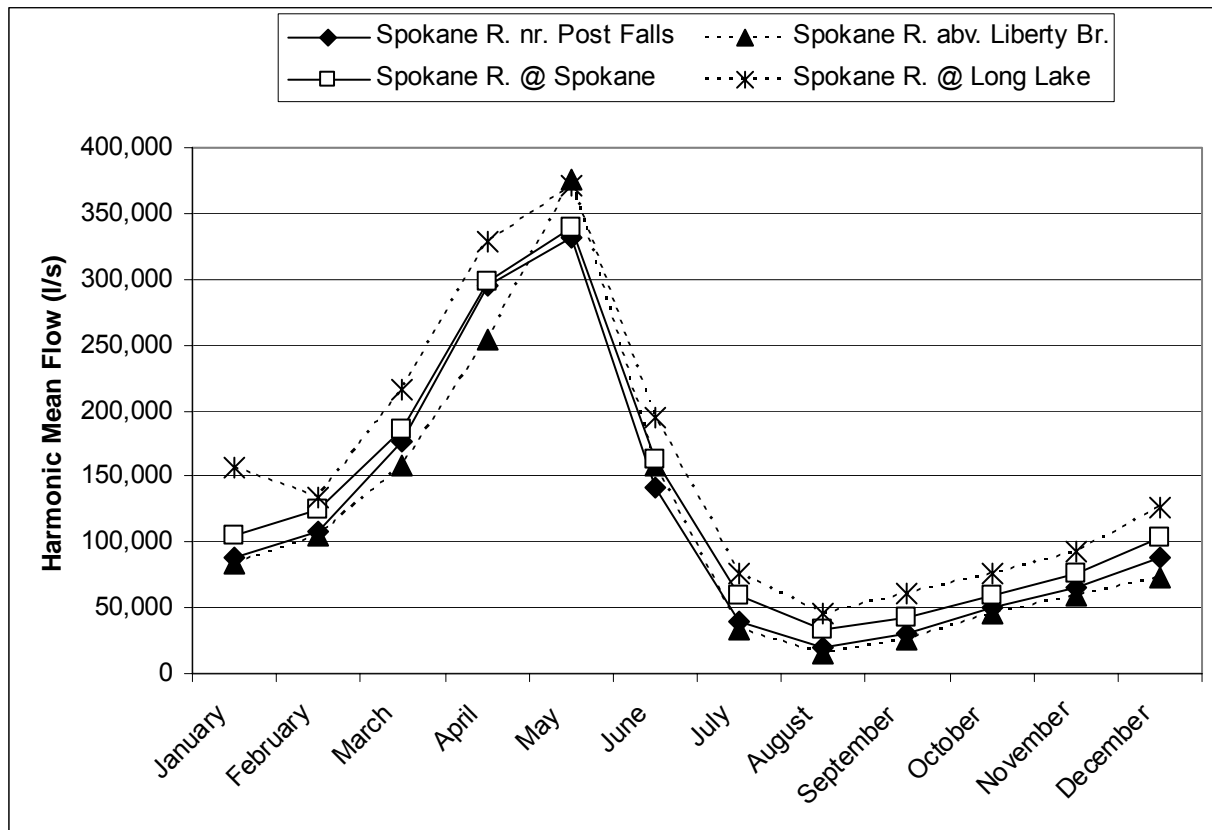


Figure 2. Spokane River Monthly Harmonic Mean Flows for Water Years 1969-2002.

Downstream of Spokane the river corridor is largely undeveloped. The two major tributaries – Latah Creek (formerly Hangman Creek) and Little Spokane River – enter the Spokane River at RM 72.2 and RM 56.3, respectively. Latah Creek has an extremely flashy flow regime and is prone to erosion of its banks, delivering substantial sediment loads to the Spokane River (SCCD, 2002). The Little Spokane River has a mean flow an order of magnitude higher than Latah Creek and also transports large sediment loads to the Spokane River, but less through the large episodic events that characterize sediment transport in Latah Creek.

One particular characteristic of the Spokane River that deserves mention is the paucity of fine depositional sediments in most of the river. Although the dams break the river into a series of pools, there are few areas of placid water above Long Lake and in most places velocities are high enough to scour the bed or prevent settling of particulate matter, even at the dam forebays. In addition, Lake Coeur d'Alene acts as a settling basin for sediments transported in the upper basin, and there are no tributaries to the river between the lake outlet and Latah Creek. As a result, almost the entire riverbed upstream of Long Lake is composed of gravel, cobble, and boulders. One exception is the narrow band of fine, organic carbon rich sediments found near the Upriver Dam forebay that constitutes the MTCA cleanup site.

## PCB Contamination of the Spokane River

### Background on PCBs

---

PCBs were first produced for commercial use in 1929. Production continued until a 1979 ban on all PCB manufacturing, processing, and distribution due to evidence that PCBs build up in the environment and concerns about possible human carcinogenicity (Sittig, 1980). Principal uses were as heat transfer fluids, plasticizers, wax and pesticide extenders, lubricants, and fluids for hydraulic machinery, vacuum pumps, and compressors.

There are 209 individual forms of PCBs known as congeners. The naming system for congeners is based on the numbers and locations of chlorine atoms on the biphenyl rings (Figure 3). In the U.S., PCBs were produced almost exclusively as Aroclors, the trade name for congener mixtures containing 21-68% chlorine by weight. The names given to the different Aroclors reflect this composition; Aroclor[PCB]-1248, for instance, contains approximately 48% chlorine by weight (12 refers to the number of carbon atoms). Many different commercial Aroclor mixtures have been quantified as to their congener composition by Frame et al. (1996).

Much of the 600 million kg of PCBs used domestically has found its way into the environment through improper disposal or by leakage of sealed systems (Sittig, 1980), although loss to the environment through their use in open systems such as hydraulic fluids in die cast machinery, heat transfer systems, and specialty inks was not uncommon (EPA, 2000a). Their primary uses are associated more with heavy industry or urban centers rather than agriculture (EPA, 1992), although direct application to the environment occurred on a lesser scale through use as pesticide extenders or as used oil mixtures applied to roads for dust control. Furthermore, many of the same properties that made PCBs commercially desirable – their stability and resistance to degradation – make them extremely persistent in the environment and they have become one of the most ubiquitous of all environmental contaminants.

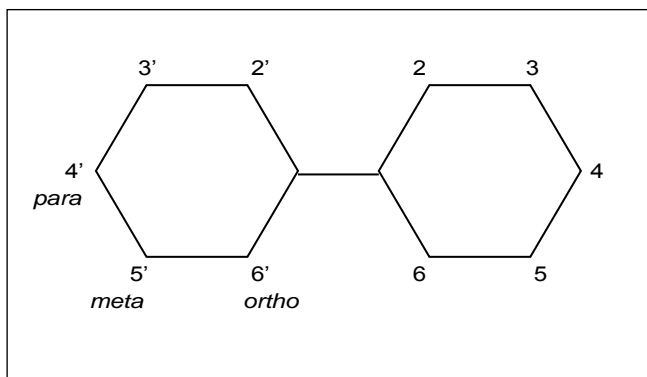


Figure 3. Generic PCB Molecular Structure and Numbering System.

PCBs have low solubilities in water and a strong tendency to sorb to organic carbon-rich sediments and accumulate in the lipids of fish tissue. Lipid solubility increases with the degree of chlorination (Mabey et al., 1982), reflected in their high octanol-water partitioning coefficients ( $K_{ow}$ ). The range of  $\log K_{ow}$  is from approximately 4.6 for monochlorinated congeners to 8.2 for decachlorobiphenyl. PCB mixtures also include relatively volatile congener compounds. Henry's Law constants generally range from approximately 1 to 400 Pa m<sup>3</sup>/mol, which indicates that volatilization is an important transport process for PCBs in the environment.

Dam spillways may be significant transformers of an Aroclor mixture, with differential loss of constituent congeners (McLachlan et al., 1990). As with solubility, this process is also partially dependent upon chlorination patterns. Losses of PCBs from the Great Lakes have been estimated by Eisenreich et al., (1992) as 66% via volatilization, 27% via sedimentation, and 7% through the outflow to other water bodies. The dams along the Spokane River likely modify the dissolved and/or particulate fractions of PCB releases as they move downstream. The combination of differential solubility, variable  $K_{ow}$ , and volatilization leads to weathering of Aroclor mixtures. In environmental samples, these abiotic processes change the composition of released PCB mixtures over time. Thus, environmental matrices such as sediment or water rarely have congener patterns which match a commercial Aroclor.

In general, PCB degradation and elimination from biota occurs via the substitution of a hydroxyl (OH) group into a meta position of the PCB molecule (Figure 3). Congeners which do not have chlorines in one or more meta positions are able to be metabolized and excreted. Once initial substitution has taken place, dechlorination is presumed to proceed to degrade the congener structure. Organisms preferentially metabolize and excrete different PCB congeners depending on their resistance to substitution.

Substitution of either a hydrogen or chlorine atom is generally required by an organism to excrete a PCB molecule. Substitution is generally more difficult for the richly chlorinated congeners, leading to preferential bioaccumulation of heavier congeners. For the most highly chlorinated compounds, bioaccumulation is less pronounced. It is speculated that congeners with  $\log K_{ow} > 7.0$  are too large to be efficiently assimilated in the fish digestive tract. Thus, peak

bioaccumulation occurs between  $\log K_{ow}$  6.5 and 7.0 (Fisk et al., 1998). There is no known way in which less chlorinated congeners might be transformed via abiotic or biotic processes into more highly chlorinated congeners. All known aerobic and anaerobic biotic processes act to dechlorinate PCBs (ATSDR, 1997).

## Historical Data on PCBs in the Spokane River

Ecology has analyzed PCBs in a variety of water, sediment, and fish tissue samples collected from the Spokane River over the past two decades. Additional data have been collected by or in cooperation with the U.S. Geological Survey (USGS) and various National Pollution Discharge Elimination System (NPDES) dischargers. More recent work has focused attention on characterizing sediments behind Upriver Dam (Table 2).

Known PCB data on the Spokane River began with statewide screening-level surveys of contaminants (Hopkins et al., 1985; Hopkins, 1991; Serdar et al., 1994). Fish from the Spokane River sampled during these surveys almost always had high PCB concentrations. For instance, total PCBs in whole fish ranged up to 2,300 ng/g in northern pikeminnow (*Ptychocheilus oregonensis*) collected in 1983. Fillet portions of mountain whitefish (*Prosopium williamsoni*) and bridgelip sucker (*Catostomus columbianus*) from Riverside State Park were also elevated with total PCB concentrations of 230 and 370 ng/g, respectively. Largescale suckers (*Catostomus macrocheilus*) sampled from Long Lake had a whole body concentration of 720 ng/g.

In 1993, Ecology began to expand its investigation of PCBs in the Spokane River by analyzing multiple fish species and sediments at reaches encompassing the entire river. Johnson et al. (1994) confirmed the high PCB levels seen earlier and found a pattern of low levels upstream of the state line and the highest tissue and sediment levels in the reach above Upriver Dam (up to 2,800 ng/g in whole largescale suckers; 3,200 ng/g in sediments) with levels gradually declining in a downstream direction. The authors of this survey recommended conducting broader investigative work to assess possible PCB sources. One year later, Ecology conducted a synoptic PCB survey of sources and aquatic media that remains the most comprehensive PCB investigation done to date (Ecology, 1995).

The 1994 Ecology study of PCBs in the Spokane River increased the number of organisms and locations analyzed, increased the sampling coverage for bottom sediments, attempted to measure *in situ* concentrations and transport of PCBs, and sampled all possible industrial/municipal sources of PCBs to the river. Results again confirmed the pattern of contamination among sites seen in 1993, but concentrations appeared to have declined substantially over the ensuing year. The 1994 study also found that Little Spokane River fish had higher than expected concentrations of PCBs since there is no known source in that watershed. Crayfish were found to accumulate very little PCBs.

The Ecology 1994 study also helped define the extent of contamination in the area behind Upriver Dam, largely by delineating the area of depositional material. Nearly the entire river was surveyed for fine sediment deposits between the state line and Long Lake, but the “hot spot” behind Upriver Dam was the only deposit found.

Table 2. PCB Data Collected on the Spokane River, 1980 – 2005.

Investigator	Data collected	Year	Comments
Ecology (Hopkins et al., 1985)	Tissue - various	1980-1983	Screening survey of contaminants in rivers statewide
Ecology (Hopkins, 1991)	Sediment	1989	Screening survey of contaminants in rivers statewide
Ecology (Serdar et al., 1994)	Tissue – fillet Tissue – whole body Sediment	1992	Screening survey of contaminants in lakes statewide
Ecology (Johnson, et al., 1994)	Tissue – fillet Tissue – whole body Sediment	1993	Screening survey for PCBs in the Spokane River
Ecology (Davis et al., 1995)	Tissue – fillet Tissue – whole body	1993	Statewide survey of pesticides and PCBs
Ecology (Ecology, 1995)	Tissue – fillet Tissue – whole body Tissue - crayfish Sediment Suspended particles Surface water Effluent Sludge	1994	Synoptic survey of PCBs in the Spokane River
Hart Crowser, (Hart Crowser, 1995)	Effluent	1994	Sampled Kaiser effluent coincidental with Ecology
Ecology (Huntamer, 1995)	Sediment	1994	Microscopic examination and PCB analysis of sediments collected behind Upriver Dam
Ecology (Golding, 1996)	Effluent Sludge	1995	Follow-up to effluent and sludge sampling conducted during the 1994 synoptic survey
Ecology (Johnson, 1997)	Tissue – fillet Tissue – whole body	1996	Survey to determine current PCB levels in Spokane River fish
Ecology and USGS (Johnson, 2000)	Tissue – fillet Tissue – whole body Tissue - crayfish	1999	Survey to determine current PCB levels in Spokane River fish
Ecology (Johnson and Norton, 2001)	Sediment	2000	Analyzed chemistry and toxicity of Spokane River sediments to bioassay organisms
Ecology (Golding, 2001)	Surface water Effluent	2000	Survey of PCBs in water around Kaiser and from Kaiser effluents
Ecology (Golding, 2002)	Effluent	2001	Survey of PCBs in industrial and WWTP effluents
Ecology (Jack and Roose, 2002)	Tissue – fillet Tissue – whole body	2001	Intensive survey of PCBs in Long Lake fish
Exponent and Anchor (Exponent and Anchor, 2001)	Sediment	2001	Survey of PCBs in sediments behind Upriver Dam
SAIC (SAIC, 2003a)	Effluent Sludge	2002	Survey of PCBs in effluent and sludge from Inland Empire
SAIC (SAIC, 2003b)	Tissue – fillet Tissue – whole body	2002	Intensive survey of PCBs in Lake Coeur d’Alene fish
Anchor Environmental (Anchor, 2004)	Surface water Ground water	2003	Remedial Investigation of PCBs in the vicinity of the Upriver Dam MTCA site
Kaiser (Kaiser, 2005)	Effluent	2004-2005	PCBs in Kaiser final Effluent
Ecology (Serdar, 2005)	Tissue – fillet Tissue – whole body	2005	Intensive survey of PCBs in Spokane River fish

Perhaps the most important findings from the 1994 study were the characterizations of PCB sources to the river. Sewage treatment plants, industrial facilities, and industrial sites along the river were sampled to assess their relative contributions of PCBs. Results of this sampling effort showed that sources upstream of the Idaho border were negligible, but downstream there was a substantial ongoing PCB source at the Kaiser Trentwood aluminum plant, potentially significant sources such as the Liberty Lake wastewater treatment plant (WWTP) and the former Inland Metals site, and a historically large source from the Spokane Industrial Park, which currently discharges to the Spokane WWTP. Low PCB concentrations were found in the Washington Water Power yard, located just above the river bank, ruling this site out as a potentially significant source. The following sections contain further discussion about PCB discharges from industrial and municipal treatment plants.

Little new has been revealed about degree, extent, and sources of PCB contamination in the Spokane River since 1994. However, numerous surveys have verified previous data, or further characterized the contamination so that its implications are better understood. The three major areas where efforts have been concentrated in the past decade are:

- Continued sampling of fish to detect temporal trends and conduct human health risk assessment
- Continued monitoring of known PCB sources
- Characterization of the Upriver Dam cleanup site

The following is a discussion of the work in each of these areas.

### PCBs in Fish Tissue, 1995-2005

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Comparisons of 1993 and 1994 fish data collected by Ecology appeared to show measurable decreases in PCB concentrations over the course of one year, possibly due to some corrective actions taken during 1992-1993. Ecology collected and analyzed fish in 1996, specifically to determine if this trend continued. The three species used most often for comparisons in the Spokane River (rainbow trout, mountain whitefish, and largescale suckers) all showed substantial decreases in PCB concentrations from earlier data (Table 3). However, concentrations continued to remain high.

In July of 1999, the USGS collaborated with Ecology to further document fish tissue concentrations in the mainstem of the Spokane (USGS, 1999; Johnson, 2000). This study found that whole largescale suckers exceeded a criterion of 110 ng/g used to protect piscivorous wildlife (Newell et al., 1987). Concentrations in five-fish composites of whole suckers were between 120 and 700 ng/g total PCBs. For mountain whitefish and rainbow trout (*Oncorhynchus mykiss*), fillets and whole fish were analyzed. Individual fillets tended to bracket the concentrations found in five-whole fish composites. This is to be expected due to the physical averaging which composite sampling provides. Peak concentrations were found in rainbow trout in the vicinity of RM 85 and in mountain whitefish in the vicinity of RM 63. Maximum concentrations were about 1,600 ng/g for both species.

Table 3. Summary of t-PCB Concentrations in Fish Tissue from the Spokane River. Concentrations Shown are the Mean of Samples Collected at Each Reach During the Year Shown (ng/g, ww).

Location and tissue type	1993 <sup>a</sup>	1994 <sup>b</sup>	1996 <sup>c</sup>	1999 <sup>d</sup>	2001 <sup>e</sup>
Rainbow trout - fillet					
Stateline	--	--	--	106	--
Plante Ferry	918	424	799	891	--
Above Monroe	--	145	76	226	--
Ninemile	490	371	76	143	--
Mountain whitefish - fillet					
Above Monroe	--	568	381	339	--
Ninemile	522	139	444	632	--
Little Spokane	--	222	145	--	--
Upper Long Lake	--		--	--	73
Lower Long Lake	780	113	--	--	--
Largescale suckers - whole					
Stateline	--	--	345	120	--
Plante Ferry	2,005	531	530	--	--
Above Monroe	--	201	116	445	--
Ninemile	1,210		--	680	--
Little Spokane	--	440	366	--	--
Upper Long Lake	--	--	--	--	265
Lower Long Lake	410	820	--	--	357

--no data

<sup>a</sup> Johnson et al., 1994

<sup>b</sup> Ecology, 1995

<sup>c</sup> Johnson, 1997

<sup>d</sup> Johnson, 2000

<sup>e</sup> Jack and Roose, 2002

In 2001, Ecology, Washington State Department of Health (WDOH), and the Washington Department of Fish and Wildlife (WDFW) collaborated in the collection of five different species to evaluate PCB concentrations in Long Lake fish tissues. Complete results are provided by Jack and Roose (2002). In general, largescale suckers and mountain whitefish had the highest PCB concentrations. Total apparent Aroclors in whole largescale suckers ranged from 160 to 340 ng/g, while mountain whitefish fillets ranged from 60 to 89 ng/g. The uptake/retention of PCBs in largescale suckers is likely influenced by their relatively high lipid content, their benthic (bottom feeding) habits, limited metabolic capabilities for PCB excretion, and their longevity. Largescale suckers in Long Lake were as old as 24 years (Jack and Roose, 2002).

Based on the elevated PCB levels in the 1999 samples, WDOH and the Spokane Regional Health District (SRHD) issued an advisory to avoid or limit consumption of fish in parts of the Spokane River ([www.srhd.org/downloads/safety\\_environment/SpokaneRiverFishAdvisory.pdf](http://www.srhd.org/downloads/safety_environment/SpokaneRiverFishAdvisory.pdf)). The advisory, issued in 2003, recommends against any consumption of fish between the Idaho border and Upriver Dam. For the reach between Upriver Dam and Ninemile Dam, WDOH and SRHD advise against eating more than one meal per month of any species. The fish downstream of Ninemile Dam are deemed safe to eat.



In order to update information on PCB levels in Spokane River fish, Ecology in 2005 collected fish from six reaches between the Idaho border and Long Lake Dam (Serdar, 2005). Samples of fillet and whole fish are currently being analyzed for PCBs as well as polybrominated diphenyl ethers (PBDEs), and metals (arsenic, cadmium, lead, and zinc). A subset of samples is also being analyzed for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The primary objective for this survey is to provide WDOH data to update their health assessment and review the fish consumption advisory for the Spokane River.

## PCB Sources, 1995-2005

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### **National Pollution Discharge Elimination System Permits**

Ecology has issued NPDES water discharge permits to a variety of industrial and municipal facilities in the Spokane River basin. Some of these facilities have discharged PCBs in the past. Although most have not been evaluated as historic contributors, recent studies have confirmed the presence of PCBs in the waste streams of some permitted Spokane River dischargers. Appendix A lists the permitted discharges to the greater Spokane watershed by Water Resource Inventory Area (WRIA) and permit number.

The NPDES permit numbers in Appendix A are coded based on the type of discharge to waters of the State. Those permit numbers beginning with ST are for the discharge of municipal and industrial effluents to ground; or industrial effluents to municipal sewer systems. The City of Spokane WWTP receives effluent from a number of these industrial dischargers. Permit numbers beginning with WAG are general NPDES permits and “WA” permits are those allowing discharge of effluents to surface waters.

In addition to the industrial and municipal discharges listed in Appendix A, the City of Spokane has a partially combined sewer-stormwater system. A combined sewer is a conjoined system of stormwater collection from areas such as roofs and parking lots, and raw sewage. During heavy rain or snowmelt events, the influx of stormwater to the combined system may overwhelm its carrying capacity. At that time, a combined sewer overflow (CSO) event occurs and a portion of the stormwater-sewage mixture bypasses the local wastewater treatment plant and discharges directly to the river. The City of Spokane has segregated about 85% of their stormwater and sewage systems. The remaining 15% are less easily separated. These sewers may discharge during high flow periods or inadvertently during maintenance activities. There are a total of 24 CSO points within the City of Spokane (City of Spokane, 2002). Because of the variety of previous uses of PCBs, they may discharge to the river via the CSO system during overflow events. Literature values from other cities indicate that PCB stormwater concentrations may be considerable (e.g., from 88,000 to 179,000 pg/L; Marsalek and Ng, 1989), suggesting that stormwater is a potential source of PCBs to the Spokane River. The City of Spokane also delivers some of the stormwater directly to the river through storm sewers and into ground via drywells or infiltration basins.

## Historic Effluent PCB Concentrations

Some effluents discharging to the Spokane River have been monitored for PCBs by Ecology and others in the past. Ecology (1995), Golding (1996), Golding (2001), Golding (2002), and SAIC (2003a) provide effluent concentration data from July 1994 through June 2002. These samples were analyzed using various techniques including Aroclor equivalents and via congener specific methods. While the methods are not directly comparable, these data are included in Table 4 to illustrate the range of loads and potential variability from these sources.

Historic PCB loads from Kaiser Trentwood were consistently higher than other facilities, although loads appear to have declined from 1994 to 2002 due to decreased PCB concentrations. Kaiser also monitored PCBs in their outfall bi-weekly in 2002 and 2003 (Merrill and Bala, 2004). The median concentration of total PCB (t-PCB) in 2002 was 2,700 pg/l (140 mg/day), decreasing to 1,200 pg/l (90 mg/day) in 2003.

PCB concentrations in Kaiser effluent during 2002-2003 were generally consistent, although variability was expressed by peaks – an order of magnitude increase from normal levels – occurring at 2-5 month intervals. The monitoring result for 4/9/2002 showed an unusually high PCB level in the effluent;  $2.2 \times 10^6$  pg/l (0.125 kg/day), which persisted for a maximum of three weeks before returning to normal levels. PCB levels jumped again in November 2002 when four consecutive monitoring events from 11/18/2002 – 12/29/2002 found effluent PCB concentrations of  $2.6 \times 10^7$  pg/l,  $3.2 \times 10^6$  pg/l,  $4.8 \times 10^7$  pg/l, and  $3.4 \times 10^6$  pg/l. Assuming an average daily load of 0.99 kg/day for a period of 6 weeks (one week prior to discovery until one week following the last elevated measurement), approximately 53 kg t-PCB was delivered to the Spokane River from the Kaiser Trentwood facility.

In late 2003 Kaiser installed a black walnut shell filtration system for their process wastewater discharge. Results of 2004-2005 effluent sampling showed an order of magnitude decrease in PCB concentrations and loads compared to 2001, presumable due to the addition of the filter (Kaiser, 2005).

Table 4. Summary Spokane Area PCB Point Source Data – Effluent/Wastewater Samples.

Source	Date	Method	Total PCBs (pg/L)	Identified Aroclor	Effluent Flow (MI/day)	PCB Load to River (mg/day)
Kaiser Trentwood	08/1/94 <sup>a</sup>	Aroclor	<b>21,000</b>	PCB-1248	109	2,290
	12/5/95 <sup>b</sup>		<b>29,000</b>	PCB-1248	67.8	1,970
	"		<b>34,000</b>	PCB-1248	"	2,300
	12/6/95 <sup>b</sup>		<b>25,000</b>	PCB-1248	68.5	1,710
	"		<b>29,000</b>	PCB-1248	"	1,990
	08/14/00 <sup>c</sup>		<b>53,000</b>	PCB-1248	96.1	5,100
	"		900 U	NA	"	0
	08/15/00 <sup>c</sup>		900 U	NA	"	0
	"		<b>25,000</b>	PCB-1248	"	2,400
	05/1/01 <sup>d</sup>		<b>10,174 NJ</b>	NA	62.1	630
	05/2/01 <sup>d</sup>	<b>5,165 NJ</b>	NA	"	320	
	6/25/04 <sup>f</sup>	congener	<b>1,170</b>	NA	63.9	75
	7/7/04 <sup>f</sup>		<b>1,230</b>	NA	64.6	79
	7/23/04 <sup>f</sup>		<b>1,340</b>	NA	66.2	89
	8/9/04 <sup>f</sup>		<b>914</b>	NA	62.4	57
	4/20/05 <sup>f</sup>		<b>669</b>	NA	56.2	38
	5/7/05 <sup>f</sup>		<b>928</b>	NA	56.1	52
	5/19/05 <sup>f</sup>		<b>1,370</b>	NA	59.7	82
6/11/05 <sup>f</sup>	<b>971</b>		NA	56.5	55	
6/14/05 <sup>f</sup>	<b>1,130</b>	NA	55.4	63		
Spokane WWTP	05/1/01 <sup>d</sup>	congener	<b>1,813 NJ</b>	NA	142	260
	05/2/01 <sup>d</sup>		<b>1,767 NJ</b>	NA	"	250
Liberty Lake WWTP	05/1/01 <sup>d</sup>	congener	<b>1,917 NJ</b>	NA	2.46	4.7
	05/2/01 <sup>d</sup>		<b>1,543 NJ</b>	NA	"	3.8
Inland Empire Paper	05/1/01 <sup>d</sup>	congener	<b>2,436 NJ</b>	NA	16.3	40
	06/5/02–a.m. <sup>e</sup>		<b>5,484</b>	NA	20.0	110
	06/5/02–p.m. <sup>e</sup>		<b>4,305</b>	NA	18.0	78
Spok. Industrial Park	07/31/94 <sup>a</sup>	Aroclor	9,000 U	NA	*	*
	08/4/94 <sup>a</sup>		31,000 U	NA	*	*
	05/1/01 <sup>d</sup>	congener	<b>9,371 NJ</b>	NA	*	*
	05/2/01 <sup>d</sup>		<b>7,108 NJ</b>	NA	*	*

**Bold** - Analyte detected

NJ - There is evidence that the analyte is present. Associated numerical result is an estimate.

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

NA – not applicable

MI/day = 0.264 MGD (million gallons per day)

\* Currently discharges to Spokane WWTP, former discharge to Spokane River

<sup>a</sup> Ecology, 1995

<sup>b</sup> Golding, 1996

<sup>c</sup> Golding, 2001

<sup>d</sup> Golding, 2002

<sup>e</sup> SAIC, 2003a

<sup>f</sup> Kaiser, 2005 (unpublished data)

## PCBs Behind Upriver Dam, 1995-2004

As mentioned previously, fine sediment deposits are sparse in the Spokane River upstream of Long Lake, with the exception of a narrow band of organically-enriched sediments behind Upriver Dam (Figure 4). Following discovery of PCB contamination of this site in 1993 and confirmation of high PCB levels in 1994, subsequent sampling consisted mainly of defining the boundary of contamination. Sediments in this band of contamination generally show PCBs at 1,000 – 5,000 ng/g dw and contain >10% TOC, gradually becoming sandier at the margins (Ecology, 1995; Johnson and Norton, 2001). Huntamer (1995) conducted a microscopic analysis of the sediments and found them to be largely composed of wood particles, consistent with unaided visual observation made earlier. Huntamer also found the sediments to be enriched with charcoal which he speculated may have originated from recent wildfires in the area.

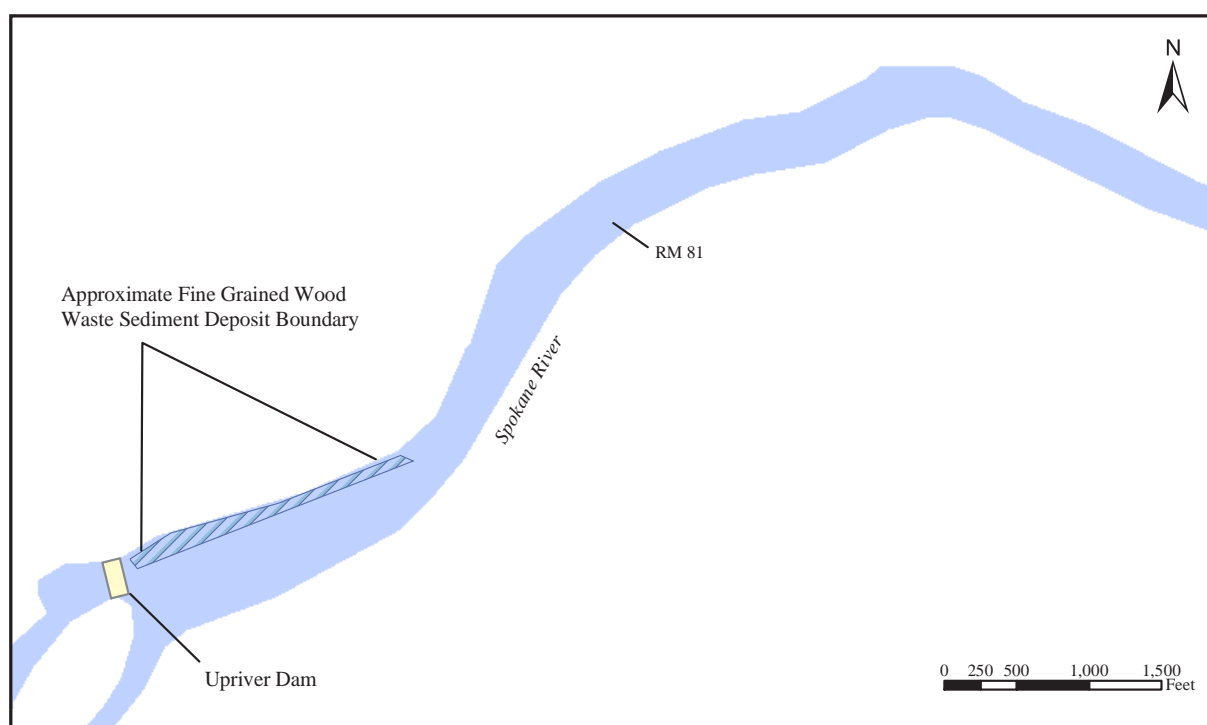


Figure 4. Location of Fine Grained Wood Waste Sediment Deposit Behind Upriver Dam

In February 2003, Ecology entered into a Consent Decree with Kaiser and Avista (formerly Washington Water Power), to evaluate site condition at Upriver Dam. The remedial investigation (RI) and feasibility study (FS) required under the Consent Decree are preliminary steps taken toward completion of a cleanup under MTCA. Aside from sediment characterization, the RI/FS study addressed other components of the aquatic ecosystem associated with the Upriver Dam contamination, such as sampling PCBs in the water column and in hydraulically-connected groundwater wells, and bathymetric surveys of the reach.

Groundwater monitoring in the area indicates there is localized exfiltration of surface water to the aquifer due to the hydraulic difference between the reservoir pool and the river surface downstream of the dam. Wells located downgradient of the dam showed low PCB concentrations (9 – 116 pg/l), lower than associated field and laboratory blanks (10 – 226 pg/l) suggesting the presence of PCBs was due to sampling or lab contamination rather than due to PCB movement from the reservoir to groundwater (Anchor, 2004).

Surface water sampling was conducted both upstream and downstream of the Upriver Dam site as part of the RI/FS investigation. Based on the results, the investigators concluded that water column PCB concentrations at the site were below the MTCA cleanup level of 170 pg/l (interpreted as the water quality standard promulgated in Chapter 173-201A WAC; Anchor, 2004). A much higher t-PCB concentration (450 pg/l) was found downstream at Riverside State Park, but the authors failed to speculate on the increase in PCB levels at this location. Another finding of potential significance was that most (approximately 70-85%) of the PCBs in the water column appeared to be particle-bound, a supposition based on the difference between whole water and the dissolved fraction. However, while this pattern was evident at locations upstream of the Upriver Dam site, an additional comparison of dissolved versus whole water concentrations at the Upriver Dam forebay actually showed higher PCB levels in the dissolved fraction.

Numerous sediment samples were analyzed in and around the known area of contamination as part of the RI/FS. Samples were also collected upstream in backwaters identified as potential depositional areas. Results did little to add to collective knowledge of sediments in the reach above Upriver Dam, but instead corroborated earlier findings that deposited fine material and elevated PCB concentrations are absent outside the known area of contamination.

Based on the sampling results of the RI/FS, Anchor (2004) concluded that cleanup actions would not be required for surface waters due to the apparent compliance with the 170 pg/l water quality standard. They also concluded that a conservative cleanup level for sediments would be 320 ng/g dw based on food web and bioaccumulation models used to establish cleanup levels at other sites.

# Water and Fish Tissue Criteria for PCBs

## Regulatory Criteria

Applicable water quality criteria for PCBs to protect human health and aquatic life have been established by the federal government under the National Toxics Rule (40 CFR 131), by Washington State as promulgated in the Water Quality Standards for Surface Waters (Ch. 173-201A WAC), and by the Spokane Tribe of Indians in their Surface Water Quality Standards (Resolution 2001-144). These regulations and other criteria are discussed separately below. The applicable numerical criteria are shown in Table 5.

Table 5. Water and Fish Criteria and Thresholds for Total PCBs<sup>a</sup>.

Threshold	Aquatic Life Water (chronic) (pg/l)	Aquatic Life Water (acute) (pg/l)	Human Health <sup>bc</sup> Water (pg/l)	Human Health <sup>bc</sup> Tissue (ng/g)	Fish Tissue Consumption Rate (kg/d)
National Toxics Rule (40 CFR 131)	--	--	170	5.3	0.0065
Washington Water Quality Standards (Ch. 173-201A WAC)	1.4 x 10 <sup>4(d)</sup>	2 x 10 <sup>6(d)</sup>	--	--	--
Spokane Tribe Water Quality Standards (Resolution 2003-259)	1.4 x 10 <sup>4(e)</sup>	2 x 10 <sup>6(f)</sup>	3.37	0.1	0.0863
EPA National Recommended Water Quality Criteria (EPA, 2002)	--	--	64	2.0	0.0175
EPA Screening Value for Recreational Fishers (EPA, 2000a)	--	--	--	2.0	0.0175
EPA Screening Value for Subsistence Fishers (EPA, 2000a)	--	--	--	0.245	0.142

<sup>a</sup>total PCBs (t-PCB, sum of Aroclors or homologue groups or isomers or congeners)

<sup>b</sup>based on a one-in-a-million (10<sup>-6</sup>) excess lifetime cancer risk

<sup>c</sup>for consumption of organisms and water

<sup>d</sup>24-hr average not to be exceeded

<sup>e</sup>A one-hour average not to be exceeded more than once every three years on average

<sup>f</sup>A four-day average not to be exceeded more than once every three years on average

### National Toxics Rule

In 1992, EPA promulgated the National Toxics Rule (NTR) which established numeric, chemical-specific water quality criteria for all priority pollutants. The CWA requires adoption of the NTR criteria in all states which do not have sufficient criteria to protect designated uses of state waters. Some of the NTR criteria are applicable in Washington, which has not developed water quality standards to protect human health from exposure to toxicants.

NTR human health criteria for PCBs (170 pg/l) were derived primarily from acceptable fish tissue concentrations, since consumption of fish is considered to be the major exposure pathway for humans (exposure through water consumption is negligible, representing approximately 1% of total intake). The most recent revisions to the NTR applicable to PCBs were effective

December 9, 1999 in which the cancer slope factor ( $q1^*$ ) was changed from 7.7 per mg/kg-d to 2 per mg/kg-d. The human health criteria (HHC) are calculated using the following equation:

$$\text{Eq. 1 } HHC = \frac{RF \times BW \times (10^9 \text{ pg/mg})}{q1^* \times [WC + (FC \times BCF)]}$$

Where:

- RF (risk factor) = the acceptable level of cancer risk. The risk level is decided by states where the NTR criteria apply. For Washington, Ecology has adopted an acceptable upper-bound excess cancer risk of one in a million ( $10^{-6}$ ) for a lifetime exposure.
- BW (body weight) = the average body weight of the consumer. The NTR uses an average consumer body weight of 70 kg.
- $q1^*$  (cancer slope factor) = the cancer potency of each chemical. The NTR uses a  $q1^*$  of 2 per mg/kg-d for PCBs.
- WC (water consumption) = the average daily consumption of water by a consumer. The NTR uses a water consumption rate of 2 l/d.
- FC (fish consumption) = the average fish tissue consumption by a consumer. The NTR uses a fish tissue consumption rate of 0.0065 kg/d.
- BCF (bioconcentration factor) = the concentration of a chemical in tissue accumulated through gill and epithelial tissue divided by the concentration in the water column. The NTR uses a BCF of 31,200 l/kg for PCBs.

When the factors described above are used, the resulting NTR HHC for PCBs in water is 170 pg/l. Since fish bioconcentrate contaminants directly from the water column through uptake by gill and epithelial tissue, HHC concentrations in water ( $C_w$ ) can be linked to fish tissue ( $C_t$ ) by BCFs, expressed as the following formula:

$$\text{Eq. 2 } BCF = C_t / C_w$$

Acceptable fish tissue concentrations may then be calculated by  $C_t = BCF \times C_w$ . The NTR HHC for PCBs in tissue is 5.3 ng/g (Table 5).

It should be noted that the values used by EPA to derive the NTR human health criteria are not necessarily used by public health agencies to establish fish consumption advisories in Washington. Agencies responsible for assessing the need for fish consumption advisories (e.g., WDOH) often examine local conditions such as consumption rates and sub-populations at risk during site-specific evaluations. Public health agencies may also consider different contaminant potencies and health endpoints than those used by EPA for criteria development.

It should also be pointed out that, although Ecology uses the edible tissue criterion to assess violations of water quality standards and consequent 303(d) listing decisions, only the water column criterion is promulgated in numerical form in 40 CFR 131. TMDLs must therefore use the numerical water concentration as the water quality goal. Any deviation from this goal requires development of a TMDL through a site-specific criteria development process.

## Washington State

Water Quality Standards for surface waters of Washington State are set in Chapter 173-201A of the Washington Administrative Code (WAC). The Spokane River from the mouth to Long Lake Dam (RM 33.9) and its tributaries are designated Class A. From Long Lake Dam to Nine Mile Bridge (RM 58.0) it is Lake Class and tributaries are designated Class AA. The remainder of the Spokane River (Nine Mile Bridge to the Idaho border [RM 96.5]) and its tributaries are designated as Class A. Characteristic uses of Class A, Class AA, and Lake Class waters include, but are not limited to:

- Water supply (domestic, industrial, agricultural)
- Stock watering
- Fish and shellfish (migration, rearing, spawning, and harvesting)
- Wildlife habitat
- Recreation (primary contact recreation, sport fishing, boating, and aesthetic enjoyment)
- Commerce and navigation

Ch. 173-201A WAC includes a provision that “Toxic, radioactive, or deleterious material concentrations shall be below those which have the potential either singularly or cumulatively to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent on those waters, or adversely affect public health as determined by the department [Ecology].” The numeric criteria to protect aquatic life from PCB exposure spelled out in Ch. 173-201A-040 WAC were originally derived by EPA to protect the most sensitive aquatic species (EPA, 1980). The acute criterion for PCBs in freshwater is  $2 \times 10^6$  pg/l. The chronic criterion is  $1.4 \times 10^4$  pg/l (Table 5)

## Spokane Tribe

The Spokane Tribe of Indians (Spokane Tribe) Surface Water Quality Standards (Resolution 2001-144) are similar to Washington State Water Quality Standards in terms of narrative as well as numerical criteria. They apply to the northern half of the river defined by a line bisecting the channel from RM 32.5 to RM 0. The Tribal standards consider the Spokane River and most of its tributaries to be Class A surface water, with the exception of Blue Creek, Orazada Creek, and Sand Creek, which are all Class AA tributaries to the Spokane Arm between RM 8 and RM 13. Designated uses for Spokane Tribe Class A and AA waters are the same as Washington State Class A and AA waters, except the Tribal standards also include primary contact ceremonial and spiritual, and cultural uses.

The narrative section for the Tribal toxic pollutant standards is nearly identical to those for Washington State, including the adoption of a  $10^{-6}$  risk level of for carcinogens. However, the Tribal numerical human health criteria are substantially lower than those adopted by Washington State through the NTR (3.37 vs. 170 pg/l) due to different values used to derive the HHC. Tribal standards spell out an aquatic organism consumption rate (i.e., FC) of 0.0863 kg/d used to determine the HHC, much greater than the 0.0065 kg/d used to derive the NTR HHC. In addition, the Spokane Tribe continues to use the  $q1^*$  of 7.7 per mg/kg-d. Using the same approach to derive the criterion as defined in the NTR (i.e., Eq. 1), the Spokane Tribe HHC of 3.37 pg/l translates to an edible tissue criterion of 0.1 ng/g. Like the NTR, however, only the



PCB water standard is promulgated in numerical form in the Spokane Tribe standards and the equivalent tissue criterion cannot be substituted without a site-specific criteria development process.

## Non-Regulatory Thresholds

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In 2002, EPA recommended new national water quality criteria including a new HHC for PCBs based on an upward revision of the fish consumption rate to 0.0175 kg/d (EPA, 2002). All other factors used to derive the recommended criterion (RF, BW, q1\*, WC and BCF) were held constant. The resulting criteria for PCBs were 64 pg/l for water and 2.0 ng/g for fish tissue (Table 5). To date, these values have not been promulgated in the NTR and therefore have no regulatory standing.

Other threshold values which have no regulatory standing but are often used to compare to sampling data are screening values (SVs) published by EPA to signal a potential public health risk or to indicate the need for further investigation (EPA, 2000a). SVs are derived in the same manner as NTR criteria and EPA's recommended national criteria for 2002, with adjustments only to the fish tissue consumption rates. The SV for recreational fishers is 2.0 ng/g based on a consumption rate representing the 90<sup>th</sup> percentile of sport fishers (0.0175 kg/d). The SV for subsistence fishers, based on a 99<sup>th</sup> percentile consumption rate (0.142 kg/d), is 0.245 ng/g (Table 5).

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# Ecology's 2003-2004 TMDL Study of PCBs in the Spokane River

## Study Approach and Objectives

Sampling for the Spokane River PCB TMDL study was conducted by the Department of Ecology, Environmental Assessment Program from September, 2003 – July, 2004. The goal of the TMDL and the water cleanup plan is to meet applicable PCB water quality criteria in the Spokane River.

Specific Objectives of the study were to:

1. Obtain representative data on PCB concentrations and ancillary parameters in the water column, NPDES permitted and stormwater discharges, bottom sediments, and fish tissue.
2. Assess trends and natural recovery rates for PCBs in sediments.
3. Determine the loading capacity for PCBs.
4. Develop a report which addresses the TMDL elements required by EPA Region 10 including proposed PCB wasteload allocations for point sources and load allocations for nonpoint sources.
5. Suggest an alternative approach to developing a TMDL using a fish tissue target and a bioaccumulation model to establish PCB loading parameters.

Historical data as well as current data was used to determine representative conditions in the Spokane River and examine trends over geographic and temporal scales. The first objective was addressed by sampling industrial and municipal effluent, surface water, suspended particulate matter, stormwater, surface and sub-surface sediments, and tissues in two species of fish. The second objective was achieved by analyzing PCBs in sediment cores.

PCB sampling using semi-permeable membrane devices was used to assess the loading capacity in the Spokane River. Load and wasteload allocations were based on loading capacity and on current PCB discharges obtained from effluent and stormwater sampling.

An alternative TMDL approach was proposed by using a bioaccumulation model to estimate site-specific critical PCB concentrations in water and sediment, based on a fish tissue target concentration. Alternative load and wasteload allocations were then determined using PCB loading capacities derived from the model.

It is important to note that the alternative TMDL approach is a useful tool to gauge the effects of PCBs in the aquatic environment under different scenarios. However, the TMDL developed using this approach has no regulatory standing without a process that establishes site-specific criteria for PCBs.

## Scope of the TMDL

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### **Geographic**

This TMDL covers the Spokane River from the Idaho border to the mouth.

### **Pollutant Parameters**

The TMDL is for total PCBs calculated as the sum of Aroclors, homologues, or congeners.

## Methods

### Field Procedures

The following sections describe field procedures used to sample surface waters, industrial and municipal effluents, stormwater, sediments, and fish tissues. Sampling station locations are shown in Figures 5-9. Coordinates and a description of each station location are in Appendix B.

“Stations” for the purpose of this report are identical to the “User Location ID” in Ecology’s Environmental Information Management (EIM) database (available on the internet at [www.ecy.wa.gov/eim/](http://www.ecy.wa.gov/eim/)). All of the data for this project are available through EIM under the “User Study ID” named DSER0010, except the Ninemile rainbow trout fillet data which are listed in EIM under the User Location ID named Spokane-F (User Study ID WSTMP03T).

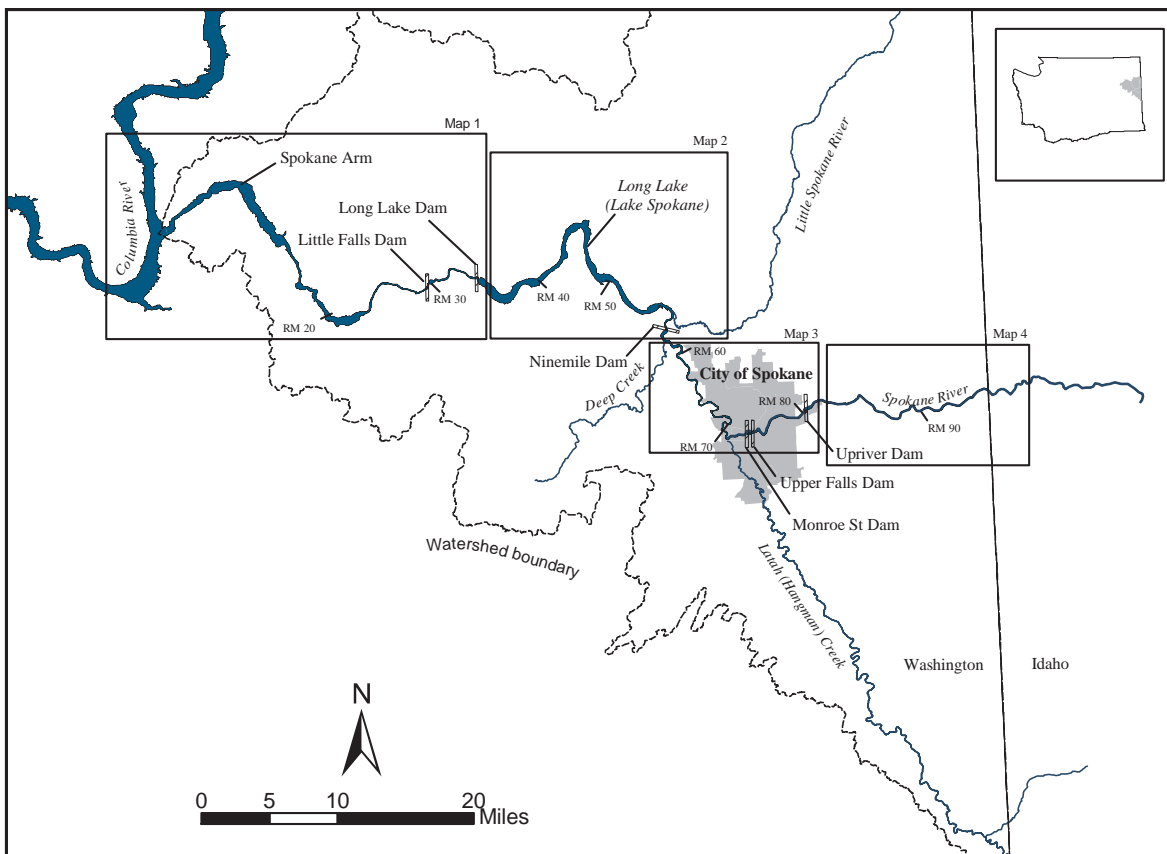


Figure 5. Location of Sampling Maps for Spokane River PCB TMDL

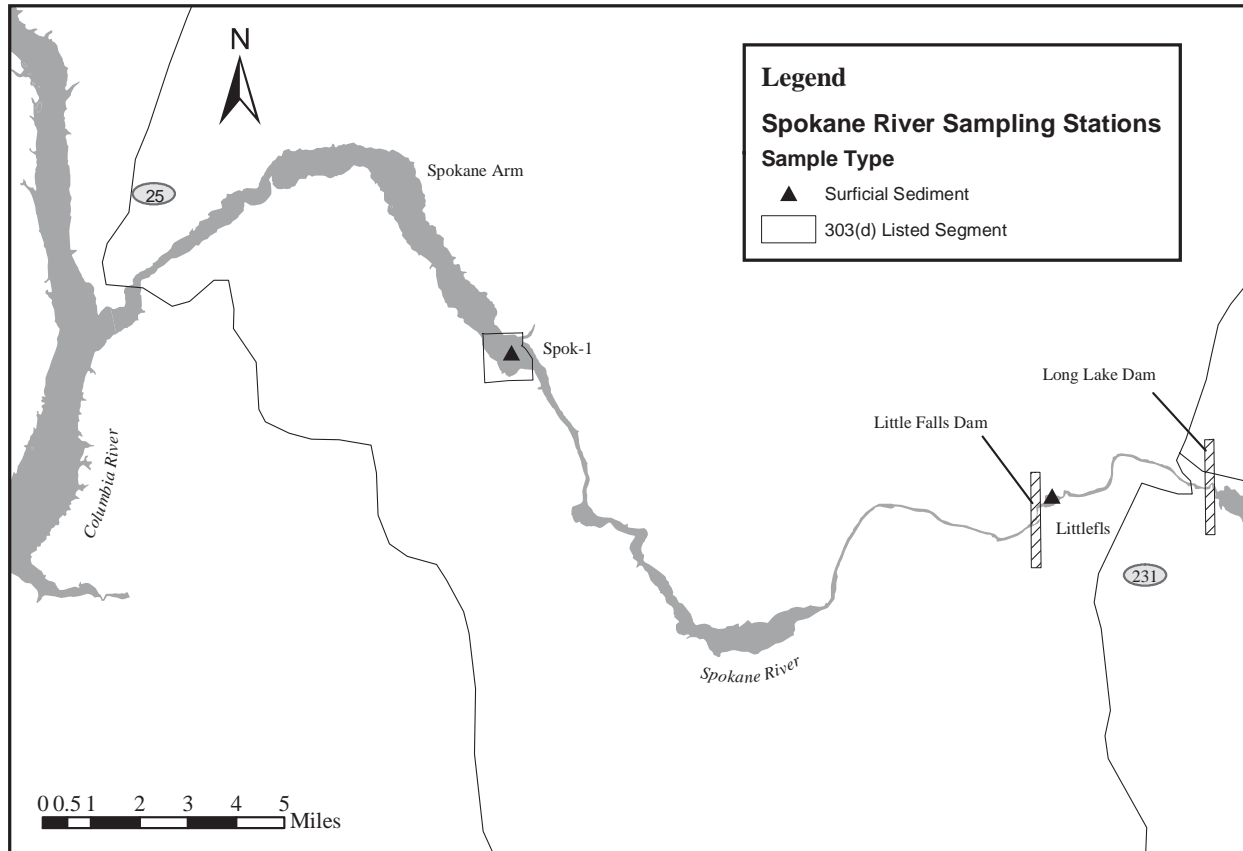


Figure 6 (Map1). Sampling Locations from Spokane River Mouth to Long Lake Dam.

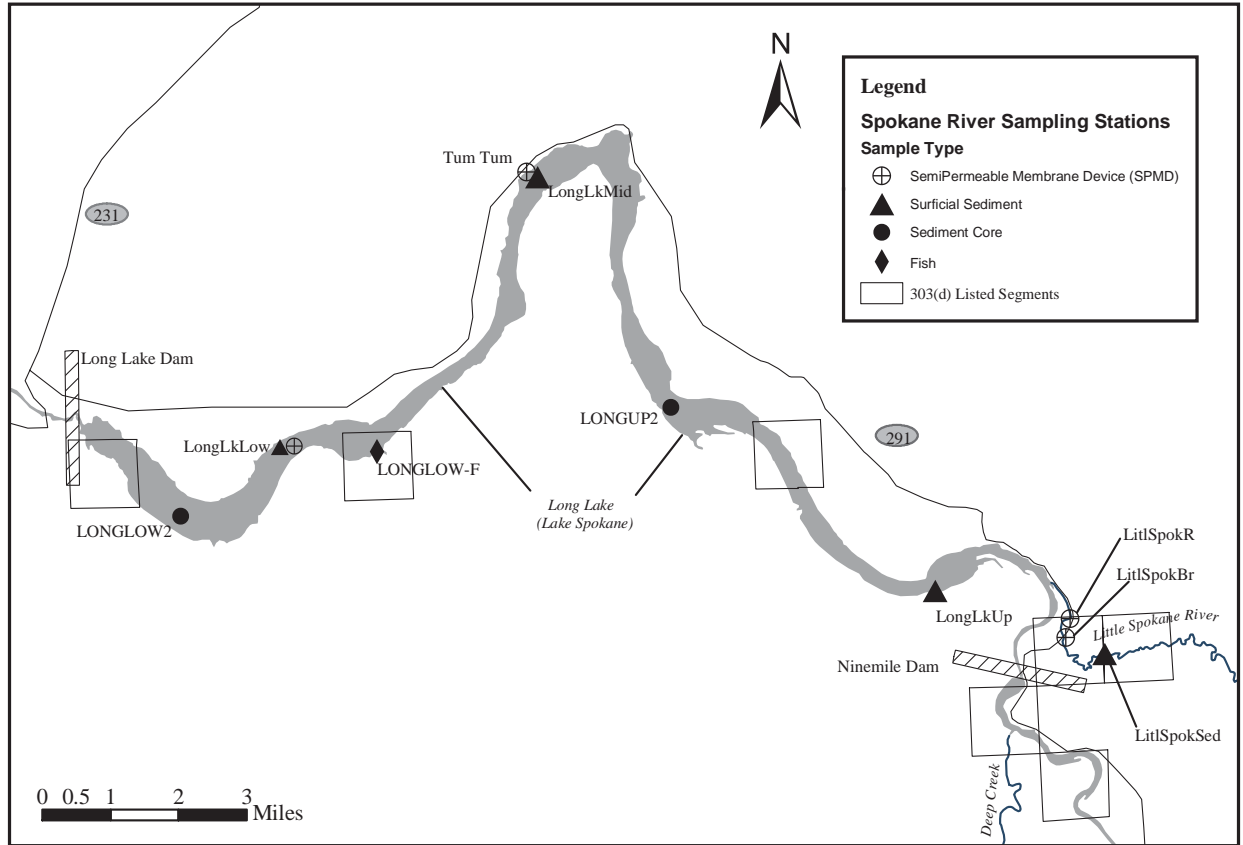


Figure 7 (Map 2). Sampling Locations from Long Lake Dam to Ninemile Dam.

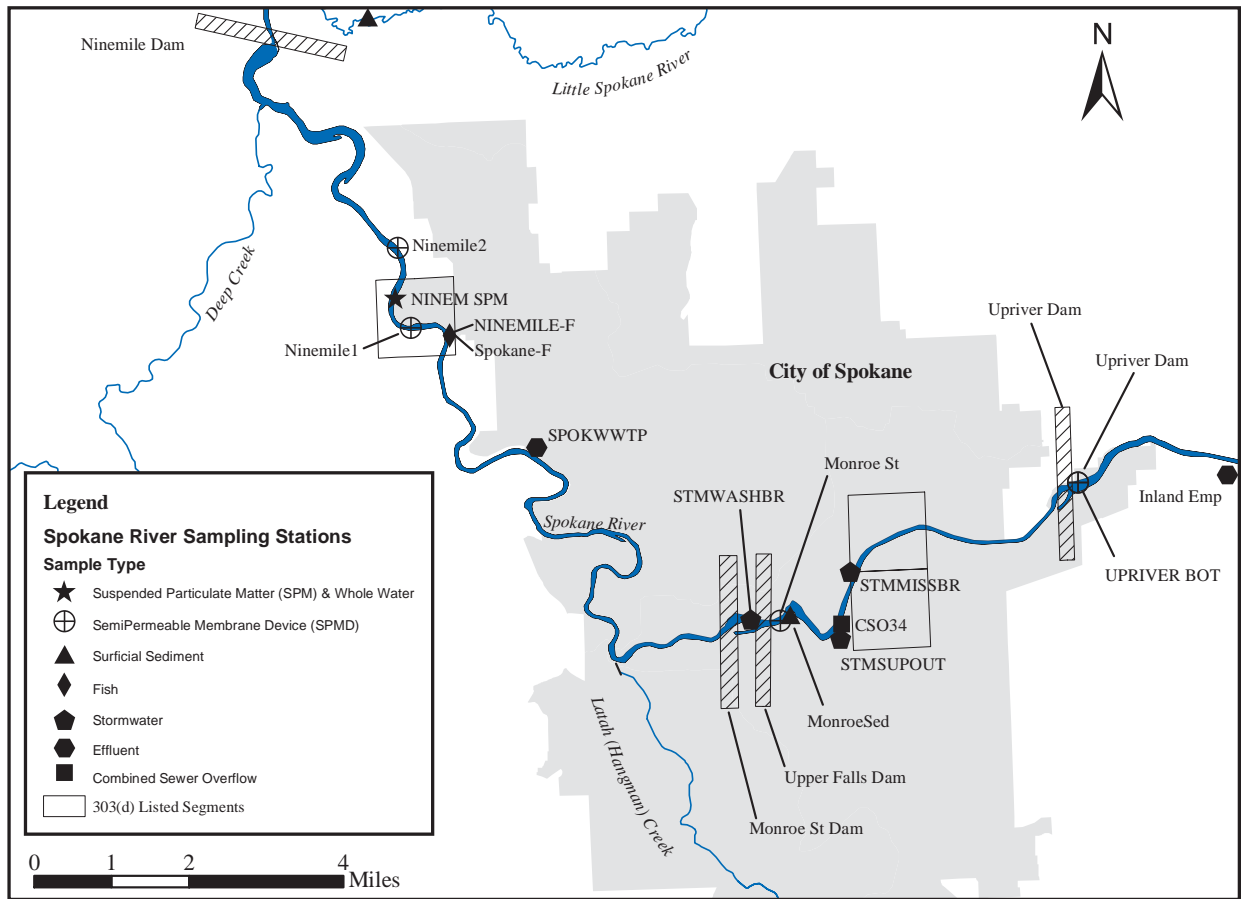


Figure 8 (Map 3). Sampling Locations from Ninemile Dam to Upriver Dam.



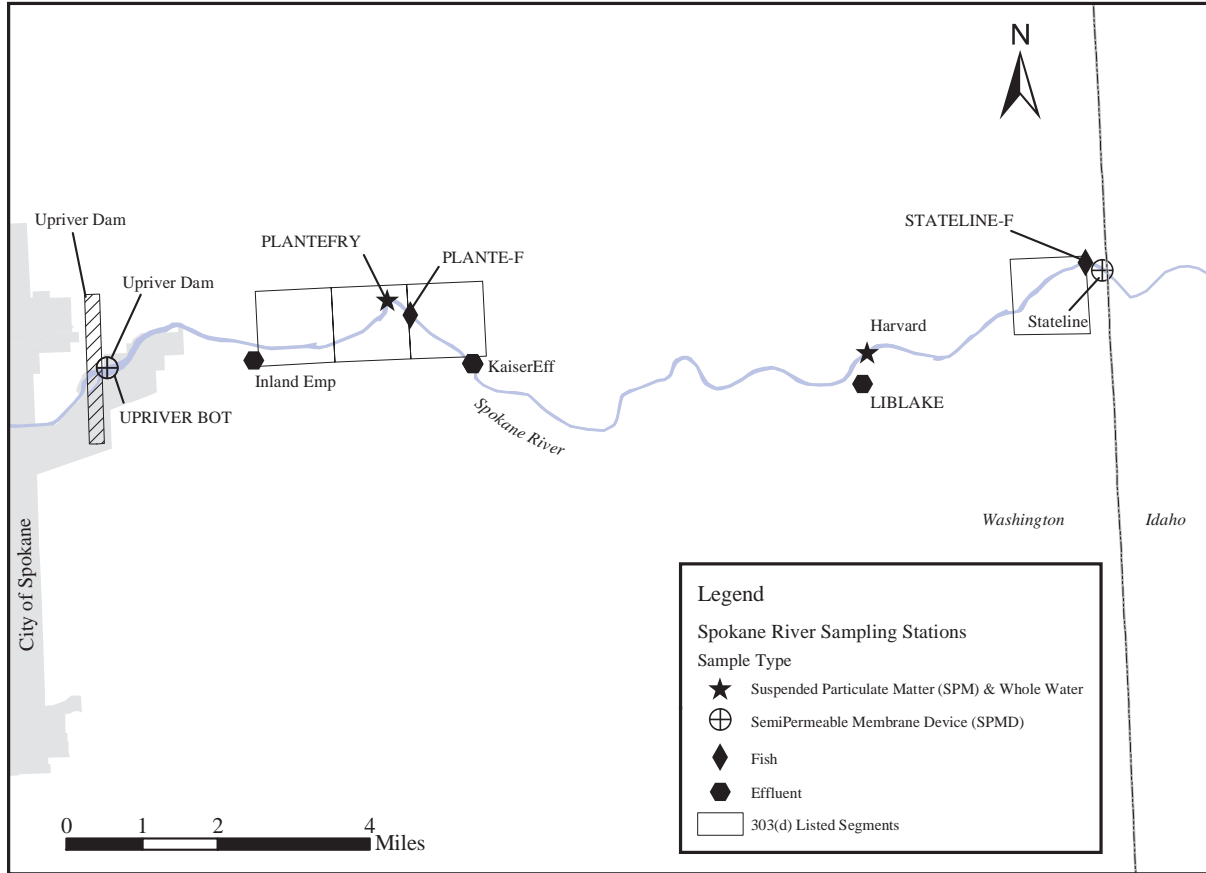


Figure 9 (Map 4). Sampling Locations from Upriver Dam to Idaho Border.

## Surface Water

### *Semipermeable Membrane Devices*

Surface waters at five Spokane River and one Little Spokane River location were sampled using semipermeable membrane devices (SPMDs). Table 6 shows locations where SPMDs were deployed.

Table 6. Locations and Dates of SPMD Deployments.

Location	Station	RM	Dates
Stateline	Stateline	96.1	10/1/2003 - 10/29/2003 1/28/2004 - 2/24/2004 4/14/2004 - 5/12/2004
Behind Upriver Dam at mid-depth	Upriver Dam	80.3	10/1/2003 - 10/29/2003 1/28/2004 - 2/25/2004 4/14/2004 - 5/12/2004
Behind Upriver Dam nr. bottom	UPRIVER BOT	80.3	10/1/2003 - 10/29/2003 1/28/2004 - 2/25/2004 4/14/2004 - 5/12/2004
Behind Monroe St./Upper Falls Dam	Monroe St	74.8	10/2/2003 - 10/29/2003 1/28/2004 - 2/25/2004 4/14/2004 - 5/12/2004
Ninemile Dam Pool upstream of Plese Flats	Ninemile1	63.6	10/1/2003 - 10/29/2003 1/28/2004 - 2/24/2004*
Ninemile Dam Pool nr. Sevenmile Bridge	Ninemile2	62.4	4/14/2004 - 5/12/2004
Tum Tum	Tum Tum	44.2	1/29/2004 - 2/24/2004
Lower Long lake	LongLkLow	38.4	10/2/2003 - 11/4/2003 4/13/2004 - 5/11/2004
Little Spokane River at Rt. 291 bridge	LitlSpokBr	1.1	1/29/2004 - 2/24/2004 4/14/2004 - 5/12/2004
Little Spokane River ½ mi. upstream of mouth	LitlSpokR	0.5	10/2/2003 - 10/30/2003

\*No SPMDs recovered

SPMDs are passive samplers which use 91 x 2.5 cm lay-flat polyethylene membranes filled with 1 ml triolein, a synthetic lipid that mimics biological uptake of dissolved organic compounds. Membranes are mounted on “spider carriers” that hold the membranes during deployment and

placed inside perforated stainless steel canisters, up to five membranes per can. Detailed information on SPMDs is in Appendix E.

Canisters were deployed in the middle of the water column at Stateline, behind Upriver Dam, behind Upper Falls Dam (Monroe St.), upstream of Seven Mile Bridge (Ninemile), in Long Lake, and in the Little Spokane River near the mouth. In addition to the mid-depth SPMDs, deployments were also done approximately one foot above the bottom at the Upriver Dam site. The project plan called for one additional SPMD deployment in the lower two miles of Deep Creek, but Deep Creek lacked the water necessary to obtain a successful sample.

SPMD deployments occurred during October 2003, January – February, 2004, and April – May, 2004. These periods were selected to represent a range of river conditions; low flow in October, moderate flow in February, and high flows during spring runoff. Exposure periods were generally 28 days.

Upon arriving at the sampling site, the cans were opened, spider carriers slid into the canisters, and the device was anchored and tethered in the water column. Because SPMDs are potent air samplers, the procedure was done as quickly as possible, typically one minute or less. Air exposure times were recorded for each event. Three SPMD membranes were used in each canister, with two canisters per sampling site. The dual canisters were used to minimize the risks of loss or vandalism. If both canisters were successfully recovered, the six membranes were combined for extraction. During each deployment period, one of the SPMD pairs from Upriver Dam was analyzed separately as a replicate. The dual canisters were deployed several meters apart at each station.

In some cases, alternative site selection was necessary due to variable flows or ice. The Long Lake SPMD was moved upstream to Tum Tum in January - February because the lower lake was frozen. April deployment at Ninemile was moved downstream due to high flows and the Little Spokane site was moved upstream from its original location for February and April sampling to improve accessibility. One of the two canisters was lost at Ninemile during October and at Stateline in April-May. In both instances the single canister (with three membranes each) contained enough material for complete analysis without compromising data quality. Both canisters were lost from Ninemile during January-February, the only event with lost data.

The SPMD retrieval procedure was essentially the opposite of deployment. Cans holding the SPMDs were sealed and shipped to Environmental Sampling Technologies (EST) for extraction. EST then shipped the extract to Pace Analytical Services Inc. for analysis.

A trip/field blank was used during each SPMD deployment by exposing dedicated membranes to air for the average time sample membranes were exposed. Trip blank membranes were treated the same as other membranes before and after sampling.

Temperature was monitored at 30-min. intervals throughout each deployment using a Tidbit® or I-button® temperature logger attached to the SPMD canister. At the beginning and end of each deployment period, grab samples for total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) were collected.

## *Suspended Particulate Matter and Whole River Water*

Suspended particulate matter was collected at several locations to assess water column PCB concentrations. Since hydrophobic organic chemicals like PCBs preferentially sorb to suspended particulate matter, concentrations are more readily detectable than in the dissolved water phase, making suspended particle sampling a useful surrogate for whole water sampling. Table 7 shows locations and dates for suspended particulate matter sampling.

Table 7. Locations and Dates of Suspended Particulate Matter and Whole River Water Samples.

Location	Station	RM	Dates
Harvard Rd.	Harvard	92.8	10/20/2003 – 10/22/2003
Plante Ferry Park	PLANTEFRY	84.8	10/28/2003 – 10/30/2003
Ninemile Pool at Plese Flats	NINEM SPM	63.2	11/3/2003 – 11/5/2003

Suspended particles were collected using Sedisamp II continuous-flow centrifuges (model 101IL) in a manner described by Serdar et al. (1997) and previously used to collect particles in the Spokane River (Ecology, 1995). A peristaltic pump set at a rate of 3 - 4 l/min. was used to draw water from an intake strainer situated in the middle of the water column approximately 10 – 20 m offshore. All tubing and fittings were Teflon®, except for Silastic® tubing used at the pump head, and all centrifuge bowl parts in contact with samples were high quality stainless steel.

Water samples for TSS were collected from the centrifuge intake and outlet water each day to estimate particle removal efficiency. TOC and DOC samples were also collected during suspended particle sampling. Aliquots of intake water were also periodically collected to provide a composite sample of whole river water for PCB analysis. At the cessation of suspended particle extraction, the centrifuges were disassembled and particulate matter was removed using a Teflon® spatula and placed in appropriate sample containers. All samples were stored on ice in locked coolers while in the field.

Total mass of particulate matter collected was 9 – 17 g (dry weight), extracted from 8,700 – 9,600 l of river water. TSS concentrations of whole river water averaged 1 – 2 mg/l and no TSS was detectable in the centrifuge outlet water at a reporting limit of 1 mg/l. Based on the average TSS values of river water and the dry weight of the particulate matter collected, the centrifuge extraction efficiencies were 71 – 89%, which is in the range of typical values using these centrifuges in similar water conditions (Yake, 1993).

## Effluents and Stormwater Samples

### *Industrial and Municipal Wastewater Effluent*

Final effluent from wastewater streams of four facilities were collected during unannounced visits on three occasions (Table 8). Samples were composites from consecutive days except at Kaiser, where final effluent was collected as discrete samples each day. Composite grab samples were also collected at the Kaiser wastewater lagoon and at the outlet of bed filters to assess the effect of particle removal on PCB concentrations.

Table 8. Outfall Locations and Dates of Industrial and Municipal Wastewater Effluent Samples.

Facility	Station	RM	Dates
Liberty Lake Sewer District WWTP	LIBLAKE	92.7	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004
Kaiser Trentwood - Effluent	KaiserEff	86.0	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004
Kaiser Trentwood - Lagoon	KaiserLag	--	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004
Kaiser Trentwood – Below Filter	KaiserFilt	--	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004
Inland Empire Paper	Inland Emp	82.5	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004
City of Spokane WWTP	SPOKWWTP	67.4	10/21/2003 – 10/22/2003 2/2/2004 – 2/3/2004 4/26/2004 – 4/27/2004

Samples were obtained by dipping a pre-cleaned glass quart container into the waste stream, either by hand or with a stainless steel pole. Two-day composites included two quart grabs per day (morning and afternoon). A transfer blank was also collected during each round of sampling by pouring deionized water prepared at Manchester Environmental Laboratory (MEL) into sample containers while on site. TSS samples were also collected as two-day grab composites at all facilities. Samples were placed on ice while in the field, and upon return to Ecology headquarters, were held in a secure cooler for later transport to MEL with a chain of custody record. MEL shipped samples to Pace Analytical Laboratory for PCB analysis.

## *Stormwater*

Three storm drains and one combined sewer overflow (CSO) were sampled during June 2004 (Table 9). Sampling was conducted by City of Spokane personnel during a runoff event produced by approximately 0.5 inches of rain in a 24-hr period. This event represented approximately one-half of the total precipitation for the month.

Table 9. Outfall Locations and Dates of Storm drain and CSO Samples.

Drain	Station	RM	Date
Mission Ave. and Perry St.	STMMISSBR	76.5	6/10/2004
CSO at Erie St.	CSO34	75.8	6/10/2004
Superior St. nr. Cataldo St.	STMSUPOUT	75.7	6/10/2004
Washington St. Bridge	STMWASHBR	74.3	6/10/2004

The storm drains and CSO were selected by City of Spokane personnel based on the following recommendations by Ecology: Drainage basins should be heavily developed with industrial land-use preferred, outfalls should be upstream of the Monroe St. Dam, and at least one should be a CSO outfall. The plan called for five storm drain/CSOs sampled during two runoff events, but a lack of precipitation, poor timing, and interference with other priorities of the City's stormwater sampling program precluded the successful completion of the plan.

Stormwater samples were collected by dipping a pre-cleaned glass quart container into the storm drain accessed through a manhole. TSS samples were also collected. Samples were placed on ice, chain of custody sealed, and shipped to Ecology headquarters.

## **Bottom Sediment**

### *Surficial Deposits*

Surficial (top 2 cm) bottom sediments were collected at several locations in the Spokane River, Little Spokane River, and a reference site. Sites were selected to assess the possibility of high concentrations of PCBs behind Monroe St. Dam, assess the longitudinal PCB concentration gradient in Long Lake, evaluate the potential of the Little Spokane River as a significant PCB source, and assess PCB concentrations in previously unexamined Spokane River reaches downstream of Long Lake.

The reference site (Buffalo Lake) was originally selected to provide reference sediments for a bioassay survey of the Spokane Arm of Lake Roosevelt (Era-Miller, 2004). It is located in a remote area of Okanogan County west of Spokane and receives contamination only through atmospheric deposition. An EPA study conducted during 2002 found low PCB concentration (5.6 ng/g t-PCB) in largemouth bass fillet from Buffalo Lake (unpublished EPA data).

The sampling plan also called for surficial sediment collection at additional locations behind the Monroe St. Dam in the vicinity of RM 76 and downstream of Little Falls Dam in the vicinity of RM 18-29, but the riverbed at these locations was composed almost entirely of gravel and cobble. Table 10 shows sampling locations for surficial sediment sampling.

Table 10. Locations and Dates of Surficial Sediment Samples.

Location	Station	RM	Date
Behind Monroe St./Upper Falls Dam	MonroeSed	74.9	4/14/2004
Long Lake	LongLkUp	54.3	5/11/2004
	LongLkMid	44.3	11/4/2003
	LongLkLow	38.4	11/4/2003
Little Falls Pool	Littlefls	29.9	11/4/2003
Spokane Arm at Porcupine Bay	SPOK-1	12.6	11/6/2003
Little Spokane River	LitlSpokSed	2.3	12/10/2003
Buffalo Lake (reference)	BUFFALO REF	--	11/5/2003

Surface sediment samples were collected from an Ecology boat using a 0.1 m<sup>2</sup> stainless steel van Veen or a 0.01 m<sup>2</sup> Petite Ponar grab sampler. Sediments from the Little Spokane were taken from the right bank using a pipe dredge.

Each sample was a composite of three grabs. Grabs were considered acceptable if the sampler was not overfull, overlying water was present but not turbid, the sediment/water interface was relatively undisturbed, and at least 5 cm of sediment depth was present. Only the top 2 cm of sediment was collected for analysis using a stainless steel spoon. Care was taken not to disturb sediments in contact with the sides of the grab sampler. Aliquots were placed together in a large stainless steel bowl or bucket, and mixed thoroughly with a stainless steel spoon to form the composite sample. Once mixed, samples were placed in appropriate containers for PCB, grain size, and TOC analysis, then stored on ice in locked coolers. Upon returning to Ecology headquarters, sediments for PCB and TOC analysis were frozen at -20°C. Samples for grain size analysis were refrigerated at 4°C.

### *Sediment Cores*

Sediment cores were collected from the upper and lower reaches of Long Lake to assess trends in historic PCB deposition and to estimate sediment recovery rates (Table 11).

Table 11. Locations and Dates of Sediment Cores.

Location	Station	RM	Date
Upper Long Lake	LONGUP2	49.2	6/9/2004
Lower Long Lake	LONGLOW2	36.0	11/4/2003

Cores were collected using a Wildco 50-cm stainless steel gravity box corer fitted with a 13 cm by 13 cm (i.d.) transparent acrylic liner. Once sufficient penetration was achieved, the corer was brought aboard the Ecology vessel and the acrylic liner was removed and stabilized on a custom built platform and extruding device. After the core was examined for varves or other distinguishing characteristics, the extruding device was used to push the core from the bottom

upward so that 1-cm horizons (layers) could be collected beginning with the top layer. Sediments touching the sides of the liner were pared away with a pre-cleaned stainless steel spatula to prevent smearing effects from influencing the stratigraphy.

Core sections were placed into appropriate sample containers for PCB and TOC analysis, then stored on ice in locked coolers. Upon returning to Ecology headquarters, sediments were frozen at -20°C until analysis.

### **Fish and Crayfish Tissue**

Fish and crayfish collected for PCB analysis were obtained from five locations in the Spokane River (Table 12). The sampling goal was to collect rainbow trout (>250 mm) and two size classes of largescale suckers (250 – 350 mm and <200 mm) at each site except Upriver Dam. Crayfish sampling at the Upriver Dam location was not part of the original sampling plan, but samples were collected due to interest regarding their possible of accumulation of PCBs at the cleanup site. Rainbow trout were not found during extensive efforts to capture them at Stateline and lower Long Lake. Largescale suckers were numerous at all sites except in the Ninemile reach where bridgelip suckers were the dominant species. The smaller size class of suckers was not found at any of the sites sampled, even when various capture methods were employed. All biological data on specimens used for analysis are in Appendix C.

Table 12. Locations and Dates of Fish and Crayfish Samples.

Location	Station	Species	Tissue	Approx. RM	Dates
Near Stateline	STATELINE-F	Largescale suckers	Whole body	96.0	7/14/2004
Near Plante Ferry Park	PLANTE-F	Rainbow trout Largescale suckers	Fillet Gut contents Whole body Gut contents	85.0	9/15/2003
Behind Upriver Dam	Upriver Dam	Crayfish	Tail muscle	80.3	5/13/2004
Upstream of Plese Flats	Spokane-F NINEMILE-F	Rainbow trout Bridgelip suckers	Fillet Gut contents Whole body Gut contents		9/16/2003 7/13/2004
Lower Long Lake	LONGLOW-F	Largescale suckers	Whole body		7/13/2004 – 7/14/2004

Fish were collected primarily using Ecology’s 16’ Smith-Root electrofishing boat. Largescale suckers from Long Lake were captured using variable mesh gillnet sets on the lake bottom. Specimens were held in the vessel’s live well and checked for species identification and desired length. Fish selected for sampling were killed with a blow to the head, weighed and measured in the field, assigned an identifier, double-wrapped in aluminum foil (dull side in), placed in nested zip-lock bags, and put on ice in locked coolers while in the field. Upon returning to Ecology headquarters, specimens were frozen at -20°C until resection.



Crayfish were collected using basket-cone style crayfish traps baited with cat food and set on the bottom overnight. Captured specimens were placed in a pre-cleaned 1-gal. jar and placed on ice in locked coolers while in the field. Upon returning to Ecology headquarters, specimens were measured, weighed, and identified using an invertebrate species key. Following identification, specimens were returned to the jar and frozen at -20°C until resection.

#### *Tissue Preparation – Whole Body*

Suckers for whole body analysis were prepared by removing them from the freezer and allowing them to partially thaw. Plans to composite specimens by sex were abandoned after numerous specimens were opened and gonads were either not found or of indeterminate type. As an alternative, specimens were grouped by length to form a small composite sample and a large composite sample, although size did not vary appreciably among fish. This allowed composites to be formed according to EPA recommendations where the smallest fish in the composite was at least 75% of the length of the largest fish (EPA, 2000a).

Scales and opercula were removed from suckers and mounted or stored for subsequent aging according to Washington Department of Fish and Wildlife (WDFW) protocols. The partially thawed fish were chopped or sawed into pieces on aluminum foil, then ground one at a time in a Hobart commercial meat grinder. After each individual was ground, tissue was mixed well using a stainless steel bowl and spoon. A 50 g aliquot from each specimen was combined to form the composite samples. The combined tissue was then passed twice more through the grinder and thoroughly mixed after each pass.

Composites of Plante Ferry and Long Lake suckers consisted of ten specimens each and composites of Stateline and Ninemile suckers were made from seven specimens each. Homogenized tissue was placed in an appropriate sample container and returned to -20°C until analysis.

#### *Tissue Preparation – Fillet*

Rainbow trout fillets were prepared by removing specimens from the freezer and allowing them to partially thaw. Scales and otoliths were removed and mounted or stored for subsequent aging according to WDFW protocols. Specimens were scaled, rinsed with deionized water, and sex was determined by visual inspection of gonads.

Plante Ferry rainbow trout were prepared as ten-fish composite samples, grouped by sex. Ninemile rainbow trout were analyzed individually. Tissue was prepared by removing a skin-on fillet from one side of the fish while on aluminum foil. Composite samples were formed in the same manner as described for whole body samples except that a Kitchen Aid® food processor was used to homogenize tissue rather than a Hobart grinder. Homogenized tissue was placed in an appropriate sample container and returned to -20°C until analysis.

### *Tissue Preparation – Gut Contents*

Gut contents were obtained from suckers other than those used for whole body analysis and from rainbow trout used for fillet samples. Thawed specimens were opened, and the entire gastrointestinal tract was removed, rinsed with deionized water, gently patted dry with a paper towel, and the contents of the stomach was extruded into a pre-cleaned glass jar. In some cases, rainbow trout stomach contents could only be obtained by slicing open the stomach wall and removing the contents. For suckers, the gut did not have distinctive anatomical components (stomach, intestine), were extremely long (approximately 3 m), and narrow. Therefore, contents from the upper half of the gut were removed for analysis.

Once removed, gut contents were weighed and visual observations were made. Approximately one-half of the rainbow trout had large masses of filamentous plant material in the stomach. In these cases, bugs, mucous bolus, or other food-like material was extracted and plant material was discarded. Entire gut contents from each specimen were combined for a composite sample, since total mass of material was small and near the minimum amount of material required for analysis. Several grams of material from each species were placed in 20% formalin for subsequent stereoscopic evaluation. The remainder of the collected material was frozen at -20°C until analysis.

### *Tissue Preparation – Crayfish Tail Muscle*

Crayfish (*Pacifastacus leniusculus*) collected from Upriver Dam were allowed to partially thaw. Sex was determined and the entire tail muscle (4 – 5 g) was removed from the exoskeleton. All tissue from the four specimens obtained were placed together in a pre-cleaned jar, finely chopped and mixed using a clean scalpel, and frozen at -20°C until analysis.

## Sample Equipment Preparation

Prior to sampling, all sampling implements and equipment were cleaned by sequentially:

1. Washing in Liquinox detergent and hot tap water
2. Rinsing with hot tap water
3. Rinsing with deionized water
4. Rinsing with pesticide grade acetone
5. Air-drying
6. Rinsing with pesticide grade hexane
7. Air drying

After drying, equipment was wrapped in aluminum foil (dull side in) until used in the field. Sampling equipment was dedicated to each station or each sample. Fish processing and tissue homogenization equipment was cleaned between each sample using the described procedure. Persons preparing tissue samples wore non-talc polyethylene or nitrile gloves and worked on aluminum foil. Gloves and foil were changed between samples.

All sample containers were pre-cleaned according to EPA (1990) QA/QC specifications (Appendix D). Samples for PCB analysis were placed in glass jars with Teflon lined lids. All

samples were cooled on ice immediately after collection and transported under chain-of-custody protocols.

## Analytical Methods

All PCB congener samples and percent lipid in tissue were analyzed at Pace Analytical Services, Inc., Minneapolis, MN. PCB Aroclors, TOC in sediments, and TOC, DOC, and TSS in water were analyzed at Manchester Laboratory. SPMD preparation and dialysis was done at Environmental Sampling Technologies (EST), St. Joseph, MO. Radioisotope analysis of sediment cores was done at Teledyne Brown Engineering, Knoxville, TN. Grain size analysis was done at Analytical Resources, Inc., Tukwila, WA. Table 13 shows analysis methods and reporting limits for sample media.

Table 13. Preparation Methods, Analytical Methods, and Reporting Limits for the Spokane River Samples.

Sample Media	Parameter	Preparation method	Analytical method	Reporting Limits
SPMD	PCB Congeners	Dialysis and ampulization - EST SOP	GC/HRMS, EPA Method 1668A	100 ng/4 ml dialysate (per congener) translates to approx. 0.1 – 1 pg/l (per congener)
Water	PCB Congeners TSS TOC DOC	-- -- -- --	GC/HRMS, EPA Method 1668A EPA Method 160.3 EPA Method 415.1 EPA Method 415.1	100 pg/l (per congener) 1 mg/l 1 mg/l 1 mg/l
Sediment (Suspended particulate matter and surficial sediment)	PCB Congeners	Soxhlet extraction	GC/HRMS, EPA Method 1668A	0.05 ng/g (per congener)
Sediment	PCB Congeners TOC (104 °C) Grain size	Soxhlet extraction -- --	GC/HRMS, EPA Method 1668A Combustion Sieve and Pipet	0.05 ng/g (per congener) 0.1% ±0.5% for each fraction
Sediment (Core)	PCB Aroclors TOC (104 °C) Pb-210	Soxhlet extraction -- --	GC/ECD, EPA Method 8082 Combustion Gamma detection	1 - 25 ng/g (per Aroclor) 0.1% --
Tissue	PCB Congeners % lipids	Soxhlet extraction --	GC/HRMS, EPA Method 1668A Gravimetric	0.01 – 0.05 ng/g (per congener) 0.1%

## Data Quality

Results of QC samples analyzed to estimate precision and accuracy are shown in Tables 14 – 17. Laboratory duplicate analysis of PCB congeners and Aroclors show generally good precision, with relative percent differences (RPDs, the difference as a percentage of the mean) less than 20% when detected (Table 14). Precision of field replicates, which integrates environmental, sampling, and laboratory variability is shown in Table 15. Results show that there is substantial variability in SPMD results (average RPD of 28%). Other matrices show lower variability and can be largely accounted for by variation in laboratory analysis.

Table 14. Precision of Laboratory Duplicates (Mean RPD of Individual PCB Congeners or Aroclors\*).

Station	Sample type	Sample Number	RPD
Harvard	Surface water	3438100	ND
LIBLAKE	Water (effluent)	4064113	ND
Litlfls	Sediment	3454113	19%
LONGUP2 *	“	4268384	8%
Spokane-F	Tissue fillet	03084282	5%

Table 15. Precision of Field Replicates (Mean RPD of Individual PCB Congeners).

Station	Sample type	Sample Number	Replicate Sample number	RPD
Upriver Dam	SPMD	3474156	3474157	9%
		4194131	4194132	55%
UPRIVER BOT	SPMD	4208136	4208137	20%
LitlSpokR	SPMD	3474162	3474163	26%
LitlSpokBr	SPMD	4194136	4194137	25%
		4208140	4208141	35%
SPOKWWTP	Water (effluent)	4188204	4188206	6%
KaiserEff	Water (effluent)	4064105	4064106	ND
NINEMILE-F	Tissue fillet	4324447	4324448	8%
Spokane-F	Tissue fillet	3084282	3084308	20%
LongLkLow	Sediment	3454112	3454114	20%

Replicate samples for conventional parameters showed little variation in most cases (Table 16). Instances of high RPD results were due to small absolute differences at low concentrations which have the effect of amplifying RPDs.

Accuracy of the PCB congener data in sediments was assessed through analysis of the National Institute of Standards & Technology (NIST) standard reference material (SRM) 1944 - New York/New Jersey Waterway Sediment. Results are shown for 12 of the 25 PCB congeners for which SRM 1944 is certified; other individual congeners in SRM 1944 match co-eluting congeners reported by Pace and were not compared (Table 17). Five of the twelve congeners were within the 95% confidence level of the certified values. Other results were approximately 20%-25% below the certified value, suggesting a low bias for PCB congener results in Spokane River sediments.

Table 16. Precision of Field Replicates for Conventional Analytes.

Station	Sample type	Parameter	Sample Number	Replicate Sample number	RPD
Ninemile 1	Surface water	TOC	4058115	4058114	0%
		DOC			17%
		TSS			0%
PLANTEFRY	Surface water	TOC	3448102	3448101	0%
		DOC			0%
		TSS			100%
Upriver Dam	Surface water	TOC	4208136	4208135	0%
		DOC			10%
		TSS			0%
Harvard	Surface water	TOC	3438103	3438102	9%
		TSS			0%
Upriver Dam	Surface water	TOC	3408967	3408972	22%
		DOC			8%
NINEM SPM	Surface water	TSS	3454107	3454106	0%
Upriver Dam	Surface water	TOC	4094045	4094044	15%
		DOC			0%
		TOC			4164043
DOC	18%				
TSS	0%				
SPOKWWTP	Water (effluent)	TSS	4188204	4188206	18%
KaiserEff	Water (effluent)	TSS	4064105	4064106	0%
LongLkLow	Sediment	Grain size	3454112	3454114	8%*
		TOC			0%
		Pct. solids			1%
NINEMILE-F	Tissue fillet	% Lipids	4324447	4324448	8%

\*Mean RPD of individual size fractions

Table 17. Analysis of NIST 1944 Standard Reference Material (New York – New Jersey Waterway Sediment) by Pace Analytical Services, Inc. (ng/g, dw).

Analyte	Certified Concentrations*	Pace Result	% Difference from mean
PCB-008	22.3 ± 2.3.	23.4	5%
PCB-031	78.7 ± 1.6	77.6	-1%
PCB-052	79.4 ± 2.0	80.3	1%
PCB-066	71.9 ± 4.3	57.1	-21%
PCB-095	65.0 ± 8.9	48.1	-26%
PCB-099	37.5 ± 2.4	29.7	-21%
PCB-105	24.5 ± 1.1	23.5	-4%
PCB-118	58.0 ± 4.3	52.9	-9%
PCB-194	11.2 ± 1.4	9.35	-17%
PCB-195	3.75 ± 0.39	3.91	4%
PCB-206	9.21 ± 0.51	7.09	-23%
PCB-209	6.81 ± 0.33	5.43	-20%

\*Mean and range of 95% confidence levels

outside certified range of values

## Results and Discussion

### Dissolved PCBs in Spokane River Water

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Ancillary water quality data collected in concert with SPMD deployment and recovery are shown in Table 18. Organic carbon concentrations in the water column were low at all sites. Dissolved OC constituted approximately 92% of the total OC on average. TSS concentrations were generally  $\leq 3$  mg/l with higher values (4-10 mg/l) occurring in February and April. With a few exceptions, average temperatures were similar at all mainstem locations during each deployment. Stateline and Long Lake were approximately 1.5°C warmer than other sites in October, but Stateline temperatures were slightly colder in February. Long Lake temperatures were also the warmest among mainstem sites in February. At the Upriver Dam site, bottom and middle water column temperatures were nearly identical, except for the 1°C difference during the April deployment.

Results of SPMD deployments are shown in Table 19. A summary of PCB accumulation in SPMD membranes (raw data) is in Appendix E. Concentrations of dissolved t-PCBs ranged from 34 pg/l at Stateline during February (2004) to a maximum of 660 pg/l at lower Long Lake during October (2003). PCBs were composed primarily of tri- through heptachlorobiphenyl congeners. Spokane River t-PCB showed a fairly consistent trend of increasing concentrations moving downstream. Generally, dissolved t-PCB concentrations were comparatively low at Stateline and Upriver Dam (34-140 pg/l), intermediate at Monroe St. and Ninemile (76-300 pg/l), and highest at Long Lake (78-660 pg/l). t-PCB concentrations in the Little Spokane River were 120-180 pg/l.

Table 18. Ancillary Parameters at SPMD Sites (mg/l).

Station Name	Sample Number	Collection Date	DOC		TOC		TSS		Mean Temp. (°C)
Stateline	3408971	10/1/2003	1.1		1.3		1	U	14.4
	3448107	10/29/2003	1.1		1.2		2		
	4058111	1/28/2004	1.4		1.3		1	U	3.2
	4094040	2/24/2004	1.2		1.3		1		
Upriver Dam	4164041	4/14/2004	1.2		1.6		3		10.8
	4208134	5/12/2004	1		1.2		2		
	3408966/72*	10/1/2003	1.2		1.5		2		
	3448108	10/29/2003	1		1.2		1		
UPRIVER	4058112	1/28/2004	1.2		1.4		1		3.5
	4094044/5*	2/25/2004	1.2		1.3		2		
	4164042/3*	4/14/2004	1.6		1.7		3		
	4208135	5/12/2004	1		1.1		2		
UPRIVER	--	10/1/2003	--		--		--		12.7
	--	10/29/2003	--		--		--		
	--	1/28/2004	--		--		--		
	4094046	2/25/2004	1.1		1.3		2		
Monroe St	4164044	4/14/2004	1.3		1.4		3		9.8
	4208136/7*	5/12/2004	1.1		1.1		2		
	3408968	10/2/2003	1	U	1	U	1		
	3448109	10/29/2003	1	U	1.1		1		
Ninemile1	4058113	1/28/2004	1	U	1.1		2		4.0
	4094047	2/25/2004	1.2		1.2		1		
	4164045	4/14/2004	1.4		1.3		3		
	4208138	5/12/2004	1	U	1.3		2		
Ninemile2	3408967	10/1/2003	1	U	1	U	1	U	12.3
	3448110	10/29/2003	1.1		1.3		2		
	4058114/5*	1/28/2004	1.2		1.3		2		
LongLkLow	4094041	2/24/2004	1.4		1.8		4		--
	4164046	4/14/2004	1.4		1.4		6		
	4208139	5/12/2004	1		1.1		2		
Tum Tum	3408969	10/2/2003	1.1		1.1		2		14.4
	3454120	11/4/2003	1	U	1	U	2		
	4164040	4/13/2004	1.1		1.5		4		
LitlSpokR	4208133	5/11/2004	1.1		1.3		3		10.8
	4058117	1/29/2004	1		1.1		2		
	4094043	2/24/2004	2.1		2.6		4		
LitlSpokBr	3408970	10/2/2003	1	U	1	U	1		14.4
	3448111	10/30/2003	1	U	1	U	2		
LitlSpokBr	4058116	1/29/2004	1	U	1	U	8		4.5
	4094042	2/24/2004	2.7		2.2		10		
	4164047	4/14/2004	1.3		1.7		7		
	4208140	5/12/2004	1.1		1	U	5		

\*Mean of replicate analysis

U - The analyte was not detected at or above the reported result.

Table 19. Dissolved PCB Concentrations Grouped by Homologues in Water (pg/l).

Station	Sample Number	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
<b>October</b>												
Stateline	474155	0.4	1.5	11	15	56	19	7.9	2.4	0.0	0.0	113
Upriver Dam	474156/7*	0.7	5.5	25	26	32	10	3.7	0.0	0.0	0.0	103
UPRIVER BOT	474158	0.4	5.0	31	48	43	13	4.8	0.7	0.0	0.0	145
Monroe St	474159	0.6	8.6	32	60	65	42	18	3.0	0.0	0.0	231
Ninemile1	474160	0.3	13	63	61	95	49	21	3.1	0.0	0.0	305
LongLkLow	474161	0.7	15	59	269	195	74	32	9.3	2.3	0.0	656
LitlSpokR	474162/3*	0.2	1.0	12	27	33	16	12	11	6.4	0.0	118
<b>February</b>												
Stateline	194130	0.0	0.0	1.8	4.6	14	8.9	5.0	0.0	0.0	0.0	34
Upriver Dam*	194131/2*	0.1	0.6	5.6	12	15	3.7	19	0.0	0.0	0.0	56
UPRIVER BOT	194133	0.0	0.3	10	40	22	4.1	0.8	0.0	0.0	0.0	78
Monroe St	194134	0.0	1.0	9.5	21	20	13	11	0.0	0.0	0.0	76
Ninemile1	--	--	--	--	--	--	--	--	--	--	--	--
Tum Tum	194135	0.0	1.4	12	24	18	8.9	13	0.1	0.0	0.0	78
LitlSpokBr*	194136/7*	0.1	0.4	9.1	35	51	16	12	13	6.9	0.0	143
<b>April</b>												
Stateline	208134	0.0	0.3	8.0	17	60	32	27	2.1	0.0	0.0	145
Upriver Dam	208135	0.0	0.0	2.1	16	14	6.6	4.6	0.9	0.0	0.0	45
UPRIVER BOT*	208136/7*	1.8	1.0	24	78	57	17	11	0.5	0.0	0.0	191
Monroe St	208138	0.1	1.8	21	53	80	40	31	4.0	0.0	0.0	231
Ninemile2	208139	0.5	2.6	25	57	68	40	28	3.9	0.0	0.0	225
LongLkLow	208133	0.6	6.0	25	94	84	34	16	3.3	0.0	0.0	263
LitlSpokBr*	208140/1*	0.4	0.8	18	37	53	19	23	14	10	3.1	178

\*Mean of replicate analysis

Note: Reporting limits were variable, 0.1 – 10 pg/l.



There was a seasonal difference in t-PCB, with concentrations highest during October and lowest during February (Figure 10). t-PCB measured during October and April appeared similar at all reaches except for a large divergence at Long Lake during April. The February t-PCB concentrations were similar among reaches, and low compared to other months. Lower concentrations during this deployment may have been more a result of colder temperatures which reduce the SPMD sampling rate but is not accounted for in the model used to translate SPMD to surface water concentrations. This may also explain the consistent t-PCB concentrations in the Little Spokane River, since February and April temperatures at this location were 2-3°C warmer. Simple flow dilution does not explain the differences among deployments since Spokane River discharge was highest during April (325 m<sup>3</sup>/s at Spokane), lowest during October (49 m<sup>3</sup>/s), and intermediate during February (114 m<sup>3</sup>/s).

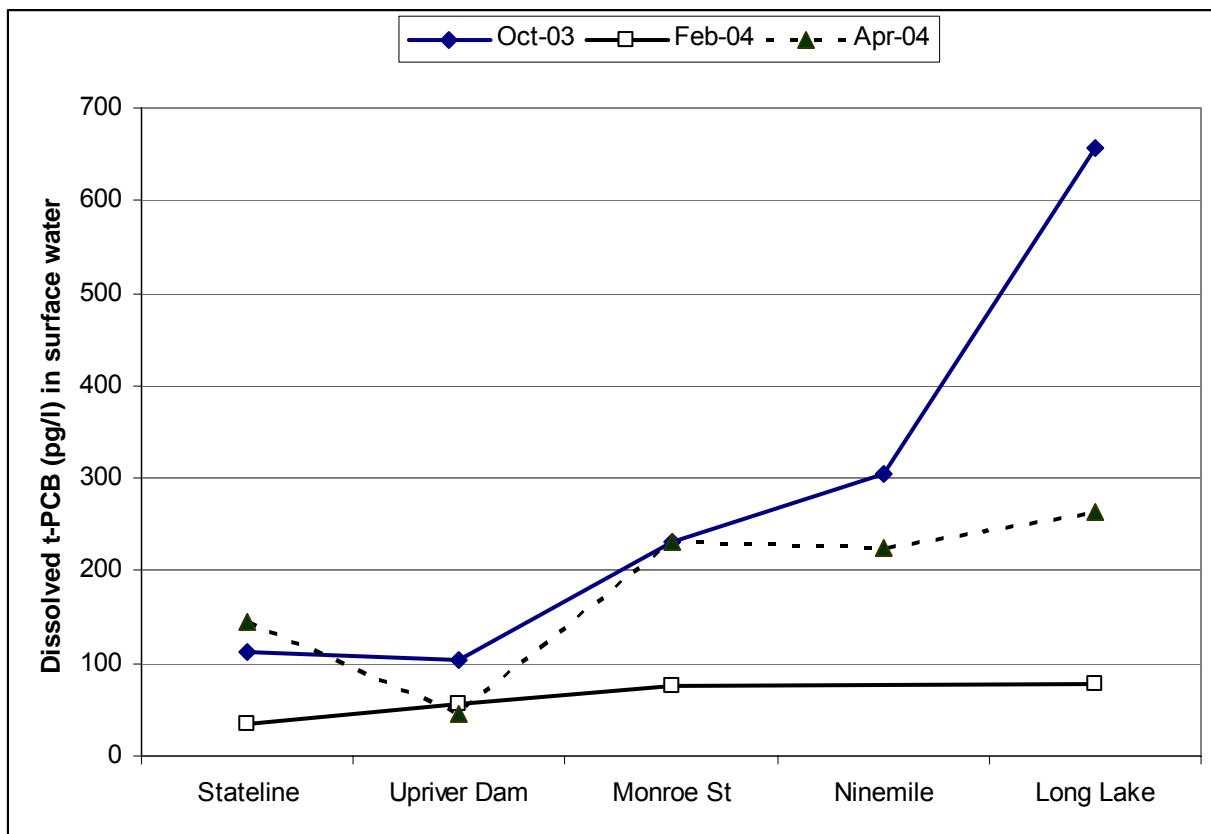


Figure 10. Dissolved t-PCB in the Spokane River, 2003-2004.

One objective of the SPMD sampling at the Upriver Dam cleanup site was to assess dissolved PCBs at different depths. Samples deployed 1-2 feet from the bottom had consistently higher concentrations than those at mid-depth (12-13 feet above bottom, Figure 11). The difference was pronounced in April when the bottom sample was four times the mid-column sample, even though the temperature was 1°C lower (and thus a lower sampling rate) at the bottom. Temperatures at both depths were identical during the other deployments.

Higher PCB concentrations near the bottom are not unexpected at this site which has very high PCB levels in the sediments. Although the high level of organic carbon in the sediments theoretically sequesters PCBs, some diffusion to the water column presumably occurs which was captured by the near-bottom SPMDs.

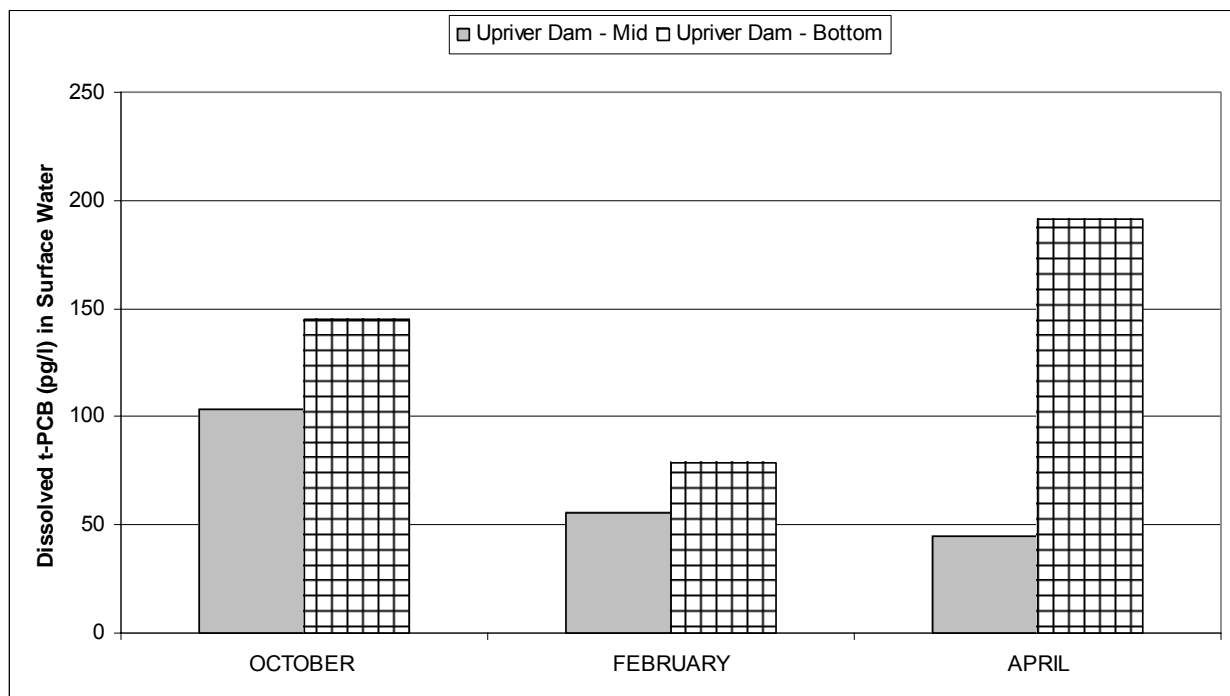


Figure 11. Dissolved t-PCB at Mid-depth and Near the Bottom at the Upriver Dam Deployment Location.

## PCBs in Spokane River Suspended Particulate Matter

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PCBs were measured in suspended particulate matter at Harvard Rd., Plante Ferry, and Ninemile using centrifugal extraction during October-November, 2003. Results are shown in Table 20. Ancillary parameters are in Appendix F. TOC and DOC values were generally  $\leq 1$  mg/l and TSS averaged 1 mg/l at Harvard Rd. and Ninemile and 2 mg/l at Plante Ferry.

PCBs were composed primarily of tetra-, penta-, and hexachlorobiphenyl congeners. t-PCB concentrations in suspended particles from Ninemile were an order of magnitude higher than those upstream. The low TSS concentrations during all three sampling events indicated that differences in t-PCB concentrations were not due to varying sediment entrainment.

Earlier (1994) suspended particulate matter sampling by Ecology at Plante Ferry yielded much higher PCB concentrations (220 ng/g) using the same collection methods as the present study (Ecology, 1995). Although that result was obtained using Aroclor rather than congener analysis, river conditions were similar, TSS was low ( $< 1$  mg/l), and the sampling site was nearly identical.

Whole surface water samples were also collected during particulate matter sampling in 2003 to assess comparability with other sampling methods (Table 20). No PCBs were detected at Harvard Rd. or Plante Ferry at the 110 pg/l level, and only a low concentration (130 pg/l) of dichlorobiphenyl congeners was detected at Ninemile, an unusual finding considering the relatively low concentration of this homologue group in SPMDs and suspended particulate matter.

To examine the proportion of solid and dissolved phase PCB concentrations in Spokane River surface water, the following partition formula was applied to the suspended particulate matter data:

$$\text{Eq. 3 } \textit{Fraction of dissolved PCB} = 1 / (1 + (f_s \times f_{oc} \times K_{oc}))$$

Where:

- $f_s$  = fraction of solid in water
- $f_{oc}$  = fraction of organic carbon in the solid phase
- $K_{oc}$  = sediment-water partition coefficient normalized for organic carbon

This formula assumes that PCBs are in equilibrium between the solid and dissolved phases, and the proportion in each phase is governed by the amount of solids in the water and the organic carbon content of the solid material.  $K_{oc}$ , the sediment-water partition coefficient normalized for organic carbon, is a field or laboratory-derived constant for each chemical. Values for  $f_s$  were from TSS measurements (1 or 2 mg/l; i.e.,  $f_s = 0.000001$  or  $0.000002$ ). Values for  $f_{oc}$  (0.15) and  $K_{oc}$  (449,000) are from EPA (1994) and DiToro et al. (1991), respectively, and are the same values used by Ecology (1995) to calculate a dissolved PCB concentration in water from earlier sampling.

Table 20. PCB Concentrations Grouped by Homologues in Suspended Particulate Matter (ng/g, dw) and Whole River Water Collected at the Centrifuge Inlet (pg/l).

Station	Sample Number	1-Cl		2-Cl		3-Cl		4-Cl		5-Cl		6-Cl		7-Cl		8-Cl		9-Cl		10-Cl		Total PCBs	
<i>Suspended Particulate Matter</i>																							
Harvard	3438100	91	U	<b>0.11</b>		<b>0.51</b>		<b>0.96</b>		<b>2.91</b>		<b>3.40</b>		<b>1.39</b>		<b>0.32</b>		0.09	U	0.09	U	<b>9.60</b>	
PLANTEFRY	3448100	51	U	<b>0.09</b>		<b>0.41</b>		<b>1.34</b>		<b>2.49</b>		<b>1.98</b>		<b>0.70</b>		<b>0.08</b>		0.05	U	0.05	U	<b>7.09</b>	
NINEM SPM	3454105	71	U	<b>0.39</b>		<b>3.71</b>		<b>12.9</b>		<b>24.6</b>		<b>18.6</b>		<b>6.30</b>		<b>1.71</b>		<b>0.39</b>		<b>0.15</b>		<b>68.8</b>	
<i>Whole Water – Centrifuge Inlet</i>																							
Harvard	3438100	111	REJ	111	UJ	111	U	111	U	111	U	111	U	111	U	111	U	111	U	122	U	111	U
PLANTEFRY	3448100	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	120	U	109	U
NINEM SPM	3454105	108	U	<b>130</b>		108	U	108	U	108	U	108	U	108	U	108	U	108	U	119	U	<b>130</b>	

Detected values in **bold**

U - The analyte was not detected at or above the reported result.

REJ - Data are unusable for all purposes

Based on the sediment-water partition formula, approximately 90% of the PCBs are in the dissolved phase. Dissolved t-PCB concentration for Harvard Rd. and Plante Ferry are 142 and 105 pg/l, respectively, similar to results derived from SPMD deployments at Stateline and Upriver Dam during the same period ( $\approx 110$  pg/l). At Ninemile, the theoretical dissolved concentration of t-PCB was 1,020 pg/l, more than three times the concentration measured with SPMDs (305 pg/l) during October.

Figure 12 shows whole water PCB concentrations calculated from the suspended particle data and illustrates the relative importance of the dissolved PCB component, at least during low flow conditions. Results also suggest that the analysis of whole surface water samples collected during particulate matter sampling underestimated actual PCB concentrations.

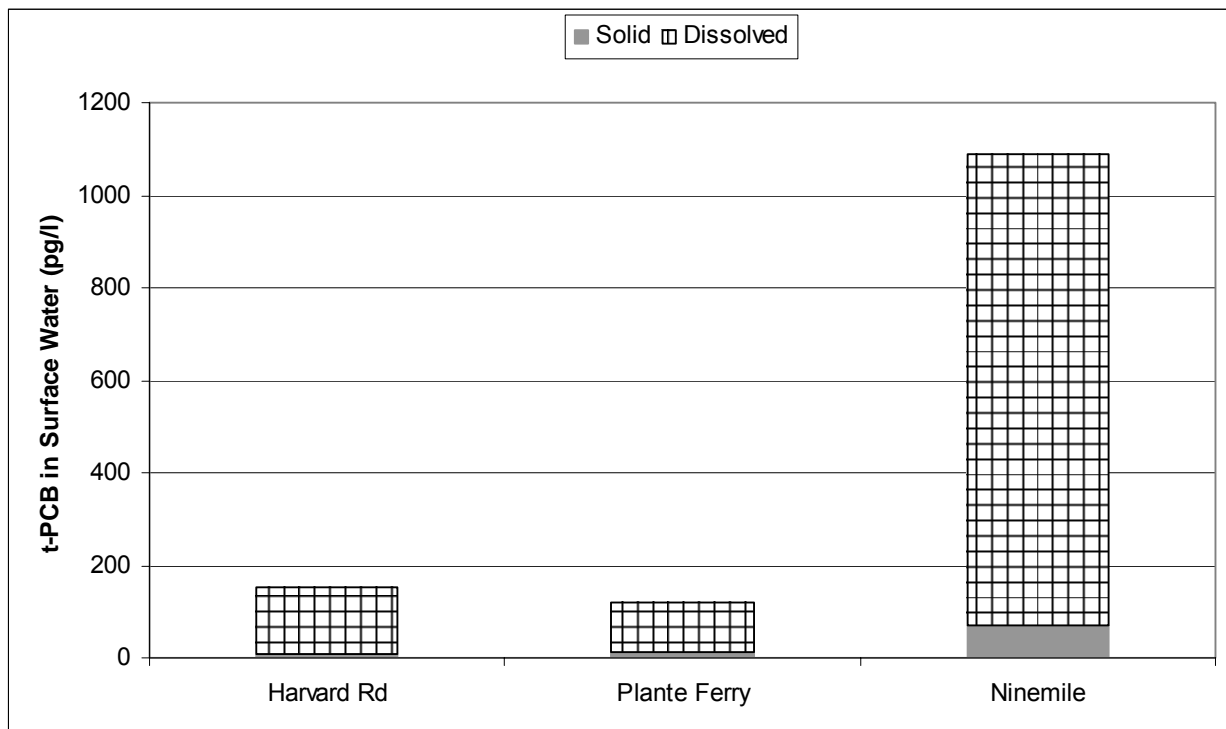


Figure 12. Measured Particle-bound PCB Concentrations and Theoretical Dissolved PCB Concentrations in Spokane River Surface Water Based on Suspended Particulate Matter Collected During 2003.

## PCBs in Industrial and Municipal Effluents Discharged to the Spokane River

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PCBs monitored in effluents from industrial and municipal facilities during three events are shown in Table 21. Spokane WWTP was the only facility where PCBs were detected during all three sampling events, with an average PCB concentration of 940 pg/l. Kaiser effluent t-PCB concentrations were generally <110 pg/l except during the October sampling when 330 pg/l was detected on 10/21/2003 but undetected at 100 pg/l the following day. Samples from the treatment lagoon at Kaiser showed much higher PCBs (110 – 7,400 pg/l) but these concentrations were reduced substantially by the bed filtration system prior to discharge.

Liberty Lake WWTP appeared to have variable concentrations, as did Inland Empire to a lesser degree. T-PCB concentrations at Liberty Lake WWTP increased an order of magnitude higher during the April sampling event while Inland Empire had only one sample with PCBs detected, 670 pg/l t-PCB in the October sample.

Overall, it appears that PCB concentrations in the effluent of the four facilities monitored have decreased substantially since previous sampling. The smallest decrease occurred at the Spokane WWTP where average concentrations were about one-half those during 2001. However, the bulk of this apparent decrease may be due to higher detection limits used for the 2003-2004 samples compared to earlier samples. Effluent samples analyzed by Golding (2002) and SAIC (2003a) typically had detection limits <5 pg/l for individual congeners and nearly all detected congeners were found at concentrations <100 pg/l. Therefore, the 2003-2004 results are likely all biased low due to the omission of these detections.

## PCBs in Stormwater Discharged to the Spokane River

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Sampling for stormwater was conducted by City of Spokane personnel during one runoff event during June, 2004. Four locations were sampled. Although the sampling plan proposed sampling at five locations during two runoff events, lack of springtime precipitation and logistical problems did not permit fulfillment of the plan.

Samples were collected at manholes nearest the outfalls draining the particular stormwater conveyance systems. Figure 13 shows the catchment areas for each sample. One of the systems, CSO34, is a combined sewer overflow (CSO) system, although an overflow event did not occur during sampling.

Table 21. PCB Concentrations Grouped by Homologues in Industrial/Municipal Effluent (pg/l).

Station	Sample ID	TSS (mg/L)	1-Cl		2-Cl		3-Cl		4-Cl		5-Cl		6-Cl		7-Cl		8-Cl		9-Cl		10-Cl		Total PCBs	
<b>October</b>																								
LIBLAKE	3434025	7	98	UJ	<b>161</b>		98	U	98	U	98	U	98	U	98	U	98	U	98	U	108	U	<b>161</b>	
KaiserEff	3434020	1	100	U	<b>100</b>	J	<b>228</b>		100	U	100	U	100	U	100	U	100	U	100	U	110	U	<b>328</b>	J
KaiserEff	3434023	1	101	U	101	U	101	U	101	U	101	U	101	U	101	U	101	U	101	U	112	U	101	U
KaiserLag	3434021	3	102	U	<b>292</b>	J	<b>911</b>		<b>1,350</b>		102	U	102	U	102	U	102	U	102	U	112	U	<b>2,550</b>	J
KaiserFilt	3434022	1	100	U	<b>167</b>	J	<b>104</b>		100	U	100	U	100	U	100	U	100	U	100	U	110	U	<b>271</b>	J
Inland Emp	3434026	5	101	UJ	<b>670</b>		101	U	101	U	101	U	101	U	101	U	101	U	101	U	111	U	<b>670</b>	
SPOKWWTP	3434027	6	99	U	<b>143</b>		99	U	<b>112</b>		<b>218</b>		99	U	99	U	99	U	99	U	108	U	<b>473</b>	
<b>February</b>																								
LIBLAKE	4064113	31	111	U	111	U	111	U	111	U	111	U	111	U	111	U	111	U	111	U	122	U	111	U
KaiserEff	4064105	1	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	123	U	112	U
“ Replicate	4064106	1	106	U	106	U	106	U	106	U	106	U	106	U	106	U	106	U	106	U	116	U	106	U
KaiserEff	4064107	1	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	119	U	109	U
KaiserLag	4064110	5	106	U	<b>422</b>		<b>2,580</b>		<b>3,720</b>		<b>647</b>	J	106	U	106	U	106	U	106	U	117	U	<b>7,370</b>	J
KaiserFilt	4064109	1	109	U	109	U	<b>307</b>		<b>125</b>	J	109	U	109	U	109	U	109	U	109	U	120	U	<b>432</b>	J
Inland Emp	4064111	9	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	109	U	120	U	109	U
SPOKWWTP	4064112	10	108	U	108	U	108	U	<b>123</b>		<b>259</b>		<b>122</b>		108	U	108	U	108	U	119	U	<b>504</b>	
<b>April</b>																								
LIBLAKE	4188205	43	<b>999</b>	NJ	112	U	112	U	<b>265</b>		112	U	112	U	112	U	112	U	112	U	123	U	<b>1,260</b>	J
KaiserEff	4188198	1	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	124	U	112	U
KaiserEff	4188199	1	107	U	107	U	107	U	107	U	107	U	107	U	107	U	107	U	107	U	117	U	107	U
KaiserLag	4188202	1	104	U	<b>112</b>	J	104	U	104	U	104	U	104	U	104	U	104	U	104	U	115	U	<b>112</b>	J
KaiserFilt	4188201	1	106	U	106	U	106	U	106	U	106	U	106	U	106	U	106	U	106	U	116	U	106	U
Inland Emp	4188203	2	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	112	U	124	U	112	U
SPOKWWTP	4188204	5	102	U	102	U	102	U	<b>342</b>		<b>588</b>		<b>329</b>		102	U	102	U	102	U	113	U	<b>1,260</b>	
“ Replicate	4188206	6	<b>865</b>	NJ	107	U	107	U	<b>360</b>		<b>826</b>		<b>358</b>		107	U	107	U	107	U	117	U	<b>2,410</b>	J

Detected values in **bold**

U - The analyte was not detected at or above the reported result

UJ - The analyte was not detected at or above the reported estimated result.

J - The analyte was positively identified. The associated numerical value is an estimate.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

## SPOKANE CITY LIMIT AND STUDY SUB-BASINS

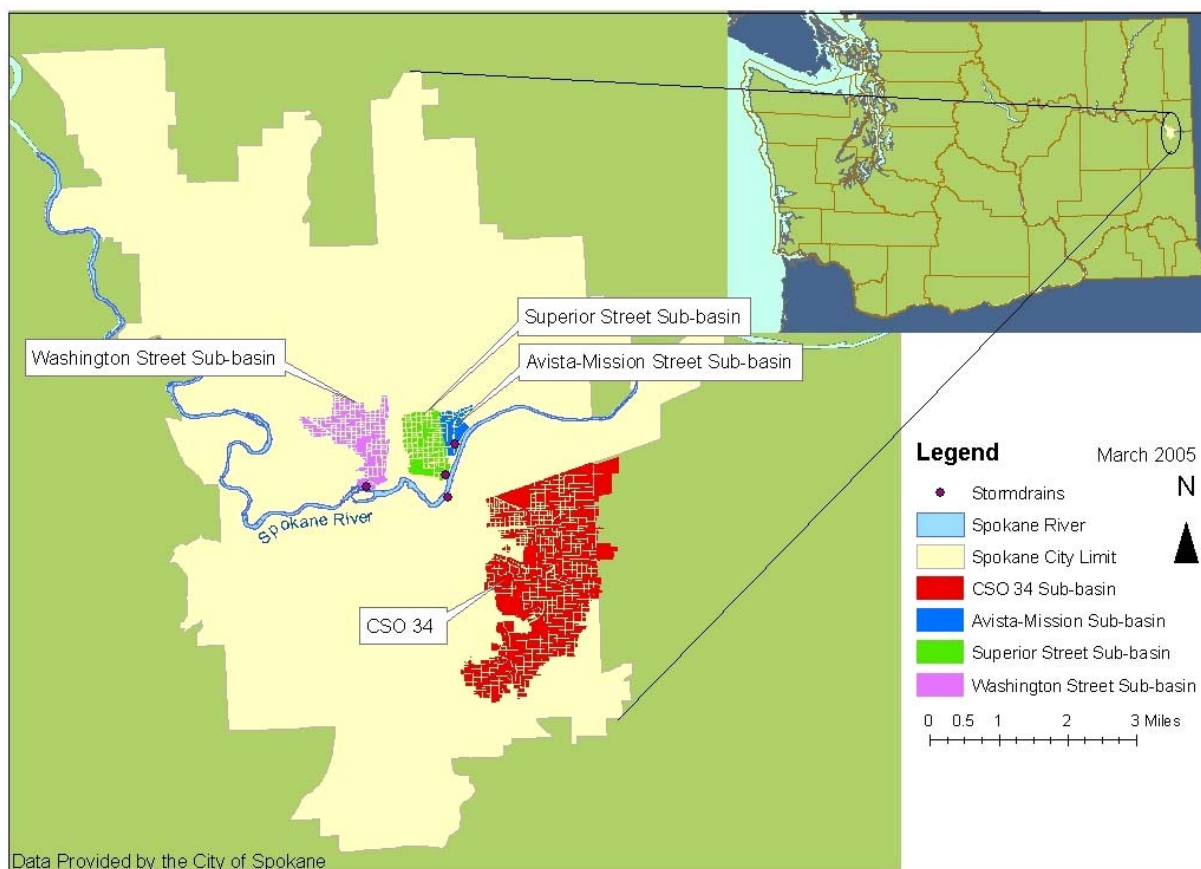


Figure 13. Stormwater Sub-Basins Sampled for PCBs During 2004.

Results of the grab samples collected from storm drains are shown in Table 22. PCB concentrations varied widely (4,900 – 83,000 pg/l t-PCB) and may have been related to the substantial TSS concentrations (26 – 126 mg/l).

Based on these TSS concentrations, it can be assumed that most of the PCBs were adsorbed to the solid component of stormwater. Approximately 85%-95% of the PCBs were estimated to be bound to the solid phase (i.e., attached to the suspended sediment) when the partitioning formula described previously was applied and an OC fraction of 0.05 is used. If this is the case, the suspended sediment carried in stormwater would have average dry weight t-PCB concentrations ranging from approximately 150 to 1,000 ng/g, or about two to fifteen times the levels seen in suspended particulate matter sampled from the surface water at Ninemile.



Table 22. PCB Concentrations Grouped by Homologues in Stormwater (pg/l).

Station Name	Sample Number	TSS (mg/L)	1-Cl		2-Cl		3-Cl		4-Cl		5-Cl		6-Cl		7-Cl		8-Cl		9-Cl		10-Cl		Total PCBs	
STMMISSBR	4254001	58	117	U	117	U	<b>117</b>		<b>5,490</b>		<b>28,800</b>	J	<b>19,200</b>		<b>6,660</b>		<b>1,600</b>		<b>283</b>		<b>254</b>		<b>62,400</b>	
CS034	4254000	126	111	U	111	U	<b>685</b>		<b>3,120</b>		<b>10,200</b>		<b>28,500</b>		<b>32,400</b>		<b>7,800</b>		<b>678</b>		123	U	<b>83,400</b>	
STMSUPOUT	4254003	26	102	U	102	U	102	U	<b>843</b>		<b>1,920</b>		<b>1,270</b>		<b>749</b>		<b>120</b>		102	U	112	U	<b>4,900</b>	
STMWASHBR	4254002	91	113	U	113	U	<b>285</b>		<b>2,560</b>		<b>8,380</b>	J	<b>5,290</b>	J	<b>2,530</b>		<b>690</b>		<b>198</b>		124	U	<b>19,900</b>	J

Detected values in **bold**

U - The analyte was not detected at or above the reported result.

J - The analyte was positively identified. The associated numerical value is an estimate.

## PCBs in Spokane River Bottom Sediments

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Grain size composition and PCBs in surficial (top 2 cm) bottom sediments from various Spokane River locations and one reference site (Buffalo Lake) are shown in Tables 23 and 24. As mentioned previously, sites were selected to assess the possibility of PCB enriched sediments behind Monroe St. Dam, assess the longitudinal PCB concentration gradient in Long Lake, evaluate the potential of the un-surveyed Little Spokane River as a significant PCB source, and assess PCB concentrations in previously sampled Spokane River reaches downstream of Long Lake. Due to the lack of fine-grained sediment deposits in the Spokane River, sampling was limited to a smaller number than planned. Sampling the fine-grained sediment deposit behind Upriver Dam was deemed unnecessary due to the intensive investigation of these sediments as part of the clean-up at this site.

Table 23. Grain Size in Bottom Sediments (%).

Station Name	Sample Number	Silt (%)	Sand (%)	Gravel (%)	Clay (%)
MonroeSed	4164049	0.8	47.1	52	34.0
LongLkUp	4208147	73.6	22	0.1	4.3
LongLkMid	3454111	76.3	3.6	0	20.2
LONGLKLOW	3454112/4*	59.1	7.0	0.1	32.3
Littlefls	3454113	9.4	88.2	0	2.3
SPOK-1	3458100	66.5	9.7	0	23.8
LitlSpokSed	3504060	13	84	0.2	2.8
BUFFALO REF	3458103	25.4	23.3	0.3	50.9

\*Mean of replicate analysis

Table 24. PCB Concentrations Grouped by Homologues in Bottom Sediments (ng/g, dw).

Station Name	Sample Number	TOC (%)	1-Cl		2-Cl		3-Cl	4-Cl	5-Cl		6-Cl		7-Cl	8-Cl		9-Cl		10-Cl		Total PCBs	
MonroeSed	4168149	0.36	0.01	U	0.01	U	<b>0.04</b>	<b>0.15</b>	<b>3.00</b>	J	<b>1.79</b>		<b>0.90</b>	<b>0.24</b>	J	<b>0.05</b>	J	0.02	U	<b>6.17</b>	J
LongLkUp	4208147	2.8	<b>0.17</b>	J	<b>0.90</b>		<b>5.99</b>	<b>16.1</b>	<b>13.1</b>	J	<b>8.52</b>	J	<b>3.50</b>	<b>1.06</b>		<b>0.23</b>		0.12		<b>49.7</b>	J
LongLkMid	3454111	2.98	0.24	U	<b>0.30</b>		<b>3.05</b>	<b>7.31</b>	<b>5.54</b>		<b>5.23</b>		<b>1.76</b>	<b>0.86</b>		<b>0.27</b>		<b>0.08</b>		<b>24.4</b>	
LONGLKLOW	3454112/4*	2.81	<b>0.09</b>		<b>0.37</b>		<b>2.80</b>	<b>8.49</b>	<b>6.89</b>		<b>4.22</b>		<b>2.23</b>	<b>0.94</b>		<b>0.22</b>		<b>0.08</b>		<b>26.3</b>	
Littlefls	3454113	0.61	0.05	U	<b>0.10</b>		<b>0.24</b>	<b>0.52</b>	<b>0.62</b>		<b>0.35</b>		<b>0.05</b>	0.05	U	0.05	U	0.05	U	<b>1.90</b>	
SPOK-1	3458100-S	1.71	0.05	U	<b>0.20</b>		<b>0.72</b>	<b>3.61</b>	<b>3.08</b>		<b>1.59</b>		<b>0.89</b>	<b>0.28</b>		<b>0.07</b>		0.05	U	<b>10.4</b>	
LitlSpokSed	3504060	0.85	0.05	U	0.05	U	<b>0.06</b>	<b>0.16</b>	<b>0.31</b>		<b>0.24</b>		<b>0.25</b>	<b>0.75</b>		<b>0.30</b>		0.05	U	<b>2.06</b>	
BUFFALO REF	3458103-S	8.24	0.05	U	<b>0.06</b>		<b>0.07</b>	<b>0.30</b>	<b>0.82</b>		<b>0.81</b>		<b>0.30</b>	<b>0.12</b>		<b>0.23</b>		<b>0.16</b>		<b>2.88</b>	

\*Mean of replicate analysis

Detected values in **bold**

U - The analyte was not detected at or above the reported result.

J - The analyte was positively identified. The associated numerical value is an estimate.

Concentrations ranged from 50 ng/g t-PCB at upper Long Lake to 1.9 ng/g at Little Falls. Upper Long Lake sediments have t-PCB concentrations similar to suspended particulate matter concentrations at Ninemile, suggesting perhaps that this material is deposited in this reach. PCB levels in the lower and middle reaches of Long Lake are half those in the upper reach possibly due to dilution from entrained bank material or Little Spokane River sediments carried downstream.

Monroe St. sediments had low PCB concentrations, (6.2 ng/g t-PCB) as did the Little Spokane River (2.1 ng/g) and Little Falls. The low concentrations probably reflected a lack of organic carbon-enriched fine material in these reaches. When PCB concentrations among sites were compared on an organic carbon normalized basis, the Long Lake stations retained the same relative PCB levels, Little Falls and the Little Spokane River were comparatively low, and Monroe St. t-PCB concentrations were as high as those from upper Long Lake (Figure 14).

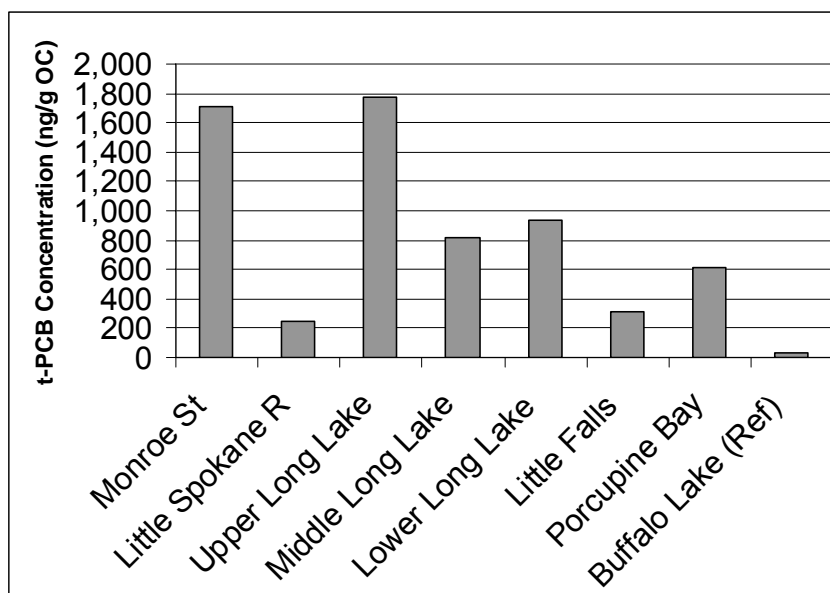


Figure 14. PCB Concentrations in Spokane River and Little Spokane River Sediments Normalized to Organic Carbon. Buffalo Lake (Okanogon County) Included as Reference.

TOC normalized t-PCB concentrations in Monroe St. and Upper Long Lake sediments were elevated 50 times the reference sediment from Buffalo Lake. Middle and lower Long Lake sediments were half that elevation. Little Spokane River and Little Falls sediments were less than ten times above PCBs in the reference sediments, while Porcupine Bay levels were 18 times higher.

Temporal trends in sediment PCBs are difficult to establish due to the higher reporting limits used in the Aroclor analysis of previous studies. For instance, Johnson and Norton (2001) found TOC-normalized t-PCB concentrations of 400, 740, and 3,800 ng/g OC at upper, middle, and lower Long Lake, respectively, but few Aroclors were detected and reporting limits were often >10 ng/g. In 1993, Ecology found 1,400 ng/g OC at lower Long Lake using essentially the same

analysis and near the same location (Ecology, 1995). Porcupine Bay sediments from the same survey showed 770 ng t-PCB/g OC, representing the only other comparable data for sediments.

To more closely examine the historical record of PCB deposition in Spokane River sediments, PCBs were analyzed at various depths in a 30-cm core collected in upper Long Lake and in a 44-cm core from lower Long Lake. Table 25 shows t-PCB concentrations at various depths in each core and Figures 15 and 16 show the chronology of PCB deposition based on radionuclide ( $^{210}\text{Pb}$ ) decay in sediments.

Table 25. t-PCB Concentrations in Sediment Cores from Upper and Lower Long Lake (ng/g, dw).

Station/Sample ID	Depth (cm)	TOC (%)	t-PCB
<i>LONGUP2</i>			
04268382	0-1	2.82	7.8
04268383	1-2	2.38	13.8
04268384	3-4	2.27	15.9
04268385	5-6	1.81	16.2
04268386	7-8	1.94	19.2
04268387	9-10	1.79	33.3
04268388	11-12	1.85	32
04268389	14-15	1.85	28
04268390	24-25	2.01	50.9
04434079	28-29	1.87	31.9
04268391	29-30	2.58	30
<i>LONGLOW2</i>			
04268372	0-1	3.08	28
04268373	1-2	2.76	75
04268374	3-4	2.83	42
04268375	5-6	2.48	40
04268376	7-8	2.41	27
04268377	9-10	2.36	32.1
04268378	11-12	2.69	54
04268379	14-15	2.74	59
04268380	24-25	2.70	233
04268381	34-35	2.70	1,000
04434078	41-42	2.70	701

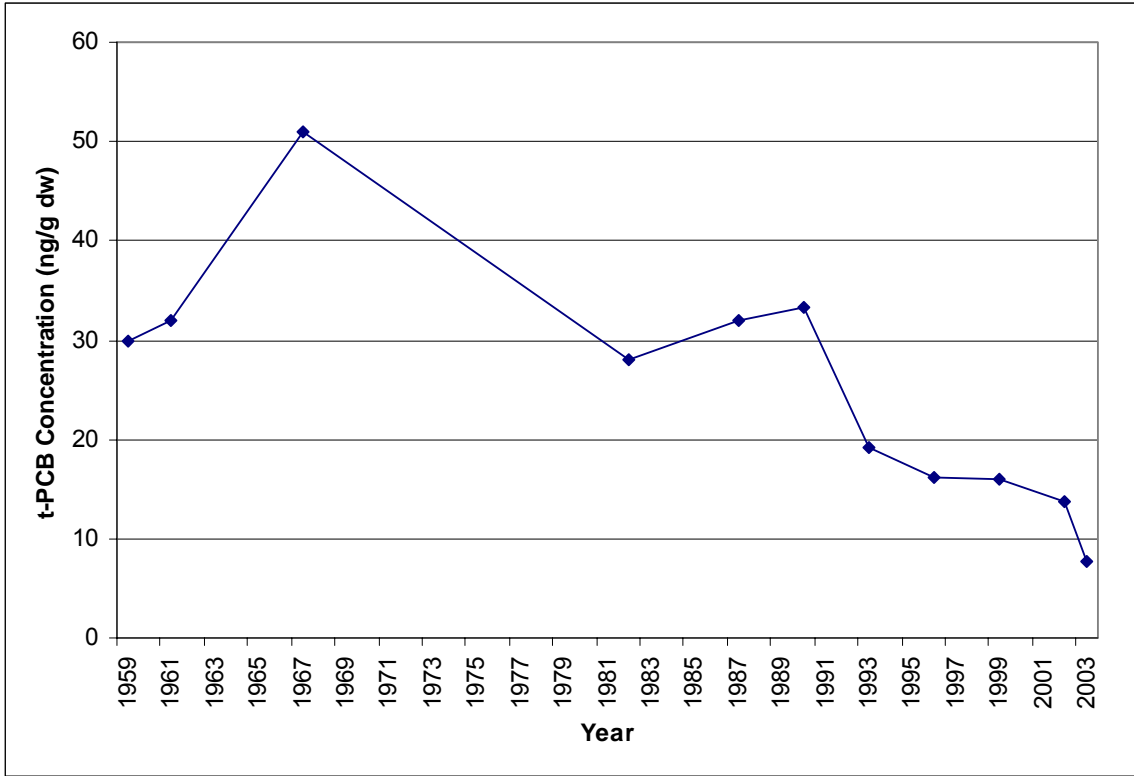


Figure 15. Chronology of PCB Concentrations in Upper Long Lake Sediments.

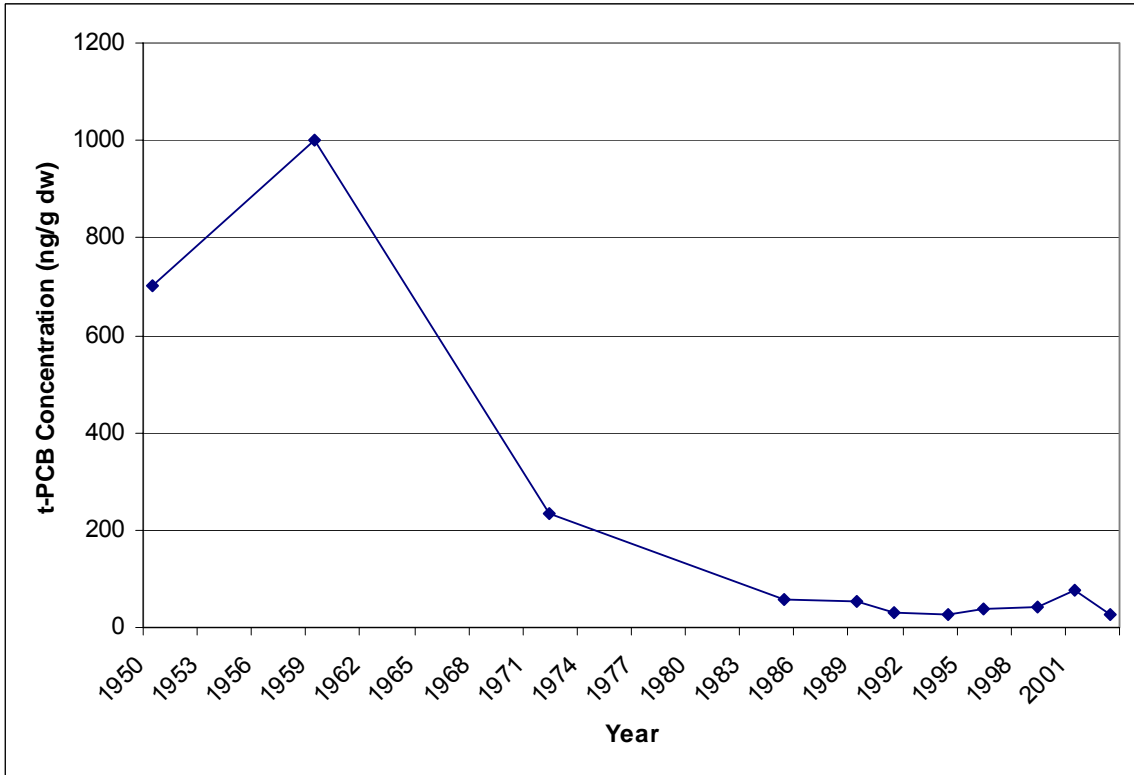


Figure 16. Chronology of PCB Concentrations in Lower Long Lake Sediments.

The sediment core from upper Long Lake was not as deep as desired due to coarser material preventing maximum corer penetration, and therefore PCB history could only be traced to circa 1959. The PCB profile showed a declining trend from 1959 to 2003, with a 1967 peak (51 ng/g), nearly coinciding with peak domestic PCB production in 1970.

The shape of the PCB profile from lower Long Lake had similarities to the upper lake. The peak occurred earlier with 1,000 ng/g circa 1959, but no horizons deposited between 1959 and 1972 were analyzed for PCBs, raising the possibility that the peak PCB concentration in this core was even higher than 1,000 ng/g. PCB concentrations in sediment deposits have leveled off significantly in the past two decades, a pattern that has been observed at other locations in Washington (e.g., Serdar, 2003).

Cores from upper and lower Long Lake differ vastly in PCB levels, with peak years showing at least a thirty fold higher concentration at the lower lake. Lower Long Lake had post-peak t-PCB concentrations 2-5 times higher than those deposited the same years in the upper lake, except during the early 1990s when PCB levels were nearly identical.

The differences in PCB concentrations between upper and lower Long Lake and the apparent variability in PCB concentrations in upper lake sediments indicate that these locations receive sediments at proportionally different rates and possibly from different sources. The high level of PCBs historically deposited in the lower lake most likely originate from PCB contamination sources in and around Spokane whereas the upper lake sediments are probably diluted with comparatively clean sediments from the Little Spokane River and Latah Creek, the latter of which provides large volumes of clean sediment. (Johnson and Norton, 2001; SCCD, 2002). The <sup>210</sup>Pb profile in the lower lake shows a steady input of newly formed material and little perturbation of sediments while upper lake sediments appear to contain older material near the surface, presumably delivered from Little Spokane River and Latah Creek, and an inconsistent decay profile suggesting physical disturbance. Future analysis of upper lake sediments should be conducted with caution and consideration for the dynamics of sedimentation in this reach.

## PCBs in Spokane River Fish

Table 26 shows concentrations of PCBs in rainbow trout fillet tissue and in gut contents. Male rainbow trout from Plante Ferry had a somewhat higher PCB concentration than females even though female fish were larger on average (391 mm vs. 363 mm). One possible explanation for the difference in concentrations is that PCBs had been mobilized along with lipids to egg production since all female trout from this location were gravid. However, lipid content was nearly identical between sexes suggesting other factors at play. Ninemile rainbow trout had slightly lower PCB concentrations than Plante Ferry possibly due to the smaller length (311 mm vs. 377 mm) or lower lipid (1.3% vs. 1.7%) on average.

The rainbow trout from Ninemile, having been analyzed individually, offer an opportunity to examine some of the factors determining PCB levels in tissue. Upon initial inspection it appears that sex differences play a large role in PCB concentrations since females have twice the average PCB levels compared to males. However, the median age of the female fish was three years

versus one year for the male fish, and the females were 20% longer on average<sup>1</sup>. Another possible factor is the origin of the specimens; the larger females were all wild fish while the majority of male specimens were hatchery-raised based on the pattern of scale checking (John Sneva, WDFW, written communication). Differences in PCB levels of wild versus hatchery fish may be due to foraging habits or prey selection, and a possible hatchery-derived contaminant burden.

Ninemile is a candidate site for an Ecology program (Washington State Toxics Monitoring Program) to evaluate long-term trends in fish tissue contaminants (Seiders and Kinney, 2004). If selected, another large group of rainbow trout from Ninemile will be sampled around 2008-2010. Specimens will be analyzed individually, and factors such as size, sex, and origin will be scrutinized to account for many of the known variables affecting PCB accumulation in tissue.

PCB concentrations in rainbow trout gut contents were approximately 15%-30% those in tissue. Many of the specimens collected at both Plante Ferry and Ninemile were engorged with filamentous plant material. There is some speculation that this material is swallowed to allow insects and other aquatic organisms to be digested while the fibrous material remains undigested. Aquatic organisms extracted from Ninemile trout stomachs and keyed under stereoscopic examination were mostly Corixidae (water boatman) adults, Chironomidae larvae, and Trichoptera larvae (probably Hydropsychidae). The gut contents of Plante Ferry rainbow trout were not examined under the stereoscope, but casual observation suggested that contents were similar to Ninemile specimens; and PCB concentrations were similar as well. Crayfish or crayfish parts were also observed in the guts of some Plante Ferry trout.

Table 27 shows PCB concentrations in suckers analyzed whole and in gut contents. Crayfish from the Upriver Dam cleanup site analyzed to assess bioavailability of PCBs from sediments are also included in Table 27. Suckers were composited by size to assess growth dilution as potential factors in PCB concentrations. Growth dilution occurs when a fish grows faster than the accumulation rate of the contaminant of concern, lowering the concentration as the fish size increases.

Largescale suckers from Stateline and Plante Ferry had similar PCB concentrations. Composites of large fish had three times the PCB level of the smaller fish composites at both sites even though average lengths were not substantially different (513 mm vs. 445 mm at Stateline; 480 mm vs. 453 mm at Plante Ferry). The higher PCB concentrations within these sites may be due to the 50% higher lipid content of the larger samples, yet even on a lipid-normalized basis, growth dilution does not appear to be a controlling factor in PCB concentrations. In the Long Lake samples, where the size disparity was similar (463 mm vs. 433 mm), the sample composed of smaller fish had 30% higher PCB levels, but here again, the difference is not necessarily due to growth dilution since the sample composed of smaller fish had a 20% higher lipid content.

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<sup>1</sup> Fish aged one year were all considered males based on observation of reproductive organs. However, reproductive organs are difficult to distinguish in immature fish, and it is therefore possible that the sex of some immature fish was misidentified.



Table 26. PCB Concentrations Grouped by Homologues (ng/g, ww) and Lipid Content in Rainbow Trout from Plante Ferry and Ninemile

Station/Tissue	Sample ID	Sex	Lip	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	t-PCB
<b>Fillet</b>														
PLANTE-F	4188308	M	1.7%	0.004 N	0.03	0.14	7.15	13.4	9.08 J	10.2 J	0.83	0.15 J	0.02	40.9 J
	4188309	F	1.7%	0.01 J	0.06 J	0.09	5.13 J	6.35 J	9.97 J	5.82 J	0.81	0.11	0.02	28.4 J
	mean=													34.7
Spokane-F	084281	M	1.5%	0.02 U	0.02	0.14	1.81	3.29	3.08	1.12	0.25	0.02 U	0.02 U	9.7
" " *	084282/308	F	2.7%	0.02	0.03	1.01	6.45	19.8	20.4	6.45	1.73	0.16	0.02	56.0
" "	084283	M	1.3%	0.02 U	0.03	0.13	2.35	5.04	4.25	1.41	0.26	0.03	0.02 U	13.5
" "	084284	M	1.9%	0.02 U	0.03	0.72	4.96	13.1	10.3	4.44	0.83	0.08	0.02 U	34.4
" "	084285	F	1.1%	0.02 U	0.02 U	0.08	4.58	16.9	19.4	7.74	1.88	0.30	0.04	50.9
" "	084286	M	1.0%	0.02 U	0.02	0.12	2.18	4.43	3.65	1.04	0.14	0.02	0.02 U	11.6
" "	084287	M	0.4%	0.03 U	0.03 U	0.53	1.73	4.87	3.68	1.24	0.30	0.03 U	0.03 U	12.3
" "	084288	M	1.9%	0.03 U	0.04	1.03	3.09	6.17	4.86	1.66	0.40	0.03 U	0.03 U	17.3
" "	084289	F	0.7%	0.02 U	0.02	0.61	3.80	12.8	15.4	7.06	2.44	0.19	0.03 J	42.4
" "	084290	M	3.3%	0.02 U	0.04	1.70	9.48	31.2	19.0	10.7	2.20	0.15	0.02 U	74.5
" "	084291	F	2.5%	0.02 U	0.04	1.36	7.33	19.5	16.3	5.95	1.25	0.16	0.03	51.9
" "	084292	M	2.0%	0.02 U	0.03	1.13	6.27	17.0	13.6	5.56	1.04	0.12	0.02 U	44.8
" "	084293	M	1.8%	0.02 U	0.03	0.39	3.75	9.98	8.96	3.23	0.65	0.09	0.02 U	27.1
" "	084294	M	1.0%	0.02 U	0.03	0.14	1.86	4.00	2.65	0.79	0.23	0.02 U	0.02 U	9.7
" "	084295	M	0.6%	0.02 U	0.03	0.14	2.70	4.91	4.59	1.94	0.27	0.03	0.02 U	14.6
" "	084296	M	0.4%	0.02 U	0.03	0.11	2.20	4.18	2.72	1.16	0.25	0.02	0.02 U	10.7
" "	084298	M	0.9%	0.02 U	0.03	0.72	2.55	4.90	4.94	1.94	0.46	0.03	0.02 U	15.6
" "	084299	M	0.2%	0.02 U	0.03	0.07	2.62	7.16	4.67	1.84	0.39	0.02	0.02 U	16.8
" "	084301	M	1.5%	0.02 U	0.03	0.89	5.72	13.6	15.7	5.37	1.59	0.16	0.02	43.2
" "	084302	M	0.8%	0.02 U	0.03	0.77	3.04	6.48	6.48	2.76	0.53	0.03	0.02 U	20.1
" "	084303	F	0.9%	0.02 U	0.03	0.60	3.29	9.30	10.7	3.28	1.35	0.11	0.02	28.7
" "	084304	M	0.3%	0.02 U	0.02 U	0.23	1.58	4.05	3.15	0.97	0.38	0.02	0.02 U	10.4
" "	084305	M	0.5%	0.03 U	0.04	0.55	1.89	4.29	3.35	1.66	0.33	0.03 U	0.03 U	12.1
" "	084306	M	1.6%	0.02 U	0.03	1.00	4.32	11.9	12.8	3.38	1.03	0.10	0.02 U	34.6
													mean of males =	22.8
													mean of females =	46.0
													mean overall =	27.6
<b>Gut Contents</b>														
PLANTE-F	4188311			0.01 N	0.03	0.06	0.11	1.77	0.97 J	0.99 J	0.14	0.02 N	0.02 U	4.1 J
NINEMILE-F	4188310			0.01 U	0.03	0.04	0.06	2.42	2.02 J	1.35	0.21	0.03 N	0.01 U	6.2 J

\*Mean of replicate analysis

U - The analyte was not detected at or above the reported result.

J - The analyte was positively identified. The associated numerical value is an estimate.

Table 27. PCB Concentration Grouped by Homologues in Suckers and Crayfish Tissue (ng/g, ww)

Station/Tissue	Sample ID	Size	Mean Length (mm)	Lip	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	t-PCB
<i>Whole Body Suckers*</i>															
STATELINE-F	4324442	Lg	513	4.5%	0.02 U	0.02 U	0.67	20.7	43.2	39.7	30.8 J	5.78 J	0.49	0.12	141.5 J
	4324443	Sm	445	3.4%	0.02 U	0.02 U	0.08	3.77	14.6	20.1 J	16.8	3.02	0.40	0.10	59.0 J
															mean=
PLANTE-F	4324440	Lg	479	4.6%	0.02 U	0.03	2.26 J	30.2	52.4	25.0	25.9 J	3.98	0.28	0.05	140.2 J
	4324441	Sm	453	3.3%	0.02 U	0.02	0.76	9.71	19.0	12.7 J	8.16	2.87 J	0.24	0.04	53.5 J
															mean=
NINEMILE-F	4324447/8†	Lg	431	2.6%	0.02 U	0.03	0.56 J	3.33 J	9.22 J	11.0 J	4.91 J	1.27	0.21 J	0.05	30.6 J
	4324450	Sm	355	4.8%	0.02 U	0.06	1.01 J	3.86	8.77	9.66	3.49	0.79	0.16	0.04 U	27.8 J
															mean=
LONGLOW-F	4324444	Lg	463	7.7%	0.02 U	0.06	3.41 J	43.4	59.7 J	53.9 J	25.5	8.17 J	1.11	0.11	195.4 J
	4324446	Sm	433	9.1%	0.02 U	0.06	4.08 J	54.7	74.4 J	78.0 J	32.0	8.59	1.05	0.18	253.1 J
															mean=
<i>Sucker Gut Contents</i>															
PLANTE-F	4324445	--	485	na	0.02 U	0.03	1.38	27.6	44.2	26.8 J	14.1	3.40	0.28	0.04	117.8 J
NINEMILE-F	4324449	--	396	na	0.02 U	0.02	0.03	0.29	1.13	1.48	0.28	0.05	0.02	0.04 U	3.3
<i>Crayfish Tail Muscle</i>															
Upriver Dam	4208148	--	40	na	0.006 U	0.02	0.01	0.03	0.036	0.05	0.54	0.18 J	0.01	0.01 U	0.87 J

\*Largescale suckers except bridgelip suckers at NINEMILE-F

†Mean of replicate analysis

U - The analyte was not detected at or above the reported result.

J - The analyte was positively identified. The associated numerical value is an estimate.

Bridgelip suckers from Ninemile had much lower PCB concentrations than suckers at other locations, possibly due to species difference or the smaller size of fish at Ninemile (large and small composites averaged 431 mm and 355 mm, respectively). However, PCB contamination of food items also appears to be a major factor since differences in PCB concentrations in whole fish from Plante Ferry and Ninemile reflect differences in PCB levels in gut contents.

Stereoscopic evaluation of gut contents from Plante Ferry largescale suckers and Ninemile bridgelip suckers revealed a diet of detritus, Chironomidae larvae, and Trichoptera larvae (probably Hydropsychidae). Simuliidae pupae and Ephemeroptera larvae (probably Leptophlebiidae) were also found in the largescale suckers, but not observed in the bridgelip suckers. The bridgelip sucker may graze algae from rocks more than the largescale sucker, but aquatic insects and crustaceans probably provide a portion of their diet (Wydoski and Whitney, 1979). Some similarities in diet between species would be expected in the Plante Ferry and Ninemile reaches where habitat conditions appear similar. This would also be true of suckers from Stateline, but largescale suckers from Long Lake (gut contents not examined) would be expected to have a much different diet based on the difference in habitat.

Both rainbow trout and suckers appear to show drastic reductions in PCB concentrations compared to previous sampling. PCBs in rainbow trout fillet from Plante Ferry and Ninemile, when compared on a lipid normalized basis to reduce covariability, have decreased an order of magnitude from 1999 (Figure 17). Largescale suckers analyzed in 2003-2004 have approximately one-fifth the PCB concentrations compared to the most recent sampling at Plante Ferry (1996) and lower Long Lake (2001) (Figure 18). Although not shown in Figure 18, bridgelip suckers collected from Ninemile in 2004 had much lower t-PCB concentrations than the most recent [largescale] sucker sampling at this location (880 ng/g lipid in 2004 vs. 31,000 ng/g lipid in 1999).

PCB concentrations in largescale suckers from Plante Ferry and lower Long Lake appear to be similar to “boundary conditions” at Stateline when compared on a lipid-normalized basis. This may suggest that PCB concentrations in Washington reaches of the Spokane River are in essence equilibrating to conditions upstream in Idaho. A recent study of PCBs in Lake Coeur D’Alene fish (SAIC, 2003b) found a t-PCB concentration of 1,580 ng/g lipid in whole largescale sucker, similar to the levels in Stateline suckers (2,440 ng/g lipid) as well as other locations analyzed during the present survey (2,340 ng/g lipid at Plante Ferry and 2,660 ng/g lipid at lower Long Lake). Rainbow trout were not analyzed from Lake Coeur D’Alene, but kokanee (another salmonid) fillets had wet weight t-PCB concentrations of 14 ng/g ww, about half those seen in rainbow trout at Plante Ferry or Ninemile.

Crayfish from the Upriver Dam fine-grained sediment site showed low levels of PCBs in tail muscle (0.87 ng/g t-PCB). This suggests little availability of PCBs, either through direct gill uptake or through diet and sediment ingestion, for this species. Previous sampling of Spokane River crayfish from various reaches has found mostly undetectable or low ( $\leq 7$  ng/g t-PCB) concentrations, indicating crayfish are a poor sentinel of PCB contamination.

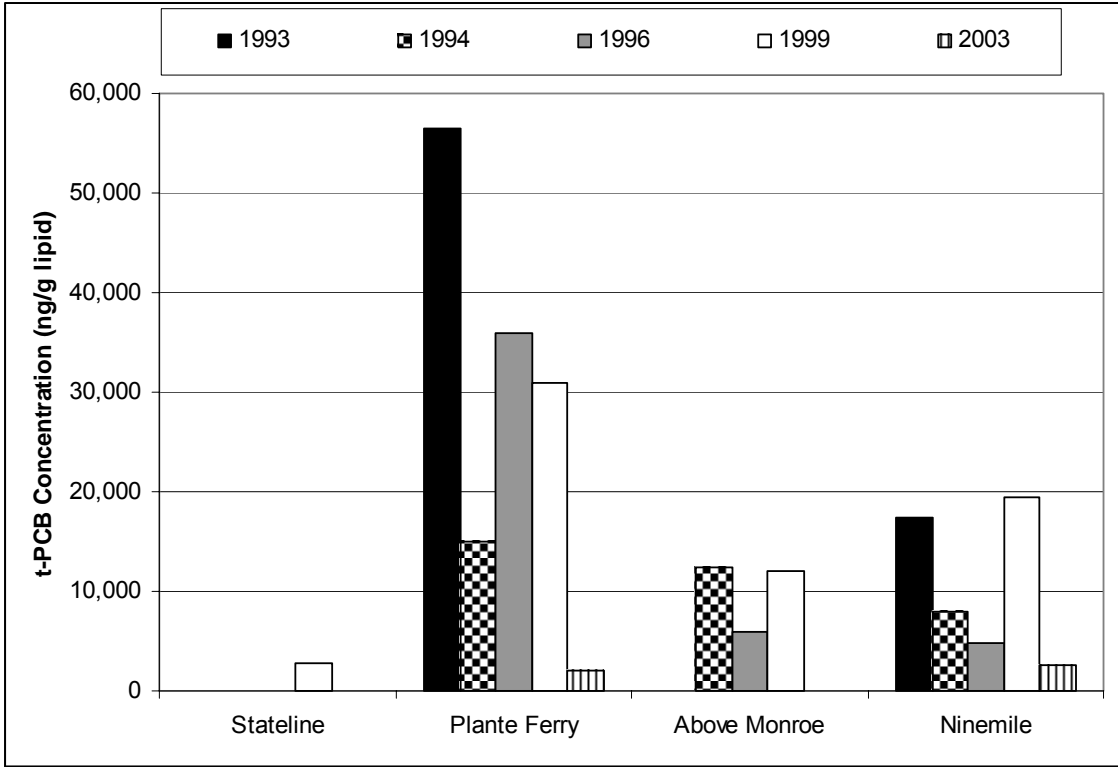


Figure 17. Lipid-Normalized Total PCB Concentrations in Spokane River Rainbow Trout Fillet, 1993-2003.

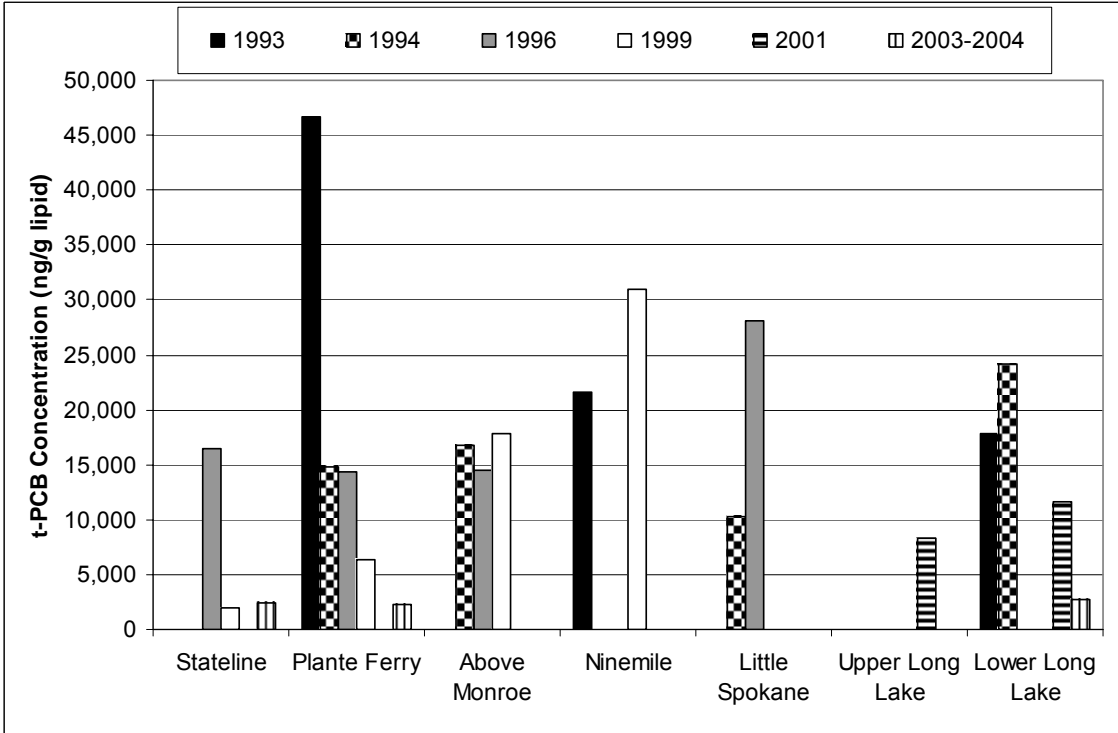


Figure 18. Lipid-Normalized Total PCB Concentrations in Spokane River Largescale Suckers Analyzed Whole, 1993-2004.

# TMDL Analysis

## PCB Source Assessment

The following section contains an assessment of PCB sources to the Spokane River which includes industrial and municipal effluents, stormwater, the Spokane River crossing into Washington from Idaho, and the Little Spokane River. Loads from other sources are considered inconsequential (Ecology, 1995; Golding, 1996, 2001, and 2002).

Deep Creek was initially considered as a potential monitoring site, but the lower section of Deep Creek appears to be a hydraulically losing reach, and no water was present. Previous monitoring of Latah Creek found no PCBs present in sediments (Johnson and Norton, 2001). The potential for other small tributaries to deliver PCBs to the Spokane River was considered low and they were not sampled.

Other possible sources are groundwater and atmospheric deposition. Groundwater has previously been monitored to assess its potential as a source of PCBs to the Spokane River, but Hart Crowser (1995) concluded that groundwater inflow was not a primary PCB transport pathway to the river.

Atmospheric deposition of PCBs has been shown to be especially pronounced in areas where cold condensation occurs, such as in the mountains of southern British Columbia and Alberta (Blais et al., 1998). This phenomenon holds the potential to deposit substantial quantities of PCBs in the mountains in the eastern portion of the Spokane River basin, eventually delivering PCBs to Lake Coeur D'Alene through the St. Joe, St. Maries, and Coeur D'Alene rivers and may partially explain concentrations of PCBs in Lake Coeur D'Alene fish higher than might be expected in a relatively unspoiled waterbody. Delivery of PCBs to Washington from this source would be integrated to a single channel – the Spokane River at Stateline. The Spokane River basin downstream of the Idaho border would not be ideal for atmospheric deposition due to aridity of the region, and PCBs that are deposited in the area would theoretically be integrated into delivery systems already considered such as the Little Spokane River and urban stormwater. Deposition of PCBs directly to the surface of the Spokane River would be minimal due to its small surface area relative to the basin area.

Although atmospheric deposition may be an unquantified source of PCBs to the Spokane River, loss of PCBs to the atmosphere through volatilization may be greater than inputs through deposition. PCB budgets for the Great Lakes area have shown atmospheric flux to be an order of magnitude greater than input and output through surface waters, with loss through volatilization approximately five times greater than atmospheric deposition (EPA, 1993).

PCB loads calculated for this TMDL assessment only include surface water inputs and outflow, generally using the following formula:

$$\text{Eq. 4 } \text{Load (mg/day)} = C_w \times (10^{-9} \text{ mg/pg}) \times Q \times (86,400 \text{ s/day})$$

Where:

- $C_w$  (concentration in whole water) = concentration of PCBs in water (pg/l)
- $Q$  (discharge) = flow of the delivery system being considered (l/s)

To simplify the amount of data and to maintain consistency with applicable criteria, loads are calculated for t-PCB only.

## PCB Loads in Industrial and Municipal Effluents Discharged to the Spokane River

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Table 28 shows PCB loads in effluents used for the TMDL analysis. PCB loads from Liberty Lake WWTP, Inland Empire, and the Spokane WWTP were calculated using a combination of results from the present survey and previous sampling (Table 4). For the Liberty Lake and Spokane WWTPs, loads were calculated using the mean t-PCB concentrations and instantaneous flows from 2001 and 2003-2004. For Inland Empire, loads were calculated using the mean t-PCB concentrations and instantaneous flows from 2001, 2002, and 2003-2004. In samples where no PCBs were detected, reporting limits were used to calculate t-PCB concentrations.

Table 28. Estimated PCB Loads in Industrial and Municipal Effluents Discharged to the Spokane River.

Station	RM	t-PCB Conc. (pg/l)	Discharge (Ml/d)	t-PCB Load (mg/d)
LIBLAKE	92.7	1,121	2.5	2.9
KaiserEff	86.0	1,080	60	65
Inland Emp	82.5	2,544	18	45
SPOKWWTP	67.4	1,364	143	194
			Total =	307

Ml/day = 0.264 MGD (million gallons per day)

PCB loads from Kaiser were based on t-PCB concentrations and instantaneous flows from nine samples collected during 2004 and 2005 (Table 4) since these represent the most current snapshot of PCBs in Kaiser effluent.

## PCB Loads in Stormwater Discharged to the Spokane River

PCB loads delivered to the Spokane River through stormwater were calculated using results from the sampling conducted during 2004 and the “Simple Method” model used to calculate contaminant loads from urban runoff ([www.stormwatercenter.net/](http://www.stormwatercenter.net/)).

The Simple Method uses the formula:

$$\mathbf{Eq. 5} \quad L = 0.226 * R * C * A$$

Where:

- L = Annual load (lbs)
- R = Annual runoff (inches)
- C = Pollutant concentration (mg/l)
- A = Area (acres)
- 0.226 = Unit conversion factor

The annual runoff is a product of annual runoff volume, and a runoff coefficient (Rv). Runoff volume is calculated as:

$$\mathbf{Eq. 6} \quad R = P * Pj * Rv$$

Where:

- R = Annual runoff (inches)
- P = Annual rainfall (inches)
- Pj = Fraction of annual rainfall events that produce runoff (usually 0.9)
- Rv = Runoff coefficient

In the Simple Method, the runoff coefficient is calculated based on impervious cover in the subwatershed. Watershed imperviousness is a reasonable predictor of Rv (Schueler, 1987), with the relationship best defined as:

$$\mathbf{Eq. 7} \quad Rv = 0.05 + 0.9Ia$$

Where:

- Ia = Impervious fraction

Geographical data were provided by The City of Spokane Wastewater Management Department. Annual rainfall was estimated to be 18 inches in Spokane based on data from Ecology’s Draft Eastern Washington Stormwater Manual. A value of 0.9 was used as the fraction of runoff.

The model was first applied to the four sub-basins sampled during 2004 (Figure 13). Table 29 shows loads calculated from the four sampled sub-basins using the Simple Method. The mass load calculated for each basin plus the roads yielded a sum total of 0.274 lb of PCBs loaded annually, or approximately 341 mg daily, in the Spokane River from these four storm drains.

Table 29. Estimated PCB Loading Through Stormwater from the Four Sub-Basins Sampled During 2004.

Sub-Basin	RM	t-PCB Conc. (pg/l)	Impervious Fraction	Area (Acres)	Annual t-PCB Load (lb)	Daily t-PCB Load (mg/d)
Avista-Mission	76.5	62,413	0.676	78	0.012	14.6
CSO 34	75.8	83,435	0.185	2,426	0.160	199.4
Superior Street	75.7	4,901	0.422	308	0.002	3.0
Washington St. Bridge	74.3	19,931	0.573	501	0.021	25.7
Roads*	--	42,700**	1.000	534	0.079	98.4
			Total =	3,847	0.274	341.0

\*Total over all four of the sub-basins.

\*\*Calculated as the average concentration of the four sub-basins.

Since the four storm drains sampled only represent approximately 10% of the entire city area, the data used for sampling and the Simple Method were used to extrapolate PCB loads in stormwater to the entire city. An average PCB concentration of 42,700 pg/l was used, and all other Simple Method model parameters were those described previously, with the exception of a city-wide impervious fraction of 0.217 provided by the City of Spokane (Wendy Corbin, City of Spokane, written and verbal communications during December, 2005).

Table 30 shows PCB loading in stormwater calculated for the entire city. The acreage represent an estimated runoff area for the city, including right-of-ways. Undeveloped land and catchments draining to dry wells were not included in the total acreage.

Table 30. Estimated Daily PCB Loading in Spokane City Stormwater.

Area Type	t-PCB Conc. (pg/l)	Impervious Fraction	Area (Acres)	Annual t-PCB Load (lb)	Daily t-PCB Load (mg/d)
Runoff Area including ROWs	42,700	0.217	22,825	0.875	1,088

ROWs=right-of-ways

Although stormwater PCB loads are three-to-four times higher than the sum of all point source loads, the characteristics of the loading is vastly different. Point sources essentially dose the Spokane River with PCBs on a continuous basis, whereas the stormwater loads are highly episodic, with each event delivering different quantities of PCBs depending on factors such as rainfall intensity and duration, and time of year. With the possible exception of Liberty Lake WWTP, PCBs in point source discharges are likely to be confined largely to the dissolved phase due to the low TSS in effluent.

Once in the Spokane River, dissolved PCBs in effluent probably remain dissolved due to low ambient TSS concentrations. PCBs delivered by stormwater, on the other hand, are probably bound to particles to a large extent. The fate of these particles in the river depends largely on their size, with larger heavier particles settling more quickly. Finally, PCB loading in stormwater is much more difficult to quantify with any degree of certainty. Factors affecting



PCB loading include, but are not limited to; intensity and duration of rainstorms or other runoff events (e.g., snowmelt), preceding runoff events, characteristics of particulate material in runoff and factors affecting mobilization of the material, characteristics of the stormwater conveyance system, and characteristics of land and land-use in the catchment.

## Instream Loads

### PCB Loads in the Spokane River at the Idaho Border

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PCB loads at the Idaho border were calculated using the average dissolved t-PCB concentration from 2003-2004 Stateline SPMD data and historic flows at USGS Gage 12419500 (Spokane River above Liberty Bridge). Two methods were used to calculate the whole water PCB concentrations; extrapolation using the dissolved fraction estimated from Equation 3 and addition of the solid component measured in Harvard Rd. suspended particulate matter (Table 31). Both methods yield an estimated t-PCB load of approximately of 480 mg/d. Results using the two methods are nearly identical since the theoretical dissolved fraction (0.92) is similar to the measured dissolved fraction (0.91).

Table 31. PCB Loads in Spokane River at Idaho Border.

Station	RM	Harm. mean flow (l/s)	Method for Calculating $C_w$	Component	Mean t-PCB $C_w$ (pg/l)	t-PCB Load (mg/d)
Stateline	96.1	52,151*	Stateline SPMD ( $C_d$ ) /diss fraction (0.92) from Equation 3	$C_w=$	106	477
Harvard	92.8	52,151*	Stateline SPMD ( $C_d$ ) + Harvard suspended partic. matter ( $C_s$ )	Diss. ( $C_d$ )	97	439
				Solid ( $C_s$ )	10	43
				Total ( $C_w$ )=	107	482

\* Flow from USGS Station 12419500 - Spokane River abv. Liberty Br (RM 93.9)

$C_w$  = Concentration in whole water

### PCB Loads in the Little Spokane River

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PCB loads in the Little Spokane River were calculated using the average Little Spokane SPMD data from 2003-2004 and historic flows at USGS Gage 12431000 (Little Spokane River at Dartford). Equation 3 was used to estimate dissolved and solid phase fractions based on TSS concentrations in the Little Spokane River.

The estimated average t-PCB load in the Little Spokane River is 97 mg/d (Table 32). Approximately 74% of this load is in the dissolved phase based on estimation using Equation 3 and an average TSS of 5 mg/l.

Table 32. PCB Loads in the Little Spokane River

Location	RM	Harm. mean flow (l/s)	Mean t-PCB C <sub>d</sub> (pg/l)	Fr <sub>x</sub> C <sub>d</sub>	Mean t-PCB C <sub>w</sub> (pg/l)	t-PCB Load (mg/d)
Little Spokane R.	56.3	5,619*	147	0.74	199	96.6

\* Flow from USGS Station - 12431000 Little Spokane River @ Dartford

## PCB Loads in the Mainstem Spokane River Downstream of the Idaho Border

PCB loads estimated from the 2003-2004 monitoring are shown in Table 33. Loads were calculated using in the matter described previously, i.e., using harmonic mean flows, mean data collected using SPMDs, and application of Equation 3 to estimate total PCB concentrations from the dissolved fraction.

Table 33. Instream PCB Loads in Spokane River Reaches and the Little Spokane River.

Location	RM	Harm. mean flow (l/s)	Mean t-PCB C <sub>d</sub> (pg/l)	Fr <sub>x</sub> C <sub>d</sub>	Mean t-PCB C <sub>w</sub> (pg/l)	t-PCB Load (mg/d)
Stateline	96.1	52,151 <sup>a</sup>	97	0.92	106	477
Upriver Dam	80.3	53,081 <sup>b</sup>	68	0.88	77	354
Upriver Dam (bottom)	80.3	53,081 <sup>b</sup>	138	0.88	157	721
Monroe St.	74.8	82,239 <sup>c</sup>	179	0.90	199	1,413
Ninemile	63.6	82,758 <sup>d</sup>	265	0.85	311	2,281
Lower Long Lake	38.4	106,329 <sup>e</sup>	332	0.83	399	3,664
Little Spokane R.	56.3	5,619 <sup>f</sup>	147	0.74	199	97

<sup>a</sup> Flow from USGS Station 12419500 - Spokane River above Liberty Br. (RM 93.9)

<sup>b</sup> Flow from USGS Station 12419500 - Spokane River above Liberty Br. (RM 93.9) plus sum of flows from municipal and industrial facilities

<sup>c</sup> Flow from USGS Station 12422500 - Spokane River at Spokane (RM 72.9)

<sup>d</sup> Sum of Flows from USGS Station 12422500 - Spokane River at Spokane (RM 72.9) and Station 12424000 - Hangman Creek at Spokane (RM 72.2)

<sup>e</sup> Flow from USGS Station 12433000 - Spokane River at Long Lake (RM 33.8)

<sup>f</sup> Flow from USGS Station 12431000 - Little Spokane River at Dartford (RM 56.3)

In the mainstem Spokane River, PCB loads spanned an order of magnitude, from 350 mg/d at Upriver Dam to 3,700 mg/d at lower Long Lake (Figure 19). Higher PCB concentrations occurred in reaches with higher flows, compounding the increase in estimated loads traveling downstream. One exception to this pattern occurs at Upriver Dam (mid-column), where all of the PCB loading can be attributed to loads moving downstream from the Idaho border (Stateline). Although PCB loads estimated at the bottom of the water column are twice those in the middle column, the mid-column loads are probably more representative of the actual river conditions whereas the bottom loads are influenced by localized conditions as discussed previously.

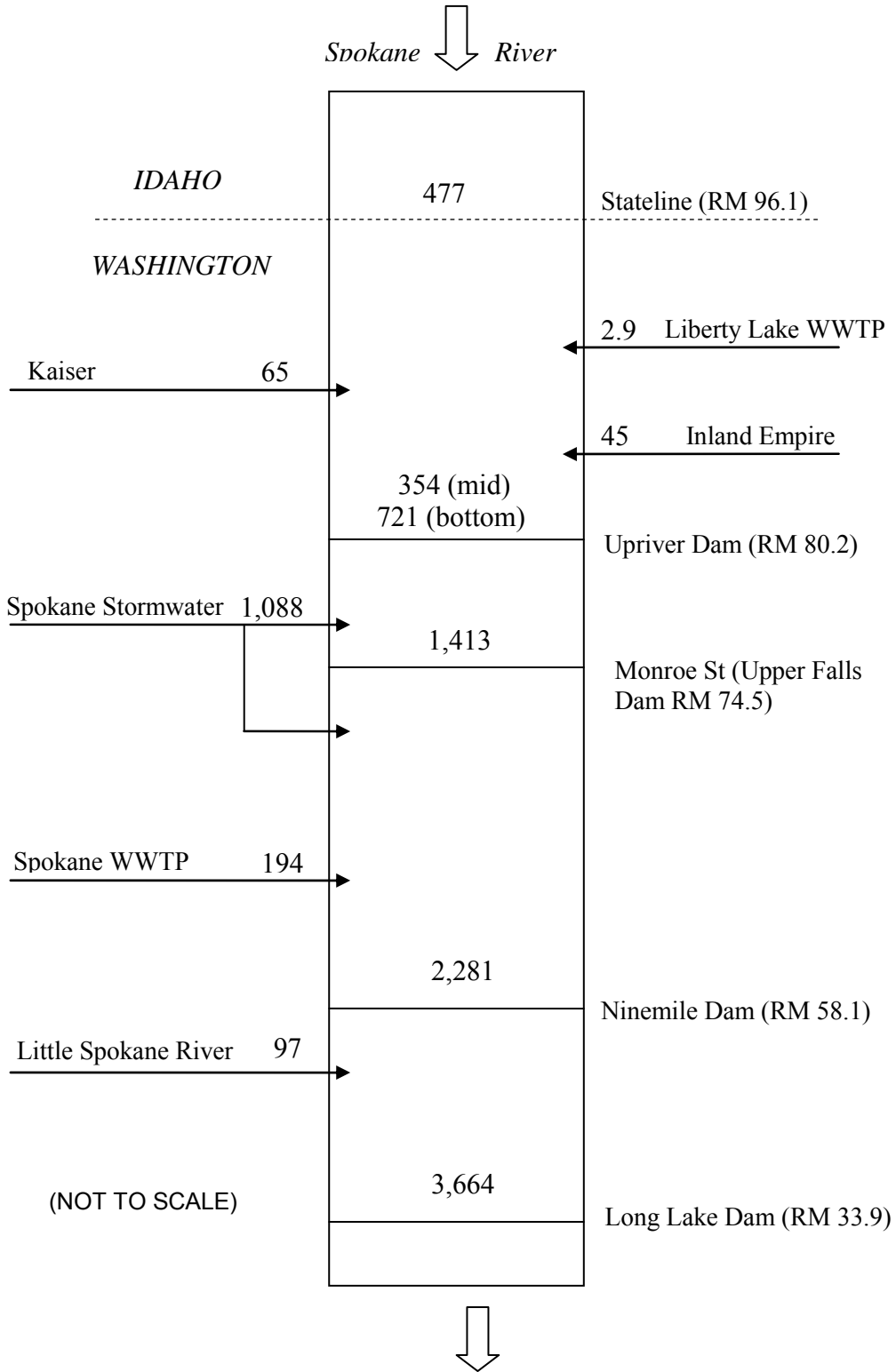


Figure 19. Schematic of PCB Sources and Instream Loads in the Spokane River (t-PCB, mg/d).

PCB loads were not calculated for Little Falls Reservoir and the Spokane Arm due to the absence of PCB data from these reaches. However, it is reasonable to assume that instream loads at Little Falls are identical to those at Long Lake since there are no known additional PCB sources to the Little Falls reservoir, flow contributions or losses to the reservoir are minor, and residence time is short since Little Falls is a run-of-the-river dam. These conditions are also true for the upstream half of the Spokane Arm which is free-flowing, but the assumption of identical loads in the lower half of the Spokane Arm (approximate delineation at Porcupine Bay [RM 13]) is tenuous due to influence of Lake Roosevelt which backs up the water in this reach during most of the year and has an undetermined effect on PCB concentrations and loads.

Limited evidence suggests that Lake Roosevelt proper contributes at most a small portion of the PCBs to the Spokane Arm and more likely has a diluting effect. Data collected by Ecology during 1993 and 1994 showed that the same or similar fish species from Long Lake had similar PCB concentrations (Ecology, 1995). In addition, PCB concentrations in Lake Roosevelt fish tissues have been low compared to fish from the lower reaches of the Spokane River (EVS, 1998; Munn, 2000).

## Necessary PCB Load Allocations and Load Reductions

### Target PCB Concentration in Water

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The Spokane Tribe criterion of 3.37 pg/l was used as the basis for calculating necessary load reductions and load allocations. Although this criterion only applies to the northern half of the Spokane River between this RM 32.5 and RM 0, it cannot be reasonably be met within these bounds unless target PCB concentrations in upstream reaches are reduced to levels near the criterion. Since a TMDL requires the incorporation of a margin of safety, the criterion was reduced by 10% to yield a target water concentration of 3.03 pg/l.

### PCB Load Allocations and Load Reductions

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PCB load allocations and load reductions required to meet Spokane Tribe criterion at Little Falls and Spokane Arm are shown in Table 34. Load allocations were calculated by first determining the assimilative capacity at Long Lake Dam, since this is the closest flow-gauging station upstream of the Spokane Tribe boundary. Based on a harmonic mean flow of  $4.51 \times 10^9$  l/d at Long Lake Dam (USGS Station 12433000), the assimilative capacity is 27.86 mg PCB/day. This load was then allocated to all known sources of PCBs in the Spokane River, apportioned by flow discharge. The mainstem Spokane River and the Little Spokane River were treated as sources and were allocated PCB loads using the same apportionment formula. No PCB load was allocated to groundwater since limited sampling suggests no loading through groundwater (Anchor Environmental, 2004).

This load allocation approach requires a 95% PCB load reduction in the Spokane River at the Idaho Border. Industrial and municipal discharges between the Idaho border and Long Lake require PCB load reductions greater than 99%. A 97% PCB load reduction is required in the Little Spokane River.

Table 34. PCB Load Allocations and Load Reductions Required to Meet Spokane Tribe Water Criterion (3.37 pg/l) at Little Falls and Spokane Arm.

Reach/Source	Current t-PCB conc. (pg/l)	Target t-PCB conc. (pg/l)	Conc. Reduct. (pg/l)	Current t-PCB load (mg/d)	Target t-PCB load (mg/d)	Load Reduct. (mg/d)	Change
<b>Stateline (RM 96.1-87.7)</b>	--	5.32	--	--	23.97	--	--
@ Idaho Border	106	5.32	100	477	23.96	453	-95.0%
Liberty Lake WWTP	1,121	5.32	1,116	2.9	0.01	2.8	-99.5%
<b>Upriver Dam (RM 87.7-80.2)</b>	--	5.32	--	--	24.39	--	--
Load from Stateline	--	--	--	--	23.97	--	--
Kaiser	1,080	5.32	1,075	65	0.32	65	-99.5%
Inland Empire	2,544	5.32	2,539	45	0.09	45	-99.8%
<b>Monroe St. (RM 80.2-74.0)</b>	--	3.44	--	--	24.42	--	--
Load from Upriver Dam	--	--	--	--	24.39	--	--
Spokane Stormwater	42,700	5.32	42,695	275	0.03	275	-99.99%
<b>Ninemile (RM 74.0-58.1)</b>	--	3.46	--	--	25.28	--	--
Load from Monroe St.	--	--	--	--	24.42	--	--
Spokane Stormwater (Latah Cr.)	42,700	5.32	42,695	7.6	0.001	7.6	-99.99%
Spokane Stormwater	42,700	5.32	42,695	806	0.10	806	-99.99%
Spokane WWTP	1,364	5.32	1,358	194	0.76	194	-99.6%
<b>Long Lake (RM 58.1-33.9)</b>	--	3.03	--	--	27.86	--	--
Load from Ninemile	--	--	--	--	25.28	--	--
Little Spokane River	199	5.32	194	97	2.58	94	-97.3%
<b>Little Falls (RM 33.9-29.3)</b>	--	3.03	--	--	27.86	--	--
Load from Long Lake	--	--	--	--	27.86	--	--
<b>Spokane Arm (RM 29.3-0)</b>	--	3.03	--	--	27.86	--	--
Load from Little Falls	--	--	--	--	27.86	--	--

Stormwater requires the largest PCB load reductions (99.99%) using the mean PCB concentration measured in stormwater (42,700 pg/l) and an estimated average flow discharge of  $2.55 \times 10^7$  l/d. The stormwater loads in Table 34 were apportioned to reaches based on relative flows in CSOs reported by the City of Spokane (City of Spokane, 2005).

## **An Alternative TMDL Approach Using of Food-Web Bioaccumulation Model to Identify Target PCB Concentrations in Water and Sediment**

Fish accumulate PCBs through a variety of pathways including bioconcentration (direct uptake of dissolved PCBs in water through the gill and epithelial tissue), diet (may also be considered indirect uptake from water and sediment), and in some cases, direct ingestion of sediment. The Spokane Tribe criterion overestimates concentration of PCBs in water that will result in a fish tissue concentration of 0.1 ng/g because bioconcentration is the only accumulation mechanism considered. Previous studies in the Spokane River have found the BCF of 31,200 l/kg used to derive this criterion to be a poor link between PCB concentrations in water and tissue. For instance, Jack et al. (2003) estimated that the BCF explained only 3-23% of the PCB accumulated in Spokane River fish tissue. To accurately relate water concentrations to fish tissue, all pathways must be considered including direct and indirect contributions from sediments.

It is widely recognized that bioaccumulation factors (BAFs) describe a much more meaningful relationship between water and tissue concentrations than BCFs (EPA, 2000b). Like BCFs, BAFs numerically describe the link between water concentrations and accumulation in tissue, but they integrate all exposure pathways (bioconcentration, diet, other sources), and therefore more accurately reflect the water-tissue relationship. Using a simplified computation method, BAFs for the Spokane River were estimated to be in the range of  $10^5$  -  $10^6$  l/kg (Jack et al., 2003).

In some cases, sediment may be a more important pathway for PCB exposure in fish, either through consumption of benthic organisms as prey or through direct ingestion of sediments. In instances where sediment exposure is more important, the relationship is described as the biota-sediment accumulation factor (BSAF), a tissue concentration divided by a sediment concentration and usually normalized to lipid in tissue and organic carbon in sediment. If a BSAF is much better than a BAF at describing the link between contaminants in the aquatic environment and tissue concentrations, then sediment recovery rates (either natural or through cleanup actions) applied to BSAFs may be used to predict contaminant declines in tissues. In Long Lake, the sediment the BSAF calculated from mean sediment and tissue concentrations was 10.9 (Jack et al., 2003).

In most instances, accumulation of PCBs in fish tissue is a result of direct and indirect water and sediment exposure pathways. Neither the BAF nor the BSAF by themselves can accurately describe the link between PCBs in the aquatic environment and fish tissue. Because of the association among water, sediments, and biota (prey items), it is impossible to account for tissue concentrations resulting from exposure to these sources when they are considered independently. Therefore, a mathematical food web bioaccumulation model was used to estimate PCB concentrations in fish tissue and prey items from concentrations in water and sediment.

As mentioned previously, numerical targets, load allocations, and other TMDL goals using this method have no regulatory standing without first meeting procedural requirements of site-specific criteria development. However, model development may be a useful exercise to determine if the existing numerical approach is adequate and if site-specific criteria are warranted.

## Food-Web Bioaccumulation Model

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A bioaccumulation food web model developed by Arnot and Gobas (2004) calculates site-specific concentrations of hydrophobic organic chemicals in multiple aquatic ecosystem compartments and is a refinement of a widely used model previously developed by Gobas (1993). The model can be used to predict PCB concentrations in fish tissue, BAFs, and BSAFs using relatively few input parameters. More importantly, and particularly applicable to TMDLs, the model can be used to back-calculate PCB concentrations in water and sediment from target PCB concentrations in fish tissue. Details of the model are in Appendix G.

## Target Water and Sediment Concentrations Calculated Using the Food-Web Bioaccumulation Model

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The Spokane Tribe tissue criterion for PCBs (0.1 ng/g) was used to calculate target PCB concentrations in water and sediment. The study area was divided into five reaches to establish target PCB loads; Stateline-Upriver Dam, Monroe Street-Ninemile, Long Lake, Little Falls, and Spokane Arm. The four reaches upstream of Long Lake were collapsed into two – Stateline-Upriver Dam and Monroe Street-Ninemile – due to the lack of input parameters for individual reaches. Some of the input parameters for Little Falls and Spokane Arm were out-of-date; Long Lake input parameters were used for these reaches with the exception of sediment TOC data which were collected at all locations for the present study. Table G-1 shows input parameters

Dissolved water and sediment t-PCB concentrations predicted to yield the Spokane Tribe criterion of 0.1 ng/g for t-PCB in rainbow trout and sucker fillet are shown in Figure 20. Results show that PCB concentrations in water and sediment one to four orders of magnitude lower than present would be required to achieve the Spokane Tribe fish tissue criterion. The model illustrates the influence of PCBs in sediments on fish tissue, either through the food web or through direct ingestion, and offers a striking contrast to the simple BCF model which ignores PCBs in sediments and diet. When sediment PCB concentrations are set to zero, effectively reducing the food-web model to the BCF model, rainbow trout fillet is predicted to have 0.1 ng/g t-PCB at whole water concentrations similar to the BCF model (3.37 pg/l).

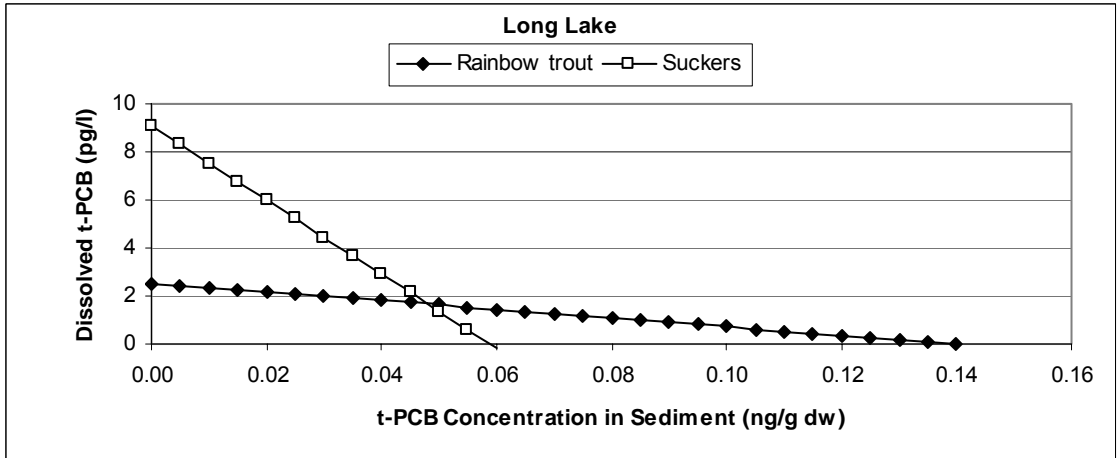
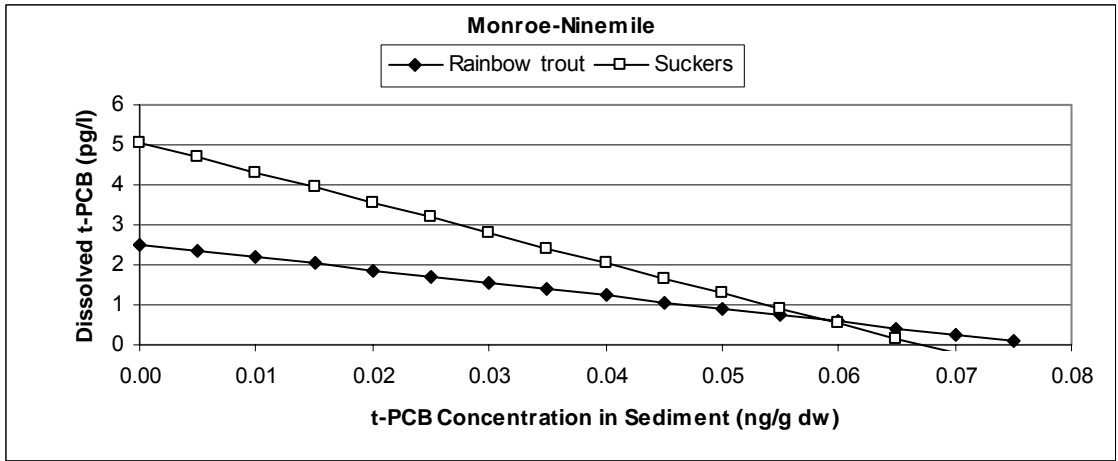
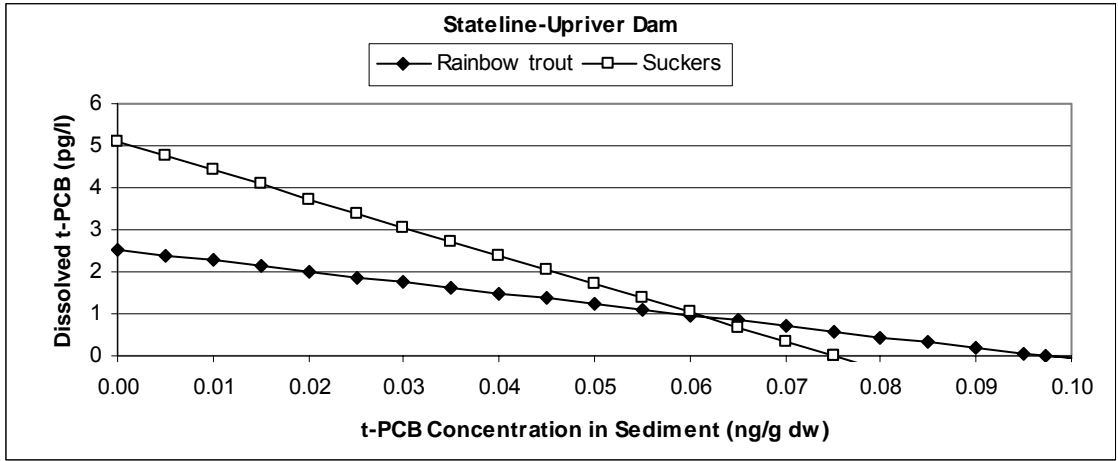


Figure 20. Dissolved Water and Sediment t-PCB Concentrations Predicted to Yield 0.1 ng/g in Rainbow Trout and Sucker Fillet.



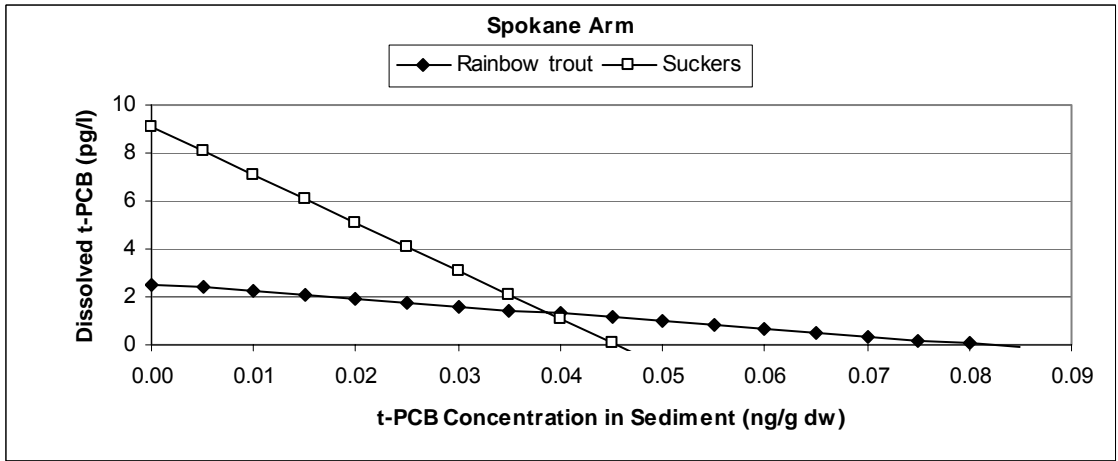
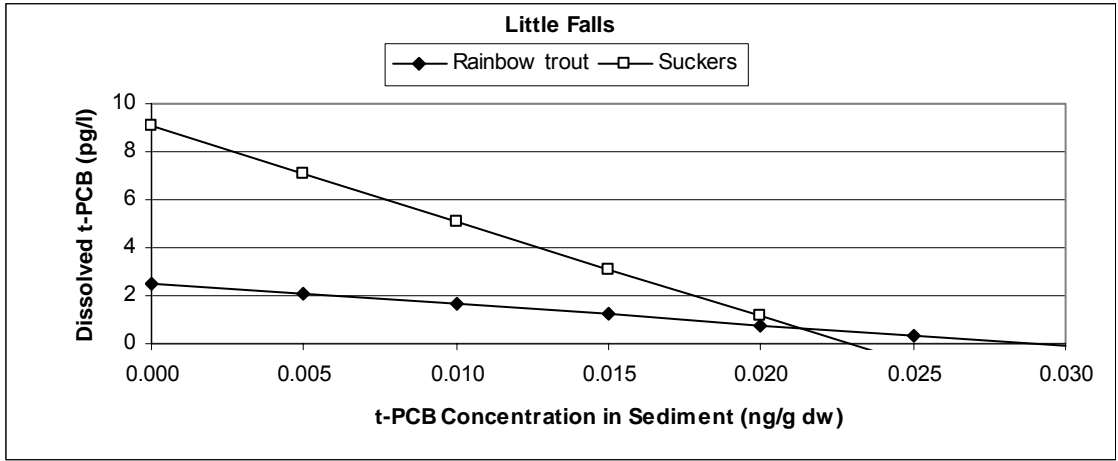


Figure 20 (cont'd). Dissolved Water and Sediment t-PCB Concentrations Predicted to Yield 0.1 ng/g in Rainbow Trout and Sucker Fillet.

Selection of water concentration targets for PCBs is subjective because it depends on sediment PCB concentrations, and conversely, target levels of PCBs in sediments depend on water PCB concentrations. In essence, both water and sediment critical values for PCBs are “moving targets” at an established tissue concentration. This is further complicated by differences in the two fish species being considered at each reach. As a practical matter, the best approach to establish target values is to select water and sediment concentrations where lines for rainbow trout and suckers intersect on each of the water-sediment plots in Figure 20. By using the intersection of two disparate species, the resulting targets will likely be protective of other species that might be consumed. The target water and sediment values may then be computed by setting the equations for each line equal to one another ( $[m \times C_s + b]_{\text{Rainbow}} = [m \times C_s + b]_{\text{Sucker}}$ ) and solving first for sediment concentration ( $C_s$ ) and then for water concentrations ( $C_d = m \times C_s + b$ ). This approach effectively halves the number of target values required (Table 35).

Table 35. Target Sediment and Water t-PCB Concentrations Needed to Yield the Spokane Tribe Fish Tissue Criterion (0.1 ng/g) in the Spokane River Based on the Arnot-Gobas Food-Web Bioaccumulation Model.

Reach	Target Tissue t-PCB conc. (ng/g)	Target Sediment t-PCB conc. (ng/g dw)	Target Dissolved water t-PCB conc. (pg/l)	Dissolved PCB fraction	Target Whole water t-PCB conc. (pg/l)	Target t-PCB Load (mg/d)
Stateline-Upriver Dam	0.1	0.06	0.9	0.90	1.0	4.5
Monroe-Ninemile	0.1	0.06	0.6	0.88	0.7	4.9
Long Lake	0.1	0.05	1.7	0.83	2.0	18.7
Little Falls	0.1	0.02	0.7	0.83	0.8	7.7
Spokane Arm	0.1	0.04	1.3	0.83	1.6	14.3

## PCB Load Allocations and Load Reductions Using Model-Derived Targets for Water and Sediment Concentrations

Table 36 shows PCB load allocations and required load reductions using water and sediment targets calculated using the food-web bioaccumulation model. PCB targets in water are two to five times lower than targets established using the Spokane Tribe water criterion.

Table 36. PCB Load Allocations and Load Reductions Required to Meet Spokane Tribe Fish Tissue Criterion (0.1 ng/g) in the Spokane River Based on the Arnot-Gobas Food-Web Bioaccumulation Model.

Reach/Source	Current t-PCB conc. (pg/l)	Target t-PCB conc. (pg/l)	Conc. Reduct. (pg/l)	Current t-PCB load (mg/d)	Target t-PCB load (mg/d)	Load Reduct. (mg/d)	Change	Necess. Reduct. in Sed. t-PCB conc.
<b>Stateline- Upriver Dam (RM 96.1-80.2)</b>	--	1.00	--	--	4.55	--	--	99.89%
@ Idaho Border	106	0.99	105	477	4.47	472.3	99.1%	--
Liberty Lake WWTP	1,121	0.99	1,120	2.9	0.00	2.9	99.91%	--
Kaiser	1,080	0.99	1,079	65	0.06	64.9	99.91%	--
Inland Empire	2,544	0.99	2,543	45	0.02	45.0	99.96%	--
<b>Monroe St.- Ninemile (RM 80.2-58.1)</b>								
Load from Upriver Dam	--		--	--	4.55	--	--	--
Spokane Stormwater	42,700	2.32	42,698	1,088	0.06	1,088.4	99.99%	--
Spokane WWTP	1,364	2.32	1,361	194	0.33	194.2	99.8%	--
<b>Long Lake (RM 58.1-33.9)</b>								
Load from Ninemile	--	--	--	--	4.94	--	--	--
Little Spokane River	199	2.04	197	97	0.99	95.6	99.0%	--
				Reserve=	12.81			
<b>Little Falls (RM 33.9-29.3)</b>								
Load from Long Lake	--	--	--	--	5.93	--	--	--
				Reserve=	1.79			
<b>Spokane Arm (RM 29.3-0)</b>								
Load from Little Falls	--	--	--	--	5.93	--	--	--
				Reserve=	8.41			

All discharges require PCB load reductions of  $\geq 99\%$  in order to meet target loads. The load reduction scenario in Table 36 yields reserve PCB capacity at Long Lake, Little Falls, and Spokane Arm. However, since target PCB concentrations in water are independent for each reach, the excess cannot be used to loosen load reduction requirements in upstream reaches.

In addition to substantial PCB reductions in water, large ( $\geq 99\%$ ) concurrent reductions in sediment PCB concentrations will also be required to meet the tissue target of 0.1 ng/g. There is currently little quantifiable data to predict how reductions in sediment PCB concentrations may occur. Intensive monitoring of sediment transport would be required to accurately project future concentrations and to set load allocations for sediment sources. However, enough information is available to assemble general conclusions regarding the dynamics of PCBs in Spokane River sediments.

Consideration needs to be given to the distribution and size of Spokane River sediments, described previously as a predominance of  $\geq$  gravel-sized particles in nearly the entire river upstream of Long Lake, with the exception of the Upriver Dam clean-up site. Due to the lack of fines, PCB concentrations in these sediments are generally very low.

Generally speaking, ongoing point sources of PCBs in the Stateline-Upriver Dam reach are not likely to be bound to settling particulate matter due to the extensive treatment of wastewater and resulting low levels of TSS in final effluent. One possible exception is the Liberty Lake WWTP which had comparatively high TSS during 2003-2004 monitoring (mean TSS = 27 mg/l vs. <10 mg/l at other facilities), but overall low discharged loads of PCBs. Historically, PCBs in this reach have been bound to settling matter, leading to the contaminated area behind Upriver Dam. In addition, Kaiser was found to have accidentally discharged a very large quantity of PCBs in late 2002 (approx 53 kg t-PCB; Merrill and Bala, 2004), apparently particle-bound but the fate of which has not been determined.

Historical discharges aside, sediments in the Stateline-Upriver Dam reach do not appear to be continuing to receive PCB enrichment. The Monroe-Ninemile reach has a similar gravelly sediment substrate, but differs in that downstream of Monroe St. it receives large quantities of relatively clean sediments from Latah Creek which are mostly sand and are ultimately deposited in the upper pool of Long Lake. The Monroe-Ninemile reach also receives potentially large doses of PCB-enriched sediments in the form of stormwater discharges from the City of Spokane. This conclusion is based on TSS concentrations in stormwater samples, which were higher than those in industrial/municipal effluents, as well as the high PCB concentrations in stormwater. Stormwater discharges also have the potential to carry a higher proportion of settling particulate matter than effluents due to the lack of high-capacity settling basins in the conveyance systems.

The fate of settling stormwater particles is unknown. Evidence from the grain-size distribution of bottom sediments suggests that heavier (i.e., sand-size) stormwater particles are deposited in the upper Long Lake Pool while smaller particles settle in middle or lower Long Lake. The record of PCB concentrations in Long Lake sediments suggests that, in the past two decades, concentrations in upper Long Lake decrease by half about every ten years, due in part to dilution from Latah Creek sediments. In lower Long Lake, where sediments are finer, PCB concentrations take approximately 20 years to decrease by half. The load allocations proposed for point sources and stormwater should result in major reductions in sediment PCB concentrations, particularly in Long Lake.

## Seasonal Variation and Margin of Safety

Seasonal differences in PCB concentrations in the Spokane River have been addressed through sampling over a range of flows and seasons. The use of SPMDs and suspended particulate matter assured data were not unrepresentative due to short-term fluctuations in water column PCB concentrations.

Human health criteria for PCBs are driven by long-term exposures to fish tissue. Acute toxicity is not considered to be a concern at PCB concentrations in the Spokane River basin. Since accumulation of PCBs by fish is a time-integrative process, and effects are based on long-term exposures, seasonal variations in loads are not an important factor in determining load allocations.

Use of the Spokane Tribe water criterion for PCBs (3.37 pg/l) is an extremely stringent standard, more than 50 times lower than the customarily used NTR criterion of 170 pg/l. In addition, a 10% margin of safety was applied.

An additional large margin of safety has been built into the TMDL through the use of harmonic mean flows to calculate loads.

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# Conclusions

This project constitutes a total maximum daily load (TMDL) assessment of PCBs in the Spokane River. The primary goal of the Spokane River TMDL and implementation strategy is to meet the Spokane Tribe water criterion of 3.37 pg/l t-PCB at the Spokane Indian Reservation boundary (RM 32.5).

Results of sampling during 2003 and 2004 indicate that average PCB concentrations in water increase with successive reaches from the Idaho border (106 pg/l) to lower Long Lake (399 pg/l), with a corresponding eight-fold increase in loads (477 – 3,664 mg/d). PCB loads delivered through industrial and sewage treatment plant effluents account for approximately 20% of instream loads. Stormwater from Spokane has the potential to deliver large PCB loads to the river (1,100 mg/d) and may account for a significant portion of loading from exogenous sources. However, stormwater sampling was limited and since data had not been previously collected from this source in the Spokane River basin, the representativeness of those data is uncertain

Current PCB concentrations in fish tissue appear to be lower than they have been historically. This may be due in part to significant reductions in point source PCB contributions during the past decade. However, a food-web bioaccumulation model used to predict PCB concentrations in fish tissue from levels in water and sediments indicates that significant reductions in sediment PCB concentrations would be required to reduce tissue to target concentrations.

Analysis of sediment cores suggest PCB concentrations at the sediment surface will decrease by half approximately every ten years in upper Long Lake, although patterns of material depositional upstream of Long Lake require further evaluation. In lower Long Lake, the ultimate sink for very fine sediments, PCBs have decreased by half during the past two decades after steep declines during the 1960s to mid-1980s.

A load allocation scenario was developed to achieve the necessary reductions in water PCB concentrations to meet the target criterion (3.37 pg/l). The scenario requires a 95% PCB load reduction in the Spokane River at the Idaho Border. Industrial and municipal discharges between the Idaho border and Long Lake require PCB load reductions greater than 99%, and stormwater from the city of Spokane requires the largest PCB load reductions (99.99%). A 97% PCB load reduction is required in the Little Spokane River.

A food-web bioaccumulation model was used to develop alternative TMDL goals. The model finds target PCB concentrations in water and sediment after a target PCB concentration in tissue has been established, in this case the Spokane Tribe PCB tissue criterion of 0.1 ng/g. Based on model-derived targets, a load allocation scenario showed that all discharges require PCB load reductions of  $\geq 99\%$  in order to meet target loads. However, reserve capacity for PCB loads would occur at Long Lake, Little Falls, and Spokane Arm under the same scenario.

Based on the food-web bioaccumulation model, PCB reductions of  $\geq 99\%$  sediments will also be required in order to meet the tissue target of 0.1 ng/g. No allocation or PCB reduction scenario was developed for sediments. However, the load reduction proposal should significantly reduce

loads of PCB-contaminated sediments to the Spokane River, particularly in Long Lake where endogenous PCB loads from sediments may remain a significant source to the water column.

The food-web bioaccumulation model is a useful tool to back-calculate water and sediment concentrations that will result in a target tissue PCB concentration.



## Recommended Load Allocations

The following PCB load allocations are recommended for adoption:

Table 37. Recommended PCB Load Allocations for the Spokane River TMDL.

Source	Load Allocation and [Wasteload allocations] (mg/d)
Spokane River @ Idaho Border	23.96
Liberty Lake WWTP	[0.01]
Kaiser	[0.32]
Inland Empire	[0.09]
Spokane Stormwater	0.13
Spokane WWTP	[0.76]
Little Spokane River	2.58

## Recommended Model Refinements

Extensive work to characterize PCBs in the Spokane River has been conducted during the past decade. As a result, little benefit would be derived from conventional sampling without consideration for how data may be used to either reduce PCB concentrations in fish tissue or to understand how and where reductions may occur. We therefore recommend further exploration and refinement of the Arnot-Gobas food-web bioaccumulation model to predict conditions necessary to reach target outcomes. Specifically, the model should be examined to determine if modifications to the organism component (both benthic and fish) of the model would yield more accurate outcomes. The model should also be examined to identify input parameters that may be better represented with additional data from the field or from literature reviews. Fish diet is a particular area where data refinement is needed.

Model input parameters in need of improvement or updating should be collected from the field where possible. Output parameters (i.e., fish tissue) should also be analyzed concurrently to assess the model's accuracy. This appears to be particularly important considering the apparent rapid change in tissue PCB concentrations.

# Implementation Strategy

## Introduction

The Washington State Department of Ecology conducted this Total Maximum Daily Load (TMDL) assessment for PCBs in the Spokane River, Washington in response to elevated PCBs in fish from multiple river segments. Sampling conducted during 2003-2004 included analysis of PCBs in river water, industrial and municipal effluents, stormwater, suspended particulate matter, bottom sediments, sediment cores, and fish tissue. The study area covered the Spokane River from the Idaho border (RM 96.1) to the mouth at the Columbia River, and the Little Spokane River.

A PCB loading scenario is proposed based on meeting the Spokane Tribe water criterion for PCBs (3.37 pg/l). The scenario requires a 95% PCB load reduction at the Idaho border, a 97% load reduction in the Little Spokane River, and  $\geq 99\%$  reductions in municipal, industrial, and stormwater discharges.

This Preliminary Implementation Strategy is intended to describe the framework for reducing PCBs discharged to the Spokane River and for ultimately meeting the Spokane Tribe water quality criterion. The anticipated roles and authorities of cleanup partners (i.e., those organizations with jurisdiction, authority, or direct responsibility for cleanup) are addressed. Necessary actions by the cleanup partners are also covered.

Once this Water Quality Improvement Report is approved by the U.S. Environmental Protection Agency (EPA), a *Water Quality Implementation Plan* will be developed. Ecology and interested and responsible parties (stakeholders) will work together to write this plan. This Preliminary Implementation Strategy is intended to provide the starting point for developing the *Water Quality Implementation Plan*. The Plan will describe and prioritize specific actions planned to improve water quality and achieve water quality standards.

## Who Needs to Participate?

Point source dischargers identified in the technical study, interested individuals and groups, and Local, State, and Federal agencies with jurisdiction are all expected to be involved with, or working toward, reducing PCBs discharged to the Spokane River. The following gives a brief description of the agencies that will be involved with the implementation of this TMDL.

### Environmental Protection Agency (EPA)

Multiple EPA programs may be involved with this TMDL. EPA is ultimately responsible for seeing that the federal Clean Water Act is implemented, and water quality criteria are met. EPA must approve the Water Quality Improvement Report and provides water quality-related funding. EPA is also responsible for issuing NPDES permits in the State of Idaho.

EPA also promulgates regulations for the proper handling, storage, and disposal of PCB contaminated material (40 CFR Part 761).

## Spokane Tribe of Indians

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The Spokane Tribe of Indians has authority to develop water quality criteria under the Clean Water Act for waters within their boundaries. For the Spokane River, Tribal criteria apply to the northern half of the river defined by a line bisecting the channel from RM 32.5 to RM 0.

## State of Idaho

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The State of Idaho has been delegated certain responsibilities under the federal Clean Water Act by the U.S. Environmental Protection Agency. The State of Idaho establishes water quality standards and coordinates water quality improvement projects (TMDLs) on waterbodies that fail to meet water quality standards.

## Washington Department of Ecology (Ecology)

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Multiple programs within Ecology are expected to be working on PCBs in the Spokane River. The State of Washington has been delegated responsibility under the federal Clean Water Act by EPA. Ecology's Water Quality Program (WQP) establishes water quality standards, issues NPDES permits, coordinates water quality improvement projects (TMDLs) on waterbodies that fail to meet water quality standards, and enforces water quality regulations under the Water Pollution Control Act, Chapter 90.48 RCW. The Water Quality Program also provides financial assistance to local governments, tribes, and citizens groups for water quality projects.

Ecology's Toxic Cleanup Program (TCP) works to address the legacy of contaminated sites resulting from past practices and on newly created and discovered soil, sediment, or groundwater contamination problems. Suspected contaminated sites undergo an initial investigation. Based on the extent and degree of contamination, a liable party may be assigned and remedial actions taken. Sites that are determined to pose a risk to human health and the environment are prioritized for cleanup actions.

## Washington Department of Health (DOH)

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Within DOH's Division of Environmental Health, the Office of Environmental Health Assessments provides technical assistance and consultation and conducts human health assessments and health education activities related to statewide and site specific releases of toxic substances. Actions may include health education—communicating protective measures to impacted residents—thus preventing illnesses associated with exposure to toxic substances being released into their environment.

The Office of Environmental Health is responsible for issuing fish consumption advisories for the Spokane River.

## Spokane Regional Health District

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The Spokane Regional Health District provides educational programs, services and printed materials about Spokane River fish consumption advisories to schools, community groups, businesses and the public.

## City of Spokane

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The City of Spokane's Wastewater Management Department provides customer services relating to wastewater collection systems, wastewater treatment, stormwater management, and combined sewer overflow reduction. The Wastewater Management Department also administers regulations for industrial users discharging wastewater to the City of Spokane sewerage system (pretreatment program). Activities include administration of waste discharge permits, inspections, enforcement, sample collection to determine compliance, and collection of surcharge and monitoring fees.

## What Needs to be Done?

In order to reduce PCBs discharged to the Spokane River and to meet the Spokane Tribe water quality criterion, reductions in multiple sources of PCBs entering the Spokane River are needed. The preliminary implementation strategy is a conceptual look on how this can be accomplished. The approach will be further refined in the *Water Quality Implementation Plan*.

The conceptual approach at reducing PCBs discharged to the Spokane River is focused on 1) PCB source identification and reduction/elimination; 2) further PCB effluent, stormwater, and groundwater characterization; 3) examination of treatment alternatives for effluent PCB removal; and 4) implementation of necessary treatment plant controls. Each item is addressed in more detail below.

Additional activities are also recommended to address current sources of PCB that may enter the environment (i.e., from printing inks and other possible sources) and to track PCB trends in water, sediment, and fish tissue. These actions are discussed in the 'What's Next' and 'Monitoring' Sections that follow.

## PCB Source Identification and Reduction/Elimination

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Based on the proposed loading scenario in this report, the largest current contributor of PCBs to the River is from the City of Spokane CSO/stormwater system (about 55% of the current loading). Reducing these levels can be accomplished by identifying potential PCB sources within the system; then reducing and/or eliminating these sources. More thorough sampling needs to be conducted as a first step in this process. Storm drainage basins where the highest PCB levels are found (either in stormwater/CSO discharges or accumulated storm drain sediments) should be prioritized for further control actions.

This type of stormwater PCB reduction/control is being implemented in other areas of the country, most notably in the San Francisco Bay area. The Santa Clara Valley Urban Runoff Pollution Prevention Program is an association of thirteen cities and towns in the Santa Clara Valley, together with Santa Clara County and the Santa Clara Valley Water District. Program participants share a common NPDES permit to discharge urban storm water to South San Francisco Bay.

The California Regional Water Quality Control Board (San Francisco Bay Region) completed a PCB TMDL for the San Francisco Bay in February, 2004 (California Regional Water Quality Control Board, 2004). Santa Clara Valley Urban Runoff Pollution Prevention Program's NPDES stormwater permit contains requirements to reduce PCBs to meet requirements of this TMDL. Valuable knowledge can be gained from the Santa Clara Program's efforts at stormwater PCB reduction/control efforts. Their approach is outlined in general below. More specific information, including detailed reports and case studies, can be found online at <http://www.scvurppp-w2k.com/pcbs.htm>.

Where high stormwater/sediment PCB concentrations have been identified, PCB source identification begins with determining how the PCBs have entered the storm drains and if ongoing sources exist (Santa Clara Valley Urban Runoff Pollution Prevention Program, 2002). The process for identifying PCB sources include mapping drainages and storm drains within these drainages; researching historical and current land uses within drainages; identifying any know PCB use, storage, and/or release for sites within the drainages; researching stormwater violations and storm drain line maintenance (e.g., flushing); and performing additional sampling and chemical analyses.

Stormwater control is then aimed at stopping PCBs from entering the stormwater system or removing PCB containing sediments in the stormwater conveyance system. Control activities may include cleanup, source control, and/or treatment. Cleanup consists of removal of PCB containing erodible soils; removal of sediments during routine maintenance of storm drain systems; and non-routine removal of sediments containing PCBs from stormwater conveyances.

Stormwater treatment has been examined using various technologies for suspended sediment removal (vortechs, treatment wetlands, swales, filters, and basins). Santa Clara Valley Urban Runoff Pollution Prevention Program has also considered diverting the first flush/wet weather stormwater flows to wastewater treatment plants.

A similar overall approach should be taken to reduce PCBs discharged to the Spokane River via storm sewers and CSOs. The *Water Quality Implementation Plan* will describe this process in more detail.

One limitation of sampling for PCB congeners at low levels (pg/L concentrations) is the high cost. For the source identification efforts, using either alternative congener methods or methods with a higher detection level (i.e., testing for aroclors) may be feasible, depending on the target concentrations and media. Based on the stormwater/CSO concentrations measured by this study, initial detection levels would have to be below about 10 ng/L (10,000 pg/L) for total PCBs. Another possibility for reducing cost would be to test for target congener homologues (i.e., those that have been detected in past stormwater/CSO samples), instead of for all 209 congeners.

A procedure for source control/identification within the sanitary sewer system will be similar to the stormwater/CSO discussed above. The only added consideration would be for commercial/industrial discharges to the municipal sewer system. Generally, those commercial and industrial dischargers which are either categorical or significant industrial users are required to have wastewater discharge permits, issued by the City of Spokane. Effluent testing would be necessary to determine if these industrial users were discharging PCBs into the sanitary sewer system. For those industrial users not required to be permitted, a survey needs to be completed to identify high priority industrial users. These high priority users would include facilities using printing inks, or any facility known or suspected of handling/using PCBs in the past. Effluent testing at these facilities would also be necessary to determine if there are active sources of PCBs to the sanitary sewer system. Ecology would work cooperatively with the City of Spokane's pretreatment staff in this source control/identification effort.

Source control investigation also needs to occur for both the Spokane River entering Washington at the Stateline and the Little Spokane River. The Spokane River at Stateline currently contributes about 25 percent of the PCB load to the system. A plan or strategy needs to be developed to reduce this load. This will be coordinated between the State of Idaho and EPA. As a first step, data needs to be gathered on the potential sources of PCBs (e.g., point sources, stormwater, contaminated and/or potential contaminated sites) in the Idaho portion of the Spokane River. To aid this data collection effort, EPA should include monitoring requirements for PCBs in NPDES permits issued in the State of Idaho that discharge to the Spokane River. Initially, test methods should be specified for measurement of PCBs to the parts per quadrillion level (pg/L). However, if high PCB concentrations are detected in these effluents, alternative methods with higher detection levels (i.e., source testing for aroclors) could be used.

For the Little Spokane River (which contributes about 5% of the PCB load to Lake Spokane), Ecology's Water Quality Program will be the lead for PCB source identification and reduction. A detailed study is necessary to further characterize the PCBs in the Little Spokane watershed. This study would address the contribution from any direct discharges to the Little Spokane River and potentially contaminated sites.

As mentioned earlier in this report, Spokane River sediments at Upriver Dam and Donkey Island are currently in the process of being remediated for PCB contamination under the Model Toxics Control Act (MTCA). At this time, no further River sediment investigations are expected to occur.

### Further PCB Effluent, Stormwater and Groundwater Characterization

Currently, Kaiser Aluminum and Chemical Corporation performs adequate effluent characterization for PCBs. Kaiser is required to sample their effluent for total PCBs once every two weeks. Sampling is done for congeners, generally achieving a 100 pg/L quantification level.

For other point sources, routine low level PCB monitoring and reporting is needed. Typically, Ecology requires effluent monitoring and testing as part of NPDES permit requirements. The current permits for these other facilities do not require routine PCB testing. Ecology plans to require PCB monitoring in these permits when they are renewed. Alternatively, Ecology can

issue Administrative Orders requiring the testing and monitoring of PCBs in effluents discharged to the Spokane River at any time.

PCB testing should be done using congener analysis (EPA method 1668A). This method provides quantification levels below 100 pg/L. This will be adequate, since the lowest effluent concentrations measured in this report were around 1,000 pg/L. In the future, analytical methods may have to improve to reliably measure PCB effluent concentrations down to the TMDL target levels (5.32 pg/L). The *Water Quality Implementation Plan* should evaluate the feasibility of using alternative technologies (e.g., semipermeable membrane devices - SPMD) to measure low PCB concentration in effluents.

For stormwater, Ecology has applied for, and received, grant money from EPA for further stormwater/CSO testing in the Spokane vicinity. As noted in the report, stormwater/CSO discharges were sampled on a limited basis. This grant will be used to further characterize stormwater/CSO discharges for PCBs and refine PCB loading estimates. Prior to this sampling, a Quality Assurance Project Plan (QAPP) will be circulated to interested parties for review and comment. This QAPP is expected to be available by the Fall of 2006 with sampling occurring in the Winter of 2006 and the Spring of 2007. However, routine monitoring is still needed for stormwater and CSO discharges both to characterize these discharges and to track the effectiveness of source identification and reduction efforts.

There are two PCB industrial cleanup sites along the Spokane River under the leadership of Ecology's Toxic Cleanup Program (General Electric Spokane and Kaiser Aluminum Trentwood sites). Groundwater present at both these sites ultimately contribute recharge to the Spokane River. Cleanup activities have been completed at General Electric, and are ongoing at Kaiser Aluminum. Further data review and/or groundwater characterizations are underway at Trentwood to assure PCBs from this site is not entering the Spokane River. The lead for these determinations will be Ecology's Toxics Cleanup Program

## Examination of Treatment Alternatives for Effluent PCB Removal

The NPDES point source dischargers are also currently participating in the Spokane River phosphorus/dissolved oxygen (DO) TMDL. As part of the phosphorus/DO TMDL, reduction of effluent phosphorus is necessary. The phosphorus/DO Water Quality Implementation Plan includes evaluating phosphorus treatment technologies on a pilot plant scale. When conducting the pilot plant tests, sampling should also include PCBs (congeners with detection levels at the pg/L level). Both influent and effluent should also be sampled to determine PCB removal through the systems.

Additionally, a thorough evaluation needs to be completed to see what treatment or best management practices (BMPs) are available for PCB removal in industrial, municipal and stormwater effluents. Ecology and EPA will work together to survey treatment technologies and best practices available for PCB removal to parts per quadrillion levels (pg/L). This survey will be either a part of, or an action item in, the *Water Quality Implementation Plan*.



## Implementation of Necessary Treatment for PCB Removal

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The evaluation of best management practices and end of pipe treatment for PCB removal will be ongoing during the PCB source control/identification and reduction/elimination efforts. Implementation of best management practices and/or treatment for PCB removal would be evaluated on a continuing basis. A process for selecting and implementing PCB best management practices and/or treatment will be outlined in the *Water Quality Implementation Plan*.

## What is the Schedule for Achieving Water Quality Standards?

The schedule for achieving water quality standards will be developed as part of the *Water Quality Implementation Plan*. Interim goals and milestones will be used to track the progress of WLA and LA implementation. It may be difficult to predict how long until the Spokane Tribal water quality criterion for PCBs are met. Nonetheless, this plan will start the process of reducing PCBs in the Spokane River system.

## Reasonable Assurances

When establishing a TMDL, reductions of a particular pollutant are allocated among the pollutant sources (point and nonpoint sources) in the waterbody – for PCBs in the Spokane River, both point sources, stormwater, and nonpoint sources exist. TMDLs (and related Action Plans) must show “reasonable assurance” that these sources will be reduced to their allocated amount. Education, outreach, technical and financial assistance, permit administration, and enforcement may all be used to ensure that the goals of this water clean up plan are met.

When developed, a goal of the Spokane River *Water Quality Implementation Plan* for PCBs will be to meet the downstream Spokane Tribe’s water quality standards. There is considerable interest and local involvement toward resolving the water quality problems in the Spokane River. Ecology expects that numerous organizations and agencies will be engaged in source correction actions that will help resolve the PCB problem. Rationale will be provided in the *Water Quality Implementation Plan* that provides reasonable assurance that the WLAs and LAs will be met by a specified target date.

The Clean Water Act requires some assurances that TMDL implementation measures will actually occur. To provide this assurance, the *Water Quality Implementation Plan* will specify actions, timelines, and funding to accomplish the stated goals.

## Adaptive Management

TMDL reductions for PCBs in the environment and reductions in point source discharges may be difficult to predict. As action items are developed, a better idea of the effectiveness of reductions will be developed. The *Water Quality Implementation Plan* will identify interim targets. These targets will be described in terms of concentrations and/or loads, as well as in terms of

implemented cleanup actions. Partners will work together to monitor progress towards these goals, evaluate successes, obstacles, and changing needs, and make adjustments to the cleanup strategy as needed.

Ultimately, Ecology will be responsible to assure that cleanup is being actively pursued and water standards are achieved.

## Summary of Public Involvement Methods

Public Involvement will include an Ecology sponsored open house which will provide an overview of the technical study and findings. A public notice will be given at least thirty days in advance of the open house. Ecology will accept comments on the technical study.

A technical advisory group will be formed to help develop the *Water Quality Implementation Plan*. This committee will be formed from members of State and Local governments, interested parties and other stakeholders. As the *Water Quality Implementation Plan* is developed and finalized, further public involvement will be necessary. This may include public notices, hearings, and/or open houses. Public notice will be thirty days in advance of any hearing and/or open house date.

## Potential Funding Sources

Potential funding sources:

- *Centennial/State Revolving Fund (SRF)/319* - These three funding sources are managed by Ecology through one combined application program. Funds are available to public entities as grants or low-interest loans. Grants require a 25% match. They may be used to provide education/outreach, technical assistance for specific water quality projects, or as seed money to establish various kinds of water quality related programs or program components. Grant funds may not be used for capital improvements to private property. Low-interest loans are available to public entities for all of the above uses.

## Next Steps

As described earlier, Ecology will consider comments on the Water Quality Improvement Report. After all comments are received, Ecology will revise the report, as determined appropriate. The Water Quality Improvement Report will then be submitted to EPA for their review and approval. Once the TMDL technical report has been approved by EPA, a *Water Quality Implementation Plan* must be developed within one year. As described above, a technical advisory group will be formed right away to help develop the *Water Quality Implementation Plan*. Ecology will work with local people to create this plan, choosing the combination of possible solutions they think will be most effective in the watershed. Elements of this plan include: who will commit to do what, how will we figure out whether it worked, what if it doesn't work, and potential funding sources.

Ecology, to the extent possible, will coordinate the implementation of both the PCB and phosphorus/DO TMDLs. This coordination will ensure that there is no duplication of efforts when collecting data, identifying targets, completing action items, and implementing treatment plant controls and/or best management practices.

On a larger scale, there are still products used today that contain PCBs (certain printing inks, feeds used in fish rearing and harvesting). Federal regulations found in 40 CFR Part 761 establishes prohibitions of, and requirements for, the manufacture, processing, distribution in commerce, use, disposal, storage, and marking of PCBs. This rule is complex, but generally, products that contain less than 50 parts per million are excluded from regulation. This includes PCBs which are inadvertently produced in manufacture of another product. The 50 parts per million level is roughly 10,000,000,000 (ten billion) times higher than the target waste load allocations listed in this report.

The National PCB rule is inadequate to control trace PCBs that continue to enter the environment. The federal rule needs to be revised to further limit PCBs in products. In the interim (or in the event that the federal rule is not revised), thorough due diligence will be needed for the screening of industrial/commercial products that may contribute to the PCB problem in the Spokane River. Alternative PCB free products must be used, either voluntarily or by legal mandate. In addition, a complete listing of products on the market that contain PCBs, including research on how the PCBs got into the product in the first place, needs to be compiled.

Also, as described previously, total PCBs includes 209 individual congeners. Both State and Tribal water quality criteria are expressed as total PCBs (the sum of all 209 congeners). Therefore, this TMDL's WLAs and LAs are appropriately expressed as total PCBs. However, there are discussions suggesting that not all of the 209 congeners are toxic to human health and the environment. The State uses the EPA promulgated human health criteria for toxic pollutants in the National Toxics Rule. Similarly, the Tribe has calculated their criterion based on procedures taken from the National Toxics Rule. Any revision to the PCB human health based criteria may have to occur through EPA at the national level.

## Monitoring plan

Monitoring will be an integral part of the TMDL process. As previously described, this preliminary implementation strategy recommends that all point sources, including stormwater, routinely monitor and report the total PCB levels in their discharges (for both Washington and Idaho dischargers). This monitoring will be used to provide feedback for adaptive management of PCB source identification and reduction/elimination measures.

Ecology will be responsible for river water, sediment and fish tissue PCB monitoring. The results of this monitoring will be used to track trends in PCB concentrations over time. A Quality Assurance Project Plan (QAPP) will be developed prior to this monitoring. This QAPP will be circulated to interested parties for review and comment.

The *Water Quality Implementation Plan* will further describe the coordinated monitoring strategy.

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# Appendices

## Appendix A - Spokane River Basin NPDES Permits

Table A-1. Spokane River Basin NPDES Permits.

Facility Name	Permit Type	Permit Number	Expiration Date	WRIA
<i>Industrial Facilities</i>				
Newman Lk Flood Control Zone Dist	Minor	WA0045438A	10-Jun-99	57
B F Goodrich	POTW	ST0008068A	8-Feb-04	57
Columbia Lighting Inc	POTW	ST0005222B	19-Feb-00	57
Group Photo	POTW	ST0005378A	12-Oct-98	57
Johnson Matthey Electronic	POTW	ST0005350B	4-Sep-03	57
Novation Inc	POTW	ST0005355B	1-Jan-01	57
Inland Empire Paper Co	Major	WA0000825B	30-Jun-02	57
Kaiser Trentwood	Major	WA0000892B	30-Jun-02	57
Dawn Mining Company	State	ST0005230C	30-Jun-02	54
Avista Corp Headquarters	Minor	WA0045195B	31-Jul-02	57
Johnson Matthey Cheney	POTW	ST0008055A	18-Apr-03	56
Key Tronic Corp (Spokane)	POTW	ST0005284B	7-Nov-01	57
Olympic Foods	POTW	ST0008051A	30-Jun-02	57
Spokane Co Util.(Mica Landfill)	POTW	ST0005356B	6-May-01	56
Wilcox Farms Inc.(Milk Plant)	POTW	ST0005399A	22-Jun-02	56
<i>Municipal Facilities</i>				
Badger Lake Estates	State	ST0008057B	1-Jun-02	56
Clayton Sewer District	State	ST0005392A	5-Nov-01	55
Freeman School District #358	Minor	WA0045403A	1-Nov-99	56
Liberty School District #362	State	ST0005397A	11-Sep-01	56
Mullen Hill Terrace Properties	State	ST0008041A	20-Oct-01	57
Snowblaze Condominiums	State	ST0008039A	25-Aug-01	57
Spokane Co Util. (Hangman Hills)	State	ST0008045A	29-Jun-02	56
Upper Columbia Academy	State	ST0008034A	20-Oct-01	56
Deer Park WWTP	State	ST0008016B	30-Jun-02	55
Diamond Lake WWTP	State	ST0008029C	30-Jun-02	55
Medical Lake RWTP	Minor	WA0021148A	30-Jun-82	54
Liberty Lake Sewer Dist #1	Minor	WA0045144B	30-Jun-02	57
Spokane AWWTP	Major	WA0024473A	30-Apr-97	54
Cheney WWTP	Minor	WA0020842B	30-Jun-00	56
Tekoa WWTP	Minor	WA0023141B	27-Jun-99	56
Fairfield Town of WWTP	Minor	WA0045489B	30-Jun-02	56
Rockford Town of WWTP	Minor	WA0044831B	21-Jan-00	56
Spangle Town of WWTP	Minor	WA0045471A	30-Jun-02	56

WRIA – Water Resource Inventory Area

POTW – Publicly-Owned Treatment Works

WWTP – Wastewater Treatment Plant

## **Appendix B – Sampling Locations for Spokane River PCB TMDL Study**

Table B-1. Sampling Locations.

Station ID <sup>1</sup>	Sampling Dates	Sample Type	Location Description	RM	Latitude North		Longitude West				
Stateline"	10/1-29/2003	SPMD	Just downstream of the I-90 bridge at Idaho stateline	96.1	47°	41'	52 "	117°	2'	29 "	
	1/28-2/24/2004			"	"	"	"	"	"	"	"
	4/14-5/12/2004			"	"	"	"	"	"	"	"
STATELINE-F	7/14/2004	Fish	Idaho stateline boundary to first downstream riffle (coordinates at midpoint)	96.0	47°	41'	54 "	117°	2'	33 "	
Harvard	10/20-22/2003	SPM/Water	Near right bank below Harvard Road Bridge	92.8	47°	41'	2 "	117°	6'	34 "	
LIBLAKE	10/21/2003	Effluent	Liberty Lake Wastewater Treatment Plant effluent*	92.3	47°	40'	40 "	117°	6'	44 "	
KaiserEff	10/21-22/2003	Effluent	Kaiser effluent before discharge to river	86.0	47°	41'	5 "	117°	13'	16 "	
	2/2-3/2004			"	"	"	"	"	"	"	
	4/26-27/2004			"	"	"	"	"	"	"	
KaiserFilt	10/21/2003	Effluent	Kaiser at Filter Outlet	86.0	47°	41'	6 "	117°	13'	17 "	
	2/2/2004			"	"	"	"	"	"	"	
	4/26/2004			"	"	"	"	"	"	"	
KaiserLag	10/21/2003	Effluent	Kaiser Lagoon	86.0	47°	41'	6 "	117°	13'	16 "	
	2/2/2004			"	"	"	"	"	"	"	
	4/26/2004			"	"	"	"	"	"	"	
PLANTE-F	9/15/2003	Fish	1/8 mi. upstream of RR bridge to riffle at lava boulders below park (coordinates at midpoint)	85.0	47°	41'	41 "	117°	14'	18 "	
PLANTEFRY	10/28-30/2003	SPM/Water	Off right bank at Plante Ferry Park	84.8	47°	41'	52 "	117°	14'	41 "	
Inland Emp	10/21/2003	Effluent	Inland Empire effluent*	82.6	47°	41'	13 "	117°	17'	2.8 "	
	2/2-3/2004			"	"	"	"	"	"	"	
	4/26/2004			"	"	"	"	"	"	"	
Upriver Dam	10/1-29/2003	SPMD	1/8 mi. upstream of Upriver Dam, off right bank	80.3	47°	41'	13 "	117°	19'	29 "	
	1/28-2/25/2004	SPMD		"	"	"	"	"	"	"	
	4/14-5/12/2004	SPMD		"	"	"	"	"	"	"	
	5/13/2004	Crayfish		"	"	"	"	"	"	"	

Table B-1 (Cont'd). Sampling Locations.

Station ID <sup>1</sup>	Sampling Dates	Sample Type	Location Description	RM	Latitude North					Longitude West				
UPRIVER BOT	10/1-29/2003	SPMD	Above Upriver Dam, off right bank, 2 feet from bottom of riverbed	80.3	47°	41'	13	"	"	117°	19	'	29	"
	1/28-2/25/2004			"	"	"	"	"	"	"	"	"	"	"
	4/14-5/12/2004			"	"	"	"	"	"	"	"	"	"	"
STMMISSBR	6/10/2004	Stormwater	Stormwater pipe near intersection of Mission and Perry on right bank	76.5	47°	40'	20	"	"	117°	23	'	20	"
STMSUPOUT	6/10/2004	Stormwater	Stormwater pipe at Superior Street near Cataldo on right bank	75.7	47°	39'	36	"	"	117°	23	'	32	"
CS034	6/10/2004	CSO	Combined sewer overflow outfall at Erie Street	75.8	47°	39'	41	"	"	117°	23	'	30	"
MonroeSed	4/14/2004	Sediment	Approximately 60 feet off left bank at first bend upstream of Monroe Street Dam	74.9	47°	39'	52	"	"	117°	24	'	22	"
Monroe St	10/2-29/2003	SPMD	Upstream of Monroe Street Dam	74.8	47°	39'	48	"	"	117°	24	'	31	"
	1/28-2/25/2004			"	"	"	"	"	"	"	"	"	"	
	4/14-5/12/2004			"	"	"	"	"	"	"	"	"	"	
STMWASHBR	6/10/2004	Stormwater	Stormwater pipe at west side of Washington Street Bridge on right bank	74.3	47°	39'	51	"	"	117°	25	'	0.8	"
SPOKWWTP	10/21/2003	Effluent	Spokane Wastewater Treatment Plant effluent*	67.4	47°	41'	51	"	"	117°	28	'	32	"
	2/2/2004			"	"	"	"	"	"	"	"	"	"	
	4/26/2004			"	"	"	"	"	"	"	"	"	"	
Ninemile1	10/1-29/2003	SPMD	Ninemile reservoir above Plese Flats boat launch	63.6	47°	43'	15	"	"	117°	30	'	29	"
	1/28-2/24/2004			"	"	"	"	"	"	"	"	"	"	
NINEM SPM	11/3-5/2003	SPM/Water	Off of right bank at Plese Flats, Riverside State Park	63.2	47°	43'	35	"	"	117°	30	'	43	"
Ninemile2	4/14-5/12/2004	SPMD	Ninemile Pool, downstream of boat launch at Plese Flats	62.4	47°	44'	9	"	"	117°	30	'	40	"
NINEMILE-F	9/16/2003	Fish Gut Contents	Nine Mile Reservoir near Seven Mile Bridge	61.7	47°	44'	35	"	"	117°	31	'	14	"
	7/13/2004	Fish		"	"	"	"	"	"	"	"	"	"	
Spokane-F	9/16/2003	Fish	"	"	"	"	"	"	"	"	"	"	"	
LongLkUp	5/11/2004	Sediment	Upper Long Lake (Lake Spokane)	54.3	47°	47'	38	"	"	117°	34	'	11	"



Table B-1 (Cont'd). Sampling Locations.

Station ID <sup>1</sup>	Sampling Dates	Sample Type	Location Description	RM	Latitude North	Longitude West
LONGUP2	6/9/2004	Sed. Core	Upper Long Lake (Lake Spokane)	49.2	47° 50' 6 "	117° 39 ' 3 "
LongLkMid	11/4/2003	Sediment	Middle Long Lake (Lake Spokane)	44.3	47° 53' 10 "	117° 41 ' 28 "
Tum Tum	1/29-2/24/2004	SPMD	Long Lake right bank near Tum Tum	44.2	47° 53' 10 "	117° 41 ' 38 "
Littlefls	11/4/2003	Sediment	Spokane River at pool above Little Falls Dam	29.9	47° 50' 10 "	117° 54 ' 38 "
LONGLOW-F	7/13-14/2004	Fish	Lower Long Lake (Lake Spokane) off left bank approx. 1 mi. upstream of DNR launch	39.4	47° 49' 40 "	117° 44 ' 39 "
LongLkLow	10/2-11/4/2003	SPMD	Lower Long Lake (Lake Spokane)	38.4	47° 49' 44 "	117° 46 ' 8.2 "
	4/13-5/11/2004	SPMD		"	" " " " "	" " " " "
	11/4/2003	Sediment		"	" " " " "	" " " " "
LONGLOW2	11/4/2003	Sed. Core	Lower Long Lake (Lake Spokane)	36.0	47° 48' 56 "	117° 48 ' 25 "
SPOK-1	11/6/2003	Sediment	Porcupine Bay - NE of boat launch (upstream)	12.6	47° 53' 3 "	118° 8 ' 59 "
LitlSpokSed	12/10/2003	Sediment	Little Spokane River approx. 1 mi. above SR291 bridge <sup>2</sup>	2.3	47° 46' 45 "	117° 31 ' 0.9 "
LitlSpokBr	1/29-2/24/2004	SPMD	Little Spokane River @ SR291 Bridge <sup>2</sup>	1.1	47° 46' 59 "	117° 31 ' 44 "
	4/14-5/12/2004	SPMD		"	" " " " "	" " " " "
LitlSpokR	10/2-30/2003	SPMD	Little Spokane R. left bend in river, adjacent to SR291 <sup>2</sup>	0.5	47° 47' 13 "	117° 31 ' 38 "
BUFFALO REF	11/5/2003	Sediment	Buffalo Lake near lake center east of boat launch		48° 3' 56 "	118° 53 ' 20 "

\*Location coordinates in North American Datum 1983 (NAD83)

<sup>1</sup> Site identification as used in Ecology's Environmental Information Management System (EIM)

<sup>2</sup> The mouth of Little Spokane River is at Spokane River mile 56.3

SPM - suspended particulate matter

SPMD - semipermeable membrane device

RM - river mile

## **Appendix C – Biological Data for Fish and Crayfish Specimens Used for PCB Analysis**

Table C-1. Biological Data for Plante Ferry Rainbow Trout Fillet Specimens.

Fillet Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Fillet Weight (g)	Sex	Age (yrs)	Comments on Sex
188308	PF6	9/15/2003	404	387	640	206	M	nd	
	PF8	9/15/2003	365	350	552	190	M	nd	
	PF11	9/15/2003	407	394	714	214	M	4	
	PF14	9/15/2003	359	342	454	206	Imm. M?	3	
	PF15	9/15/2003	323	308	363	126	M	3	
	PF16	9/15/2003	300	284	291	106	M	2	
	PF17	9/15/2003	380	364	582	212	M	3	
	PF18	9/15/2003	422	401	782	202	M	3	
	PF23	9/15/2003	345	328	452	126	Imm. M?	2	
	PF27	9/15/2003	321	301	332	136	Imm. M?	2	
	Mean=		363	346	516	172		3	
188309	PF4	9/15/2003	385	363	551	196	F	3	eggs visble
	PF5	9/15/2003	410	387	670	208	F	4	eggs visble
	PF13	9/15/2003	388	369	585	238	F	3	eggs visble
	PF19	9/15/2003	412	385	667	210	F	4	eggs visble
	PF20	9/15/2003	427	408	760	258	F	3	eggs visble
	PF21	9/15/2003	376	356	583	178	F	3	eggs visble
	PF22	9/15/2003	387	366	560	178	F	4	eggs visble
	PF24	9/15/2003	378	359	517	220	F	3	eggs visble
	PF25	9/15/2003	401	387	663	216	F	3	eggs visble
	PF26	9/15/2003	345	325	427	202	F	2	eggs visble
	Mean=		391	371	598	210		3	

Table C-2. Biological Data for Plante Ferry Rainbow Trout Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Gut Contents (g)*	Sex	Age (yrs)
188311	PF4	9/15/2003	385	363	551		F	3
	PF5	9/15/2003	410	387	670	7	F	4
	PF6	9/15/2003	404	387	640	1	M	nd
	PF8	9/15/2003	365	350	552	15	M	nd
	PF11	9/15/2003	407	394	714	1	M	4
	PF13	9/15/2003	388	369	585	9	F	3
	PF14	9/15/2003	359	342	454	5	Imm. M?	3
	PF15	9/15/2003	323	308	363	1	M	3
	PF16	9/15/2003	300	284	291	4	M	2
	PF17	9/15/2003	380	364	582	3	M	3
	PF18	9/15/2003	422	401	782	19	M	3
	PF19	9/15/2003	412	385	667	12	F	4
	PF20	9/15/2003	427	408	760	11	F	3
	PF21	9/15/2003	376	356	583	14	F	3
	PF22	9/15/2003	387	366	560	nm	F	4
	PF23	9/15/2003	345	328	452	1	Imm. M?	2
	PF24	9/15/2003	378	359	517	nm	F	3
	PF25	9/15/2003	401	387	663	empty	F	3
PF26	9/15/2003	345	325	427	nm	F	2	
PF27	9/15/2003	321	301	332	nm	Imm. M?	2	
	Mean=		373	355	546			3

\* total sample weight = 16 g

Table C-3. Biological Data for Ninemile Rainbow Trout Fillet Specimens.

Fillet Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Lipids (%)	Sex	Age (yrs)	Origin
084281	NM1	9/16/2003	334	321	413	1.5	M im?	1	hatchery
084282	NM2	9/16/2003	357	340	454	2.6	F	2	wild
084283	NM3	9/16/2003	320	307	306	1.3	M im?	1	hatchery
084284	NM4	9/16/2003	308	290	306	1.9	M	1	wild
084285	NM5	9/16/2003	350	332	471	1.1	F	3	wild
084286	NM6	9/16/2003	300	282	289	1.0	M im?	1	hatchery
084287	NM7	9/16/2003	290	272	290	0.4	M im?	1	hatchery
084288	NM8	9/16/2003	333	321	425	1.9	M	1	hatchery
084289	NM9	9/16/2003	377	365	483	0.7	F	3	wild
084290	NM10	9/16/2003	328	315	380	3.3	M	3	wild
084291	NM11	9/16/2003	333	316	376	2.5	F	3	wild
084292	NM12	9/16/2003	342	325	421	2.0	M im?	1	hatchery
084293	NM13	9/16/2003	296	281	266	1.8	M im?	1	wild
084294	NM14	9/16/2003	289	273	257	1.0	M	1	hatchery
084295	NM15	9/16/2003	283	273	268	0.6	M im?	1	hatchery
084296	NM16	9/16/2003	295	280	251	0.4	M im?	1	hatchery
084298	NM18	9/16/2003	296	285	320	0.9	M	1	hatchery
084299	NM19	9/16/2003	275	261	227	0.2	M im?	1	hatchery
084301	NM21	9/16/2003	297	282	255	1.5	M im?	1	wild
084302	NM22	9/16/2003	282	269	250	0.8	M im?	1	hatchery
084303	NM23	9/16/2003	362	352	503	0.9	F	2	wild
084304	NM24	9/16/2003	265	251	231	0.3	M im?	1	hatchery
084305	NM25	9/16/2003	286	270	244	0.5	M im?	1	hatchery
084306	NM26	9/16/2003	268	252	201	1.6	M	1	wild
		Mean=	311	296	329	1.3		1	

Table C-4. Biological Data for Ninemile Rainbow Trout Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Gut Contents (g)*	Sex	Age (yrs)
188310	NM3	9/16/2003	320	307	306	1	Imm. M?	1
	NM5	9/16/2003	350	332	471	2	F	3
	NM6	9/16/2003	300	282	289	4	Imm. M?	1
	NM9	9/16/2003	377	365	483	1	F	3
	NM11	9/16/2003	333	316	376	1	F	3
	NM13	9/16/2003	296	281	266	3	Imm. M?	1
	NM14	9/16/2003	289	273	257	5	M	1
	NM17	9/16/2003	260	245	190	1	Imm. M?	
	NM18	9/16/2003	296	285	320	5	Imm. M?	1
	NM19	9/16/2003	275	261	227	5	Imm. M?	1
	NM23	9/16/2003	362	352	503	2	F	2
	NM25	9/16/2003	286	270	244	2	Imm. M?	1
	NM26	9/16/2003	268	252	201	1	M	1
		Mean=	309	294	318			2

\* total sample weight = 22 g

Table C-5. Biological Data for Stateline Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328442	SL-5	7/14/2004	556	1584	13
	SL-6	7/14/2004	566	1618	18
	SL-7	7/14/2004	483	984	11
	SL-8	7/14/2004	521	1168	13
	SL-12	7/14/2004	492	1070	8
	SL-15	7/14/2004	499	1028	10
	SL-16	7/14/2004	476	979	8
		Mean=	513	1204	12
328443	SL-4	9/17/2003	460	909	9
	SL-9	7/14/2004	459	940	11
	SL-10	7/14/2004	457	973	11
	SL-11	7/14/2004	427	707	7
	SL-13	7/14/2004	433	765	7
	SL-14	7/14/2004	471	868	9
	SL-17	7/14/2004	408	731	6
		Mean=	445	842	9

Table C-6. Biological Data for Plante Ferry Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328440	PF-32	9/15/2003	463	1093	10
	PF-33	9/15/2003	515	1325	8
	PF-38	9/15/2003	458	1099	8
	PF-40	9/15/2003	485	1117	7
	PF-42	9/15/2003	502	1210	7
	PF-43	9/15/2003	465	1061	7
	PF-46	9/15/2003	440	981	6
	PF-47	9/15/2003	501	1250	9
	PF-50	9/15/2003	476	1095	9
	PF-51	9/15/2003	489	1097	8
		Mean=	479	1133	8
328441	PF-28	9/15/2003	475	1094	11
	PF-31	9/15/2003	454	1082	8
	PF-35	9/15/2003	477	992	7
	PF-36	9/15/2003	435	903	5
	PF-41	9/15/2003	416	797	6
	PF-48	9/15/2003	433	800	7
	PF-49	9/15/2003	442	843	9
	PF-52	9/15/2003	454	1127	7
	PF-53	9/15/2003	460	1043	8
	PF-54	9/15/2003	482	963	7
		Mean=	453	964	8

Table C-7. Biological Data for Plante Ferry Largescale Sucker Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Gut Contents (g)*	Age (yrs)
328445	PF-29	9/15/2003	443	775	5	8
	PF-34	9/15/2003	506	1205	17	10
	PF-37	9/15/2003	460	893	8	9
	PF-39	9/15/2003	424	704	2	6
	PF-44	9/15/2003	532	1599	12	10
	PF-45	9/15/2003	544	1379	9	8
		Mean=		485	1093	

\* total sample weight = 53 g

Table C-8. Biological Data for Ninemile Bridgelip Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328447/8	NM-31	7/13/2004	475	980	15
	NM-33	7/13/2004	414	820	6
	NM-34	7/13/2004	442	693	10
	NM-40	7/13/2004	432	881	7
	NM-41	7/13/2004	406	673	9
	NM-47	7/13/2004	427	616	9
	NM-51	7/13/2004	421	826	8
		Mean=		431	784
328450	NM-36	7/13/2004	358	466	5
	NM-42	7/13/2004	356	468	5
	NM-43	7/13/2004	351	476	5
	NM-44	7/13/2004	358	511	6
	NM-48	7/13/2004	355	426	6
	NM-49	7/13/2004	357	486	6
	NM-50	7/13/2004	351	460	5
		Mean=		355	470

Table C-9. Biological Data for Ninemile Bridgelip Sucker Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Gut Contents (g)*	Age (yrs)
328449	NM-32	7/13/2004	393	695	3	5
	NM-35	7/13/2004	401	631	8	5
	NM-37	7/13/2004	411	665	6	7
	NM-38	7/13/2004	408	732	16	6
	NM-39	7/13/2004	408	626	4	6
	NM-45	7/13/2004	366	533	6	6
	NM-46	7/13/2004	385	536	12	7
		Mean=		396	631	

\* total sample weight = 55 g

Table C-10. Biological Data for Long Lake Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328444	LL-2	7/13-7/14/2004	463	950	10
	LL-7	7/13-7/14/2004	475	897	10
	LL-14	7/13-7/14/2004	458	1155	11
	LL-17	7/13-7/14/2004	445	1003	7
	LL-18	7/13-7/14/2004	444	897	7
	LL-19	7/13-7/14/2004	457	934	6
	LL-21	7/13-7/14/2004	501	1335	9
	LL-23	7/13-7/14/2004	466	986	5
	LL-24	7/13-7/14/2004	473	1004	9
	LL-25	7/13-7/14/2004	450	966	8
		Mean=	463	1013	8
328446	LL-1	7/13-7/14/2004	440	733	8
	LL-4	7/13-7/14/2004	425	707	7
	LL-5	7/13-7/14/2004	439	895	8
	LL-9	7/13-7/14/2004	416	742	8
	LL-10	7/13-7/14/2004	433	950	8
	LL-11	7/13-7/14/2004	442	881	9
	LL-15	7/13-7/14/2004	439	856	6
	LL-16	7/13-7/14/2004	458	939	11
	LL-20	7/13-7/14/2004	415	700	6
	LL-22	7/13-7/14/2004	425	799	5
		Mean=	433	820	8

Table C-11. Biological Data for Crayfish Tail Muscle Analysis Specimens.

Sample No.	Field ID	Carapace Length (mm)	Date Collected	Weight (g)	Tail Muscle Weight (g)	Sex
208148	1	37	5/12-5/13/2004	41	5	F
	2	42	5/12-5/13/2004	53	5	M
	3	39	5/12-5/13/2004	53	4	M
	4	36	5/12-5/13/2004	46	4	M

## Appendix D – Containers and Holding Times for Samples



Table D-1. Containers and Holding Times for Spokane River Samples.

Media	Parameter	Sample Size	Container	Holding Time
Effluent, Stormwater	PCB Congeners	4 L	1 gal. glass w/Teflon lined lid	1 year
	TSS	1 L	1000 mL polyethylene	7 days
Surface Water	PCB Congeners	4 L	1 gal. glass w/Teflon lined lid	1 year
	SPMD extract (PCB Congeners)	-	Extracted by contract lab	1 year
	TOC	50 mL	60 mL n/m polyethylene	28 days
	DOC	50 mL	60 mL n/m polyethylene, 0.45 µm filtered	28 days
	TSS	1 L	1000 mL polyethylene	7 days
Suspended Particulate Matter	PCB Congeners	100 g	8 oz. glass w/ Teflon lined lid	1 year (frozen)
	TOC (104 °C)	25 g	2 oz. glass w/ Teflon lined lid	6 months (frozen)
Surface Sediment	PCB Congeners	100 g	8 oz. glass w/ Teflon lined lid	1 year (frozen)
	Grain size	100 g	8 oz. polyethylene w/ Teflon lined lid	1 year
	TOC (104 °C)	25 g	2 oz. glass w/ Teflon lined lid	6 months (frozen)
Sediment Core Sections	PCB Aroclors	300 g	8 oz. glass w/Teflon lined lid	1 year (frozen)
	TOC (104 °C)	25 g	2 oz. glass w/ Teflon lined lid	6 months frozen)
	Pb-210	-	Provided by contract lab	-
Fish Tissue	PCB Congeners	30 g	4 oz. glass w/ Teflon lined lid	1 year (frozen)
	% lipids	20 g	2 oz. glass w/ Teflon lined lid	28 days
Gut contents	PCB Congeners	30 g	4 oz. glass w/ Teflon lined lid	1 year (frozen)

## **Appendix E – Method Used to Convert PCB Concentrations in SPMD to Water**

## Background on SPMDs

Semipermeable membrane devices (SPMDs) are used to concentrate dissolved hydrophobic contaminants from the water column. Each SPMD consists of a 91 x 2.5 cm lay-flat low density polyethylene tube filled with 1 ml of highly purified triolein. The tube is thin-walled and generally considered nonporous except for small ( $\leq 10 \text{ \AA}$ ) cavities created by the random thermal motions of the polymer chains (see Figure D-1). Freely dissolved hydrophobic contaminants are able to pass through the pores and are sequestered and concentrated in both the triolein and the polyethylene itself.

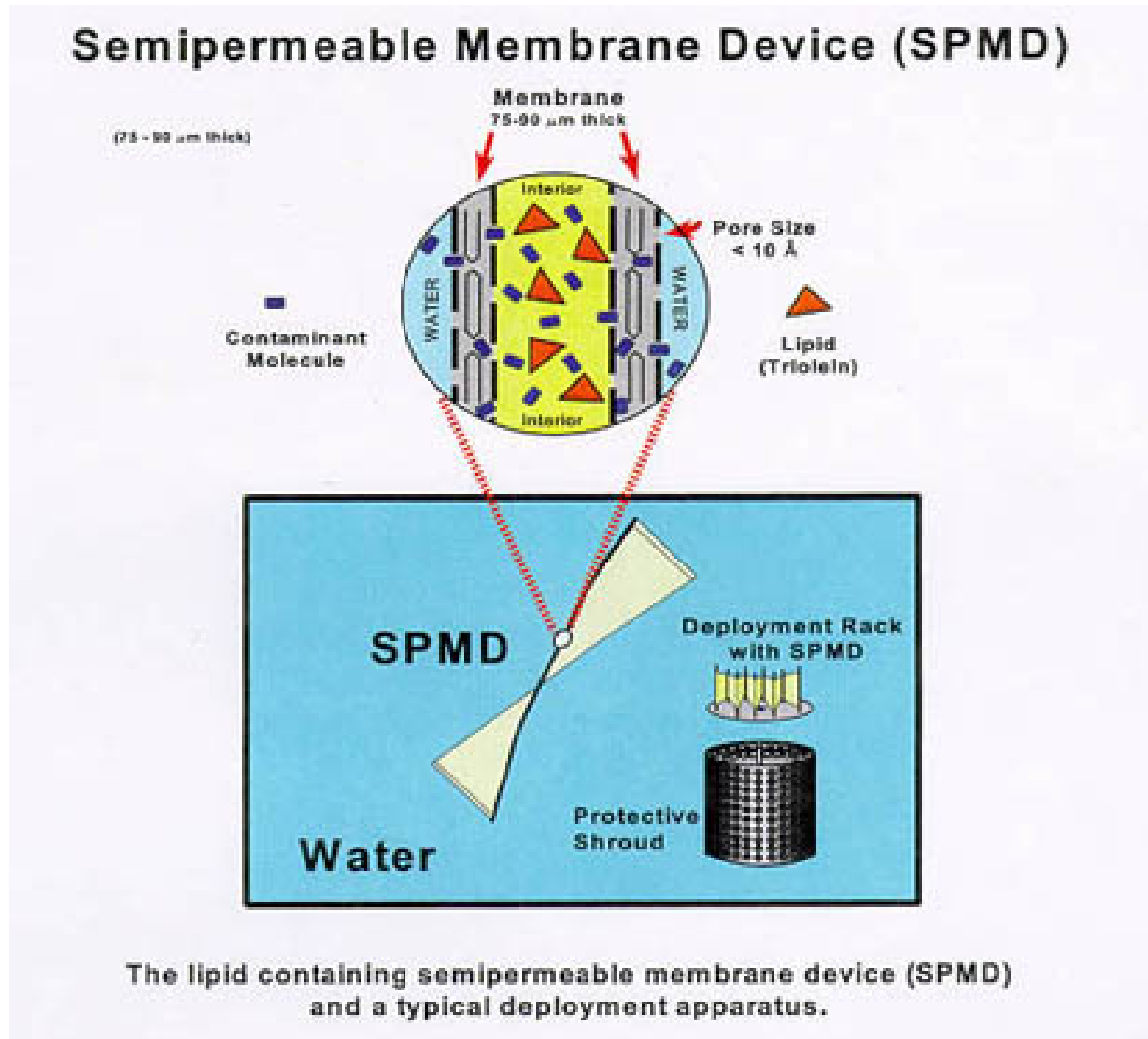


Figure E-1. Illustration of SPMD theory and mechanical design (from Duane Chapman, USGS Columbia Environmental Research Center, [www.aux.cerc.cr.usgs.gov/spmd/index.htm](http://www.aux.cerc.cr.usgs.gov/spmd/index.htm))

The SPMDs are mounted on deployment racks (a.k.a. spider carriers) which permit nearly full surface are exposure to water. The spider carriers (anywhere from one to five) are then mounted inside a protective mesh-skinned stainless steel canister which is placed in the water column for approximately one month.

After removal from the water column, SPMDs are sent to a laboratory for dialytic extraction of the solutes. Prior to dialysis, material coating the SPMD (periphyton, sediments, etc.) is removed and the membrane is inspected for holes and tears. The dialysate is concentrated to approximately 4 ml in a hexane solvent and stored in an ampule until it is ready for chromatographic or other analysis.

SPMDs are potent samplers of atmospheric organics which presents major challenges in avoiding contamination while preparing, deploying, and dialyzing these samplers. To minimize contamination due to air exposure, SPMDs are stored in argon-filled cans following preparation except during their water deployment. Field blank SPMDs are also used to assess the degree of on-site contamination by exposing them to the atmosphere for the same duration as the inevitable exposure of the water sampling SPMDs. Laboratory blank SPMDs are also prepared and analyzed to assess the degree of contamination from the lab environment.

Performance reference compounds (PRCs) are spiked into each membrane prior to deployment in order to assess sampling rates. The recovery of PRCs, along with other factors such as temperature, water velocity, degree of biofouling, and exposure duration is used to adjust the site/event-specific sampling rate from sampling rates determined in a laboratory setting. This adjustment factor, commonly referred to as the exposure adjustment factor (EAF), can be applied to the algorithms used to translate chemical concentrations in membrane extract to concentrations in the waterbody sampled.

## **Methods Used for the 2003-2004 Spokane River PCB TMDL Study**

### *Contamination of SPMDs*

For the 2003-2004 Spokane River PCB TMDL study, field (air) blanks were used to adjust laboratory results to account for laboratory and field contamination. The field blank was used for this purpose because it integrates contamination stemming from the field as well as the laboratory. Results for field blanks used during each round of sampling were subtracted (on a per membrane basis) from the sample results.

### *Exposure Adjustment Factors*

PRCs were spiked into all membranes prior to deployment. Selection of PCB congeners for PRCs was based on the congeners found during recent effluent and fish tissue sampling in the Spokane River (Golding, 2002; Jack and Roose, 2002). Four congeners – PCB-23, 55, 106, and 161 – which were absent or only present in very small amounts in these previous analyses were used for the spiking solution. 50 ng of each PRC was spiked into each membrane.

Average PRC recovery was higher than anticipated at 94%. More than a quarter of the PRCs were recovered at  $\geq 100\%$ . Subsequent consultation with Dr. David Alvarez and Dr. Jim Huckins of the USGS Columbia Environmental Research Center indicated that the fugacity of these congeners is too low to be suitable for calculation of EAFs (PCB-4 and 23 are recommended). Instead, they proposed using laboratory-derived sampling rates to calculate water concentrations.

#### *Calculation of PCB Concentrations in Water*

The following equation is the formula, in its simplest form, used to translate chemicals in SPMDs to water column concentrations:

$$C_w = C_{SPMD} / K_{SPMD} (1 - \exp[-k_e t])$$

Where:

$C_w$  = analyte concentration in water

$C_{SPMD}$  = analyte concentration in the SPMD

$K_{SPMD}$  = equilibrium SPMD-water partition coefficient

$k_e$  = first-order loss rate constant

t = time

Derivation of each term is beyond the scope of the present report but can be found at [http://www.waux.cerc.cr.usgs.gov/spmd/SPMD-Tech\\_Tutorial.htm#MODELING](http://www.waux.cerc.cr.usgs.gov/spmd/SPMD-Tech_Tutorial.htm#MODELING) or in Huckins, J.N. Petty, J.D., Priest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., and Johnson, B.T, 2000. A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants. Report for the American Petroleum Institute (API), Washington, D.C. API Publication No. 4690.

To facilitate translation of SPMD analyte concentrations to water, David Alvarez has developed a spreadsheet which requires relatively few input parameters to make the necessary calculations. Necessary input parameters are temperature, exposure duration, volume and mass of SPMD, total mass of analyte in SPMD, and EAF if PRCs are used to adjust sampling rates. The spreadsheet includes default values for Log  $K_{ow}$  and for laboratory sampling rates in cases where EAFs are not used (Table E-1). All calculations are made using the input parameters and the default values in Table E-1 and using the river conditions and exposure periods described earlier in this report. Total analyte mass by PCB homologue group is shown in Table E-2.

Table E-1. Log K<sub>ow</sub> and Sampling Rates Used to Calculate PCB Concentrations in Water.

Individual PCB Congeners	Log K <sub>ow</sub>		Laboratory Sampling Rate ( L/d )
4	5.1	k,m	12.8
5	5.1	k,m	12.8
6	5.1	g	12.8
7	5.1	k,m	12.8
8	5.1	k,m	12.8
9	5.1	k,m	12.8
10	5.1	k,m	12.8
11	5.1	k,m	12.8
15	5.1	k,m	12.8
16	5.5	k,m	6.7
17	5.5	k,m	6.7
18	5.2	g	9.2
19	5.0	g	5.3
20	5.5	k,m	6.7
22	5.6	g	5.7
24	5.5	k,m	6.7
25	5.7	g	5.7
26	5.7	g	5.7
27	5.5	k,m	6.7
28	5.7	g	8.4
31	5.7	g	7.0
32	5.5	k,m	6.7
33	5.5	k,m	6.7
34	5.5	k,m	6.7
35	5.5	k,m	6.7
37	5.5	k,m	6.7
40	5.7	g	6.6
41	5.7	g	6.2
42	5.8	g	6.2
43	5.8	g	6.2
44	5.8	g	7.5
45	5.5	g	7.9
46	5.5	g	4.4
47	5.8	g	7.5
48	5.8	g	3.5
49	5.8	g	5.3
51	5.6	g	4.8
52	5.8	g	6.2
53	5.6	g	4.8
54	5.9	k,m	5.7

Table E-1 (Cont'd). Log K<sub>ow</sub> and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K <sub>ow</sub>		Laboratory Sampling Rate ( L/d )
55	5.9	k,m	5.7
56	5.9	k,m	5.7
57	5.9	k,m	5.7
58	5.9	k,m	5.7
59	5.9	k,m	5.7
60	5.9	k,m	5.7
63	6.2	g	5.3
64	6.0	g	7.5
66	6.2	g	5.3
67	6.2	g	5.3
69	5.9	k,m	5.7
70	6.2	g	7.0
71	5.9	k,m	5.7
72	5.9	k,m	5.7
74	6.2	g	6.2
75	5.9	k,m	5.7
77	6.2	a, h	2.9
78	6.4	a, h, k	4.4
79	6.4	a, h, k	5.1
81	6.4	g, h	4.3
82	6.2	g	4.4
83	6.3	g	4.8
84	6.0	g	4.4
85	6.3	g	4.8
86	6.4	k,m	4.7
87	6.3	g	5.3
90	6.4	g	6.2
91	6.1	g	4.4
92	6.4	g	5.3
95	6.1	g	6.2
96	6.4	k,m	4.7
97	6.3	g	4.4
99	6.4	g	4.4
101	6.4	g	6.2
102	6.4	k,m	4.7
105	6.6	g	4.0
107	6.7	g	5.3
109	6.4	k,m	4.7
110	6.5	g	5.7
112	6.4	k,m	4.7
113	6.4	k,m	4.7

Table E-1 (Cont'd). Log K<sub>ow</sub> and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K <sub>ow</sub>		Laboratory Sampling Rate ( L/d )
114	6.6	g	4.4
115	6.4	k,m	4.7
117	6.4	k,m	4.7
118	6.7	g	4.8
119	6.6	g	4.4
122	6.4	k,m	4.7
123	6.4	k,m	4.7
126	6.7	a, h, k	2.2
127	6.7	a, h, k	1.6
128	6.7	g	4.4
129	6.7	g	3.5
130	6.8	g	4.0
131	6.8	k,m	4.1
132	6.8	k,m	4.1
133	6.8	k,m	4.1
134	6.6	g	4.8
136	6.2	g	5.3
137	6.8	g	3.5
138	6.8	g	4.8
139	6.8	k,m	4.1
141	6.8	g	4.8
144	6.8	k,m	4.1
146	6.9	g	4.8
147	6.8	k,m	4.1
149	6.7	g	5.7
151	6.6	g	5.3
153	6.9	g	3.2
156	7.2	g	2.6
157	7.2	g	2.6
158	7.0	g	3.5
163	6.8	k,m	4.1
164	6.8	k,m	4.1
166	6.8	k,m	4.1
167	6.8	k,m	4.1
169	7.4	a, h	2.1
170	7.1	k,m	2.6
171	7.1	k,m	2.6
172	7.3	g	1.3
173	7.1	k,m	2.6
174	7.1	g	3.1
175	7.1	k,m	2.6



Table E-1 (Cont'd). Log K<sub>ow</sub> and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K <sub>ow</sub>		Laboratory Sampling Rate ( L/d )
176	6.8	<sup>g</sup>	2.2
177	7.1	<sup>k,m</sup>	2.6
178	7.1	<sup>g</sup>	3.1
179	6.7	<sup>g</sup>	2.2
180	7.4	<sup>g</sup>	2.6
183	7.2	<sup>g</sup>	3.1
185	7.1	<sup>k,m</sup>	2.6
187	7.2	<sup>g</sup>	3.5
189	7.1	<sup>k,m</sup>	2.6
190	7.1	<sup>k,m</sup>	2.6
191	7.1	<sup>k,m</sup>	2.6
193	7.1	<sup>k,m</sup>	2.6
194	7.8	<sup>g</sup>	1.3
195	7.6	<sup>k,m</sup>	1.6
196	7.6	<sup>k,m</sup>	1.6
197	7.6	<sup>k,m</sup>	1.6
198	7.6	<sup>k,m</sup>	1.6
199	7.6	<sup>g</sup>	1.6
200	7.6	<sup>k,m</sup>	1.6
201	7.3	<sup>g</sup>	1.6
202	7.6	<sup>k,m</sup>	1.6
203	7.6	<sup>k,m</sup>	1.6
205	7.6	<sup>k,m</sup>	1.6
206	7.7	<sup>k,m</sup>	1.6
207	7.7	<sup>g</sup>	1.6
208	7.7	<sup>k,m</sup>	1.6
Total PCB <sup>g, h</sup>	6.4	<sup>g, h</sup>	4.8

Compounds are listed in general order of their chromatographic elution on a DB-35MS and a DB-5 GC-column for the organochlorine pesticides and PAHs respectively.

The linear model of estimation was used in cases where a compound's log K<sub>ow</sub>>6.

This calculator applies only to SPMDs which conform to the surface area-to-volume ratio of a standard SPMD.

If multiple log K<sub>ow</sub> values were found in the literature, a mean value was selected using the t test at 95% Confidence for rejection of outliers.

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

<sup>g</sup> Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillit, D.E. Environ. Sci. Technol., 1998, 32, 1847-1852.

<sup>h</sup> Rantalainen, A.L.; Cretney, W.; Ikonou, M.G. Chemosphere, 2000, 40, 147-158.

<sup>k</sup> Log K<sub>ow</sub> values estimated from similar congeners.

<sup>m</sup> R<sub>s</sub> values estimated as the average of known R<sub>s</sub> values of similarly substituted congeners

Table E-2. PCB homologue groups in SPMDs (pg per membrane)

Station Name	Sample Number	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
<b>October</b>												
STATELINE	474155	42	729	2,117	2,557	7,628	2,173	602	108	0	0	15,957
UPRIVER DAM	474156	74	2,385	4,787	4,196	4,194	970	237	0	0	0	16,843
UPRIVER DAM(REP)	474157	71	2,301	5,208	4,272	4,565	1,324	323	0	0	0	18,063
UPRIVER BOT	474158	35	1,994	6,125	7,974	5,888	1,476	365	35	0	0	23,891
MONROEST	474159	64	4,159	6,224	9,594	9,033	4,940	1,312	128	0	0	35,454
NINEMILE	474160	39	6,847	12,144	10,254	13,492	5,864	1,605	144	0	0	50,389
LONGLOW	474161	80	7,395	14,935	51,689	32,233	10,102	2,747	484	30	0	119,693
LITTLSPOK	474162	0	634	3,605	5,814	5,191	2,321	849	514	69	0	18,998
LITTLSPMS	474163	41	154	1,336	3,217	4,352	1,415	989	450	74	0	12,030
<b>February</b>												
STATELINE	194130	0	24	359	767	1,982	1,007	373	0	0	0	4,511
UPRIVER DAM	194131	7	337	1,126	2,089	2,025	441	1,384	0	0	0	7,409
UPRIVER DAM(REP)	194132	0	125	86	271	338	62	6	0	0	0	888
UPRIVEBOT	194133	2	176	2,087	6,796	3,158	486	69	0	0	0	12,774
MONROEST	194134	0	561	1,903	3,596	2,873	1,552	841	0	0	0	11,326
TUMTUM	194135	4	698	2,317	3,834	2,368	988	895	6	0	0	11,109
LSPOKBR	194136	10	274	2,323	6,929	7,818	2,096	1,146	598	84	0	21,278
LSPOKBRMS	194137	14	83	1,063	4,342	5,711	1,388	639	477	60	0	13,778
<b>April</b>												
STATELINE	208134	0	61	1,564	2,781	8,261	3,737	2,022	88	0	0	18,513
UPRIVER DAM	208135	0	0	411	2,663	2,001	748	350	36	0	0	6,208
UPRIVER BOT(REP)	208137	75	432	5,345	11,499	6,211	1,898	758	48	0	0	26,266
UPRIVER BOT	208136	343	184	4,330	14,517	9,800	2,144	902	0	0	0	32,219
MONROE ST	208138	17	815	4,211	8,830	11,189	4,663	2,299	176	0	0	32,198
NINEMILE2	208139	49	1,202	4,870	9,609	9,742	4,747	2,079	174	0	0	32,470
LONGLKLOW	208133	62	3,086	5,083	15,707	12,072	4,026	1,211	143	0	0	41,389
LITLSPOKBR	208140	0	261	3,560	8,285	9,617	2,779	1,424	720	131	0	26,778
LSPOKBRMS	208141	65	367	3,491	4,126	5,386	1,464	2,071	581	91	70	17,712

## **Appendix F – Ancillary Parameters for Suspended Particulate Matter Sampling**

Table F-1. Ancillary Data Taken at Centrifuge Locations During Suspended Particulate Matter Sampling (mg/L).

Station Name	Sample Number	Collection Date	TOC		DOC		TSS	
			inlet	outlet	inlet	outlet	inlet	outlet
Harvard	3438100	10/20/2003	1.2	---	---	---	2	---
	3438101	10/21/2003	1.1	---	---	---	1 U	---
	3438102	10/21/2003	1.2	---	---	---	1	---
	3438103	10/21/2003	1.1	---	---	---	1	---
	3438104	10/21/2003	---	1.2	---	---	---	1 U
	3438105	10/22/2003	1.1	---	---	---	1	---
	3438106	10/22/2003	1.2	---	---	---	1 U	---
	3438107	10/22/2003	---	2.3	---	---	---	1 U
PLANTEFRY	3448100	10/28/2003	1.1	---	1.1	---	1	---
	3448101	10/29/2003	1.1	---	1	---	3	---
	3448102	10/29/2003	1.1	---	1	---	1	---
	3448103	10/29/2003	---	1.1	---	1 U	---	1 U
	3448104	10/29/2003	1.1	---	1	---	2	---
	3448105	10/30/2003	---	1	---	1 U	---	1 U
	3448106	10/30/2003	1.1	---	1	---	2	---
NINEM SPM	3454105	11/3/2003	1	---	1 U	---	1	---
	3454106	11/4/2003	1 U	---	1 U	---	1	---
	3454107	11/4/2003	1 U	---	1 U	---	1	---
	3454108	11/4/2003	---	1 U	---	1 U	---	1 U
	3454109	11/4/2003	1 U	---	1 U	---	2	---
	3454128	11/5/2003	1 U	---	1 U	---	1	---
	3454129	11/5/2003	---	1 U	---	1 U	---	1 U

U=Undetected at Value shown

## **Appendix G – Details of Arnot-Gobas Food-Web Bioaccumulation Model**

## Overview of Arnot-Gobas Food-Web Bioaccumulation Model

Models to track hydrophobic organic chemicals through the food-web have increased in their accuracy and complexity as investigators have built upon previous models to make iterative improvements. One of the most recently available models, the food-web bioaccumulation model developed by Arnot and Gobas (2004), was selected to estimate PCB concentrations for the Spokane River PCB TMDL for several reasons. First, the model was built upon a widely accepted kinetic model developed to predict bioaccumulation of hydrophobic organic compounds in the food web of Lake Ontario and other lakes (Gobas, 1993). Second, the model is programmed in Excel spreadsheets and is simple to use, make adjustments, and perform backward calculations (find values for input parameters needed to derive a defined model output). Third and last, validation runs indicated the model could predict PCB concentrations in at least two Spokane River fish species with a fairly high degree of accuracy.

The model accounts for major routes of PCB accumulation through diet and the gills, while depuration occurs through elimination by the gills and feces, and by metabolic transformation (Figure G-1). The model also accounts for decreases in contaminant concentration through growth dilution.

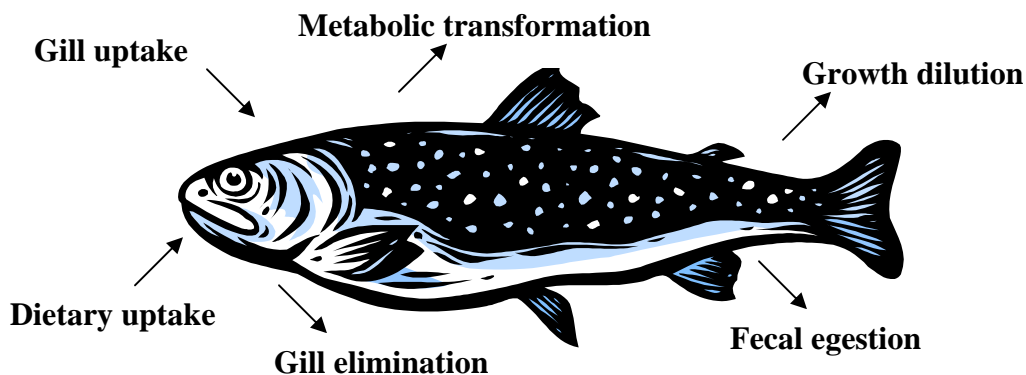


Figure G-1. Conceptual Diagram of the Major Routes of Contaminant Uptake and Depuration (Adapted from Arnot and Gobas, 2004).

The basic equation which describes the general model is:

$$dM_B/d_t = \left\{ W_B \cdot \left( k_1 \cdot [m_o \cdot \Phi \cdot C_{wT,0} + m_p \cdot C_{wD,S}] + K_D \cdot \Sigma(P_i \cdot C_{d,i}) \right) \right\} - (k_2 + k_E + k_M) \cdot M_B$$

Where:

$M_B$  = mass of the chemical in the organism (g)

$t$  = time (d)

$dM_B/d_t$  = net flux of chemical in the organism at any point in time

$W_B$  = weight of the organism at  $t$  (kg)

$k_1$  = clearance rate constant for the chemical uptake via gills and skin (l/kg • d)

$M_o$  = fraction of respiratory ventilation in overlying water

$M_p$  = fraction of respiratory ventilation in pore water

$\Phi$  = fraction of total chemical concentration that is freely dissolved in overlying water

$C_{wT,0}$  = total chemical concentration in water above sediments (g/l)

$C_{wD,S}$  = chemical concentration freely dissolved in pore water (g/l)

$K_D$  = clearance rate constant for the chemical uptake via diet (kg/kg • d)

$P_i$  = fraction of diet consisting of prey item  $i$

$C_{d,i}$  = chemical concentration in prey item  $i$  (g/kg)

$k_2$  = rate constant for the chemical elimination via gills and skin (d<sup>-1</sup>)

$k_E$  = rate constant for the chemical elimination via fecal egestion (d<sup>-1</sup>)

$k_M$  = rate constant for metabolic transformation of the chemical (d<sup>-1</sup>)

The general equation can be simplified by assuming steady state conditions (i.e.,  $dM_B/d_t = 0$ ), which results in a re-expression of the equation to:

$$C_B = \left\{ k_1 \cdot \left( m_o \cdot \Phi \cdot C_{wT,0} + m_p \cdot C_{wD,S} \right) + K_D \cdot \Sigma(P_i \cdot C_{d,i}) \right\} / (k_2 + k_E + k_M + k_G)$$

Where  $C_B$  = chemical concentration in the organism ( $M_B/W_B$ ). It is noteworthy that the steady-state assumption necessitates a growth dilution term ( $k_G$ ) which can be represented by a constant fraction of the organism's body weight. The reader is referred to Arnot and Gobas (2004) for detailed explanations of the sub-models used to derive all of the terms in the general equation. Assumptions and input parameters used to apply the model to the Spokane River are discussed below. All other environmental characteristics were those used for Lake Erie modeling and were supplied by J. Arnot.

### *Environmental characteristics*

Environmental characteristic input parameters for the Spokane River model included mean annual water temperature, DOC, TSS, particulate OC (POC) and sediment TOC. Table G-1 shows the values used. Mean annual temperatures, DOC, and TSS were mean values of the reaches modeled from data collected during SPMD deployment and recovery. One-half the detection limits were used for non-detects. Since January-February data were temperature were lost at Ninemile, the Monroe – Ninemile model was run using mean temperature data only from Monroe St. POC was calculated as the fraction organic carbon ( $f_{oc}$ ) in suspended particulate matter (0.15, see Eq. 3) multiplied by TSS.

Sediment TOC concentrations were more difficult to estimate due to lack of depositional material in the upstream reaches. For the Stateline – Upriver model run, the TOC was the mean of five sediments from RM 81.5 – RM 94.8 analyzed by Ecology (1994). Sediments from the Upriver Dam PCB “hot spot” were not used to derive this value. For the Monroe – Ninemile model run, the TOC value was the mean TOC of five Monroe St. (RM 74.9 – RM 78.7) sediments collected during 1994 averaged with a single Ninemile sediment collected during 1993 (Ecology, 1994).

### *Species characteristics*

Fish species used for target PCB concentrations were rainbow trout and suckers. The model has output parameters built in for rainbow trout. The sucker species built into the model is white sucker (*Catostomus commersoni*). This species has similar habits and foraging characteristics as largescale and bridgelip suckers, and may even interbreed with largescale suckers where their ranges overlap (Wydoski and Whitney, 1979), and was therefore deemed a suitable substitute.

The model also allows for yellow perch, smallmouth bass, and largemouth bass as target endpoints. These species are found in Long Lake and the Spokane Arm, with limited populations of smallmouth bass in upstream reaches. However, these species were not selected to establish critical PCB concentrations because they generally have much lower PCB concentrations than lipid-rich species such as trout and sucker (e.g., Ecology, 1995; Jack and Roose, 2002). For these species, the target tissue concentration of 0.1 ng/g would be achieved with much higher water and sediment PCB levels.

Rainbow trout lipid content used in Table G-1 was the average of rainbow trout analyzed whole from four Spokane River locations. Weight was an approximation of present and historical Spokane River rainbow trout collected for analysis. For largescale suckers, lipid fraction in Table G-1 was an average of whole bodies from all available Spokane River samples, historic and present. Weight was the average of all suckers analyzed whole for the present study.

Diet of target fish species in Table G-1 was based on observations of gut contents. Diet composition of fish prey items (zooplankton and benthic species) was based on likelihood rather than site-specific observations.



### *Whole body to fillet conversion*

The model produces a whole organism output for PCB concentrations in fish, which assumes that the chemical is distributed homogeneously among tissues of an organism. This limitation of the model may be an over-simplification when applied to complex organisms such as fish. To achieve the target concentration in fillet tissue, a conversion factor of 1.47 was applied based on the work of Amrhein et al. (1999). Limited data on paired whole fish-fillet data from the Spokane River (Johnson, 2000) yielded a conversion factor of 1.18 for rainbow trout and 2.73 for largescale suckers. This indicates that the water and sediment PCB concentrations used in the model along with the published conversion factor may be conservative for predicting target concentrations in suckers, while those used to predict rainbow trout targets may contain a slightly high bias.

### *Chemical characteristics*

Total PCB was analyzed as the chemical of interest in the model to provide a simplified method of calculating PCB endpoints. The log  $K_{ow}$  and Henry's Law constant for total PCB that were used for the model were the same as those used to translate SPMD concentrations to water concentrations (Table G-1). For SPMDs, these parameters yield values similar to total PCBs calculated by summing individual congeners calculated separately.

### *Validation and Sensitivity*

Prior to use, the model was validated using input parameters representative of the Spokane River and reach-specific fish weight and lipid data from recent sampling. Predicted and observed tissue concentrations were similar (Table G-2).

It should be noted that the model was not calibrated by adjusting the algorithms to match predicted and observed results. It is also noteworthy that the decision to apply this model was made only after sampling had been completed. However, the necessary input parameters were easily obtained from current or historical data, and default values for physical, chemical, and species characteristics – originally used to model PCBs in the Lake Ontario food web – are applicable to the Spokane River.

A cursory assessment of model sensitivity was done by inserting ranges of values for the input parameters discussed in previous sections. The model is somewhat sensitive to changes in POC, sediment TOC, percent lipid in target fish, and prey composition for target fish. A 50% change in these model parameters results in an approximate 15% change in the target fish PCB concentrations when other model parameters are held at values typical for the Spokane River.

The model is particularly sensitive to log  $K_{ow}$  values, which can be expected due to the log  $K_{ow}$  as one of the most important factors driving the partitioning of PCBs between water and lipid soluble compartments. The response to changes in log  $K_{ow}$  is an approximate 10% decrease in target fish PCB concentrations with each 0.1 decrease in log  $K_{ow}$  around the value used for the Spokane River (log  $K_{ow}$  = 6.4). Increases of 0.1 in log  $K_{ow}$  result in approximately 10% increases in fish PCB concentrations. Of course, these responses are not linear and the limited information provided here cannot be used to calculate target fish PCB concentrations, but they offer a glimpse at how the model output responds to certain input parameters.

Table G-1. Input Parameters for the Arnot-Gobas Bioaccumulation Food Web Model.

	Reach				
	Stateline-Upriver	Monroe-Ninemile	Long Lake	Little Falls	Spokane Arm
<i>Water</i>					
Mean annual water temp. (°C)	9.2	8.9	10.0	10.0	10.0
DOC (mg/l)	1.2	1.0	1.1	1.1	1.1
TSS (mg/l)	1.6	2.2	2.8	2.8	2.8
Particulate OC (mg/l)	0.24	0.33	0.42	0.42	0.42
<i>Sediment</i>					
TOC (%)	2.0	1.6	2.9	0.6	1.7
<i>Zooplankton</i>					
Diet	100% phytoplankton				
<i>Benthic Species</i>					
Diet	50% phytoplankton, 50% sediment				
<i>Rainbow Trout</i>					
Weight (kg)	0.5				
Lipid (%)	5.6				
Diet	50% zooplankton, 12.5% each mayfly larvae, chironomid larvae, <i>Gammarus</i> , crayfish				
<i>Sucker</i>					
Weight (kg)	0.918				
Lipid (%)	3.8				
Diet	33% phytoplankton, 33% chironomids, 34% sediment		50% chironomids, 50% sediment		
<i>Chemical (Total PCBs)</i>					
Log K <sub>ow</sub>	6.4				
Henry's Law Constant (Pa. m <sup>3</sup> /mol)	3.9				

Table G-2. PCB Concentrations in Fish Tissue Predicted Using the Arnot-Gobas Food-Web Bioaccumulation Model vs. Observed PCB Concentrations.

	Reach				
	Stateline-Upriver	Monroe-Ninemile	Long Lake	Little Falls	Spokane Arm
<i>Measured PCB conc. in water and sediment</i>					
Diss. t-PCB conc. in water (pg/l)	83	222	332	na	na
t-PCB conc. in sediment (ng/g dw)	54	78	33	1.9	10
<i>t-PCB conc. in whole rainbow trout (ng/g ww)</i>					
Predicted	87	31**	55	--	--
Observed*	51	40**	na	na	na
<i>t-PCB conc. in whole suckers (ng/g ww)</i>					
Predicted	110	26**	98	--	--
Observed*	99	29**	224	na	na

\*PCB concentrations in fillet converted to whole fish by multiplying by 1.47

\*\*Ninemile only. Recent tissue data not available for Monroe St.

na=not available