Quality Assurance Project Plan

Total Maximum Daily Load Study for PCBs in the Spokane River

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303(d) listings addressed in this study: Spokane River, Idaho border to the mouth, and the Little Spokane River in its entirety

Waterbody numbers: WA-54-1010, WA-54-1020, WA-55-1010, and WA-57-1010

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Abstract

PCBs in fish from the Spokane River have been documented at concentrations well above the National Toxics Rule (NTR) criterion and are currently at levels high enough to warrant consumption advisories for parts of the river. Although there is an abundance of data on PCBs in Spokane River fish, there has not been a recent analysis of PCB loading and dynamics in the river. There also has yet to be an examination of PCB accumulation pathways in fish.

This Quality Assurance Project Plan (QAPP) describes the sampling and analysis required to adequately assess PCB loading, dynamics, and accumulation pathways in the Spokane River. Sampling will be done to assess PCB concentrations in industrial effluent, stormwater, whole surface water, dissolved and particulate phases of surface water, surficial bottom sediments, sediment cores, whole fish, fish fillet, and gut contents from two species of fish. The data obtained will be used to develop a Total Maximum Daily Load (TMDL) for PCBs. The goal of the TMDL and the ensuing water cleanup plan is to meet the NTR criteria in Spokane River fish tissue.

Background and Problem Statement

In the Spokane River, elevated levels of polychlorinated biphenyls (PCBs) have historically been detected in surface waters, effluents, sediments, and fish tissue (Ecology, 1995; Johnson, 1997; Johnson, 2000; Golding, 2002). Concentrations in fish tissue from the Spokane River have been high enough to warrant an ecological risk assessment (Johnson, 2001) and the issuance of human fish consumption advisories for parts of the river (Spokane Regional Health District and Washington State Department of Health, 2003).

Nearly all fish samples analyzed from the Spokane River have PCB concentrations exceeding the human health criterion from the National Toxics Rule (NTR, 40 CFR Part 131.36). This criterion (5.3 ng/g) was established to protect humans from a lifetime cancer risk due to fish consumption, and can be translated to an equivalent water concentration of 0.17 ng/l.

All reaches of the Spokane River, from the mouth to the Idaho border with the exception of the Little Falls Pool, and the Little Spokane River have been included on the most recent (1998) federal Clean Water Act Section 303(d) list due to non-attainment of the NTR human health criteria. The listings are based on Johnson et al. (1994) and Ecology (1995) and are summarized in Table 1.

Table 1. Waterbodies listed in 1998 for PCBs under Clean Water Act Section 303(d).

Waterbody	Old Segment Number	New Segment Number	Parameters	Medium
Spokane River	WA-57-1010	QZ45UE	PCB-1242, PCB-1248, PCB 1254, and PCB-1260	Tissue
"	WA-54-1010	"	PCB-1248, PCB-1254, and PCB-1260	"
"	WA-54-1020	"	PCB-1242, PCB-1248, PCB- 1254, and PCB-1260	"
"	WA-54-9040	"	PCB-1242, PCB-1248, PCB- 1254, and PCB-1260	"
Little Spokane River	WA-55-1010	JZ70CP	PCB-1248, PCB 1254, and PCB-1260	"

The U.S. Environmental Protection Agency (USEPA) requires states to set priorities for cleaning up 303(d) listed waters and to establish a Total Maximum Daily Load (TMDL) for each. A TMDL includes an analysis of how much of a pollutant a particular waterbody can assimilate without violating water quality standards. TMDLs allocate the allowable load of a pollutant to point, nonpoint, and background sources and the reductions necessary to meet water quality standards.

The TMDL study for PCBs in the Spokane River will be conducted by the Department of Ecology, Environmental Assessment Program. This Quality Assurance (QA) Project Plan describes the technical study to monitor levels of PCBs in the Spokane River system and will form the basis for a water cleanup plan. The technical study includes sampling effluent, surface water, sediment, and multiple sizes and species of fish. The study will use these data to allocate PCBs in water and fish tissues to sources.

The study objectives include:

- Obtain representative data on PCB concentrations and ancillary parameters in the water column, NPDES permitted and stormwater discharges, bottom sediments, and fish tissue.
- Determine trends and natural recovery rates for PCBs in sediments.
- Determine the proportional contributions of surface water and sediment to fish tissue concentrations.
- Incorporate the above data into a site-specific conceptual model of PCB bioaccumulation.
- Determine the loading capacity for PCBs.
- Develop a report which addresses the elements required by USEPA Region 10 including proposed PCB waste load allocations for point sources and load allocations for nonpoint sources.

The goal of the TMDL and the water cleanup plan will be to meet the NTR water quality criteria in Spokane River fish tissue.

Basin Description

Impoundments

The Spokane River begins in northern Idaho at the outlet of Lake Coeur d'Alene. The cities of Wallace and Kellogg, among others, are upstream from Lake Coeur d'Alene while the cities of Post Falls and Coeur d'Alene are in Idaho downstream of the lake's natural outlet. There is one dam along the Spokane River in Idaho downstream from Lake Coeur d'Alene near Post Falls at river mile (RM) 100.8. At RM 96.1 the mainstem of the Spokane River enters Washington State. Larger Washington communities within the watershed include the cities of Spokane and Liberty Lake, Deer Park, and Medical Lake.

There are six dams in Washington along the Spokane River before it empties into Lake Roosevelt, an impoundment of the Columbia River (Figure 1). From the city of Spokane moving downstream they are:

1. Upriver Dam at RM 80.2
2. Upper Falls Dam at RM 74.5
3. Monroe Street Dam at RM 74.0
4. Nine Mile Dam at RM 58.1
5. Long Lake Dam at RM 33.9
6. Little Falls Dam at RM 29.3

The dams create a series of pools which vary in length, the largest being Long Lake 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 (Columbia River mile 639.0).

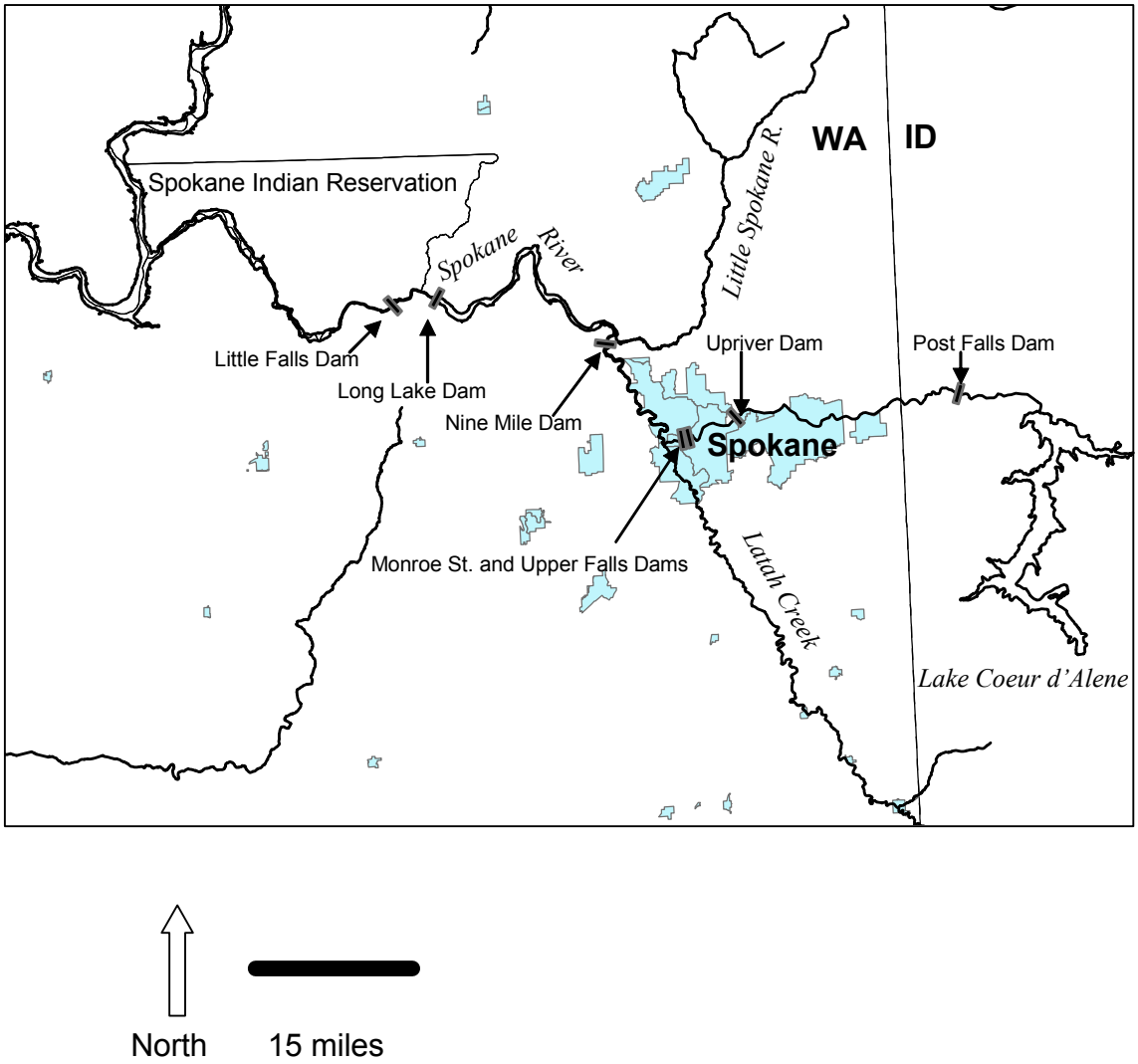

Figure 1. Spokane River basin

Flows and Drainage Areas

Prior to 1968, there were unquantified agricultural diversions from the Spokane River at Post Falls, Idaho. These diversions ceased in 1967. Thus, the following descriptions have used the 1968-2001 period to describe flow conditions. This time frame is noted as the period of record. Flow data from the U.S. Geological Survey (USGS) have been previously used by Ecology for evaluations of allowable phosphorus loading (Patmont et al., 1987) and metals TMDLs (Pelletier and Merrill, 1998), and an ongoing dissolved oxygen TMDL. Harmonic means have been used to describe the historic flows as recommended by USEPA (1991).

The Spokane River at Post Falls drains approximately 3,800 square miles. The maximum flow for the period of record is 44,400 cubic feet per second (cfs). The harmonic mean for this period is 2,151 cfs. Downstream, the mean flow of the Spokane River at Spokane increases to 2,897 cfs. Because there are few tributaries between Post Falls and Spokane, this increase predominantly reflects the influx of groundwater through this river reach. The Spokane River loses flow, especially during flood events, from the outlet of Lake Coeur d'Alene to about RM 90.4 at Barker Road. Below Barker Road, the river begins gaining flow from groundwater again. Hart Crowser (1995) concluded that groundwater inflow was not a primary PCB transport pathway to the river.

The two main tributaries to the Spokane River are the Little Spokane River and Latah (Hangman) Creek. The Little Spokane River is about an order of magnitude larger, with a mean flow of 197 cfs. Latah Creek periodically discharges large quantities of highly turbid water into the Spokane River (SCCD, 2002) at RM 72.2. Its maximum flow for the period of record is 18,000 cfs. This is a reflection of the highly disturbed, predominantly agricultural watershed. Latah Creek's harmonic mean flow is 17.7 cfs. Suspended sediment near the mouth of Latah Creek has been measured as high as 1,460 mg/L (SCCD, 2002). Gauge data from the USGS are summarized in Table 2.

Table 2. Flows for the greater Spokane watersheds, 1968-2001 (cfs).

Name	Harmonic mean	Minimum	Maximum
Spokane River @ Post Falls	2,151	67	50,000
Spokane River @ Spokane	2,897	466	49,000
Latah Creek	18	0.81	18,000
Little Spokane @ Dartford	197	66	3,710

The flow regime at Spokane basically represents the flow pattern throughout the watershed, although Latah Creek is an anomaly due to its disturbed watershed area. Figure 2 illustrates the harmonic mean flows at Spokane by month from 1968 to 2001. These data were also derived from USGS measurements. The flow exhibits strong seasonal variation, with a late summer low-flow period in August and September gradually rising throughout the winter and spring to a peak flow in May. Flows generally rapidly decline in June and July.

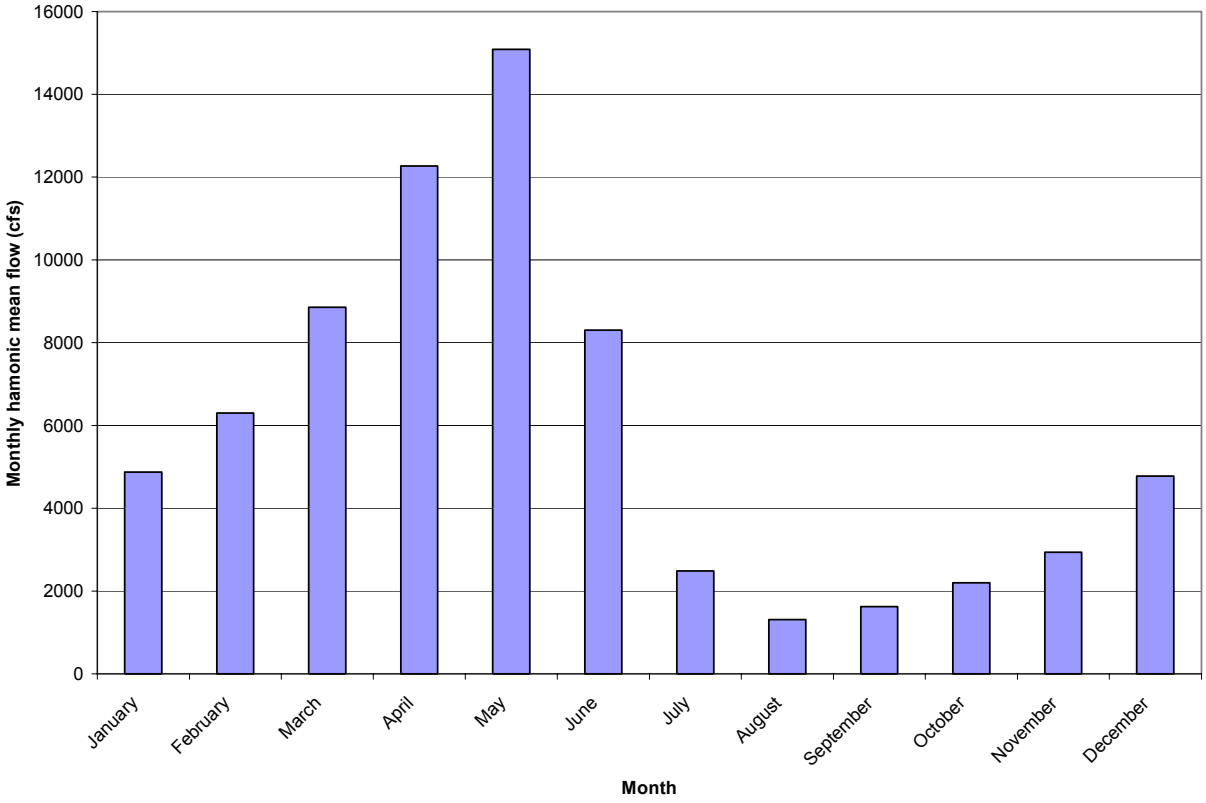

Figure 2. Spokane River monthly harmonic mean flow at Spokane, 1968-2001.

Ecology has divided the watershed into four Water Resource Inventory Areas (WRIAs). The mainstem of the Spokane River and all its tributaries from Latah Creek to the Idaho border is WRIA 57 (Middle Spokane River). Downstream from Latah Creek, the mainstem of the Spokane River comprises the Lower Spokane WRIA 54. This WRIA extends to Chamokane Creek. The Little Spokane River and Latah Creek are WRIAs 55 and 56, respectively. The drainage area of each WRIA is listed in Table 3.

Table 3. Drainage area for the greater Spokane watersheds (square miles).

Name	WRIA	Drainage Area in WA	Drainage Area in ID
Middle Spokane	57	286	4004
Lower Spokane	54	885	NA
Little Spokane	55	677	NA
Latah Creek	56	454	189

NA = Not Available

National Pollution Discharge Elimination System (NPDES) 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 wastestreams of some permitted Spokane River dischargers. Table A-1 (Appendix A) lists the permitted discharges to the greater Spokane watershed by WRIA and permit number.

The NPDES permit numbers in Table A-1 are coded based on the type of discharge to waters of the state. Those permit numbers beginning with "ST" are for the discharge of effluents to the ground or groundwater, although some metal finishers may discharge waste to the Spokane Advanced Wastewater Treatment Plant. 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 Table A-1, 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 overwhelms 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 (WWTP) 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 suggest that PCB stormwater concentrations may be above water quality criteria (e.g., from 88 to 179 ng/L), and a source to the total Spokane River loading (Marsalek and Ng, 1989). However, annual PCB loads from CSOs probably represent less than 0.2% of the annual loading from the City of Spokane WWTP due to the comparatively high flows from the WWTP (City of Spokane, 2002).

Current TMDL guidance requires the development of a numeric waste load allocation for all NPDES regulated discharges, including intermittent sources like stormwater and CSOs (Wayland and Hanlon, 2002). This TMDL will sample stormwater and CSO discharges to assess representative PCB loads transported via both delivery pathways.

Background on Polychlorinated Biphenyls

PCB Chemical Structure

Polychlorinated biphenyls are a group of synthetically manufactured organic chemicals. There are no known natural sources of PCBs. There are 209 individual forms of PCBs known as congeners, and they can exist as oily liquids or solids, with no known taste or smell. The 209 individual congeners have been assigned numbers based on the position of chlorine atoms in their structure. Figure 3 illustrates a generic PCB molecule with the potential chlorine positions labeled.

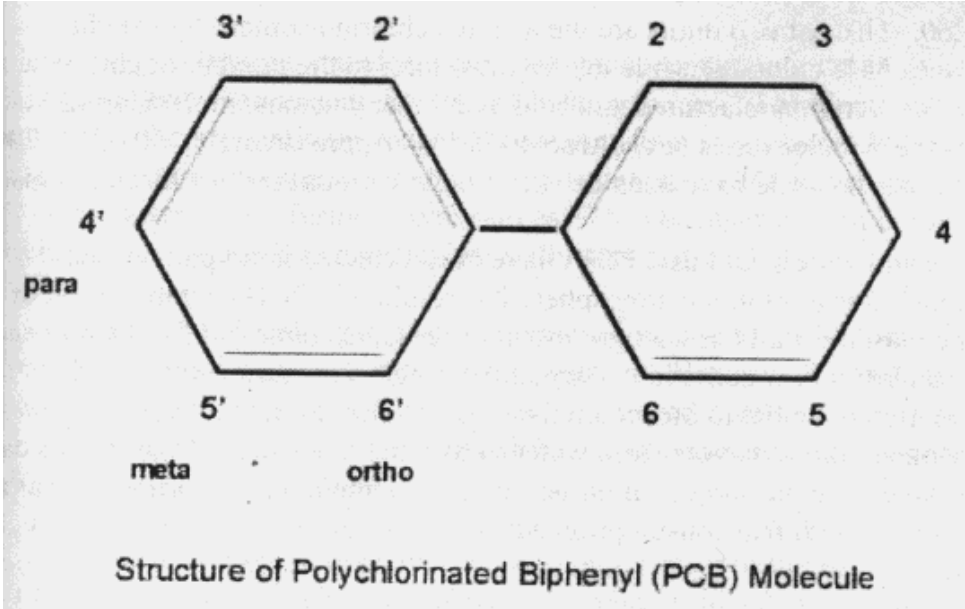

Figure 3. Generic PCB molecular structure.

PCBs were manufactured from 1929 until 1977. The production-based manufacture of PCBs stopped because of growing evidence that PCBs build up in the environment and cause harmful effects. Prior to 1977, PCBs were discharged to the air, water, and soil via their manufacture and through their use and disposal. PCBs were commonly used in capacitors, transformers, and hydraulic fluids, where their dielectric and insulating capacities were considered beneficial. In these types of applications, PCBs were not used as individual congeners; rather they were produced and sold as mixtures.

A trade name for such a mixture is Aroclor; Aroclors were the primary PCB products used in the U.S. An Aroclor is comprised of a mixture of PCB congeners, and upon manufacture they were given numerical designators describing their chlorine content. For example, Aroclor 1248 contains 48% chlorine by weight while Aroclor 1254 contains 54% chlorine by weight. The 12 refers to dual six-member carbon rings. Many different commercial Aroclor mixtures have been quantified as to their congener composition by Frame et al. (1996).

PCB Abiotic Behavior

PCB mixtures behave in the environment differently. This is a function of both their varying congener composition and of the differences in behavior of the component congeners. When mixed with water, PCBs are generally resistant to dissolution. Their general insolubility is reflected in their high octanol-water partitioning coefficient (log K_{ow}). Aroclor log K_{ow} are known to range from 4.7 to 6.8 (ATSDR, 1997). The more highly chlorinated Aroclors have higher log K_{ow}s, are less soluble, and have a high affinity for organic carbon and sediments. PCBs with the highest log K_{ow} would be expected to have the greatest organic carbon, lipid, and sediment affinity.

PCB mixtures also include relatively volatile congener compounds. PCB Henry's law constants range from $2.9x10^{-4}$ to $4.6x10^{-3}$ 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. The overall loss of PCBs from the Great Lakes has been estimated by Eisenreich et al. (1992). Average losses of PCBs in the Great Lakes via volatilization are 65.8%; via sedimentation 27.2%; and the outflow to other waterbodies is 7%. The six 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}s, 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.

PCB Biotic Behavior

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 more highly chlorinated congeners, leading to preferential bioaccumulation of heavier congeners. For the most chlorinated compounds, bioaccumulation is less pronounced. It is speculated that congeners with log K_{ow}s > 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).

Historic Data

In environmental media such as water, sediment, or fish tissue, the detected congeners often bear little resemblance to the parent Aroclor(s) which may have been released. Older laboratory analytical methods, such as EPA Method SW-846-8082 do not quantify individual congeners. These methods provide a chromatographic pattern which is then hand-matched by the analyst to a known Aroclor distribution pattern. Typical chromatographic patterns in environmental media such as fish tissue or sediment rarely match commercial Aroclor patterns exactly due to the weathering or biotic degradation of the mixture which occurs in the environment, the differential uptake and excretion of congeners in fish, and the presence of co-eluting compounds such as chlorinated pesticides which confound Aroclor pattern matching.

Ecology has analyzed PCBs in a variety of water, sediment, and fish tissue samples collected from the Spokane River over approximately the past 15 years. Additional data have been collected by or in cooperation with the USGS and various NPDES dischargers in the greater Spokane watershed. Most of these data were reported in "Aroclor equivalents", despite the limitations described above. Other, more recent data are reported as individual congeners. The following sections will review the data currently available. Because the 303(d) listing is for fish tissue concentrations, the following discussion will emphasize these data.

1983-1999 Fish Tissue Concentrations

Little data from the 1980s are available, although Hopkins et al. (1985) provide a few data in an appendix. Their total PCB values for whole fish ranged up to 2,300 µg/Kg in northern pikeminnow (*Pychocheilus oregonensis*) collected in 1983. Fillet portions of mountain whitefish (*Prosopium williamsoni*) and bridgelip sucker (*Catostomus columbianus*) from Riverside State Park in Spokane were also elevated, with total PCB concentrations of 226 and 369 µg/Kg, respectively.

More extensive fish tissue data are available from Ecology (1995). Concentrations of total PCBs (Aroclors) varied by river reach and species analyzed. Anywhere from 9 to 20 different samples were analyzed within each river reach. Some results from these composite samples are summarized by species and river reach in Figure 4. Some of the composites within a reach varied, and thus the arithmetic mean concentrations in Figure 4 have been weighted by composite size.

The only area of the Spokane watershed outside of the mainstem which has been sampled for PCBs in fish tissues is the Little Spokane River. In 1994, concentrations in whole largescale suckers (*Catostomus macrocheilus*) were 440 µg/Kg (Ecology, 1995). This concentration is similar to that found in Long Lake whole largescale suckers from 1993 to1994. The five fish for the composite sample were collected about 0.5 miles upstream from the mouth of the Little Spokane River. In these samples, the PCB mixture resembled Aroclor 1260, suggesting either a different source than the mainstem, an older source which was difficult for the analyst to pattern match after weathering of lighter congeners, or analytical variability and uncertainty.

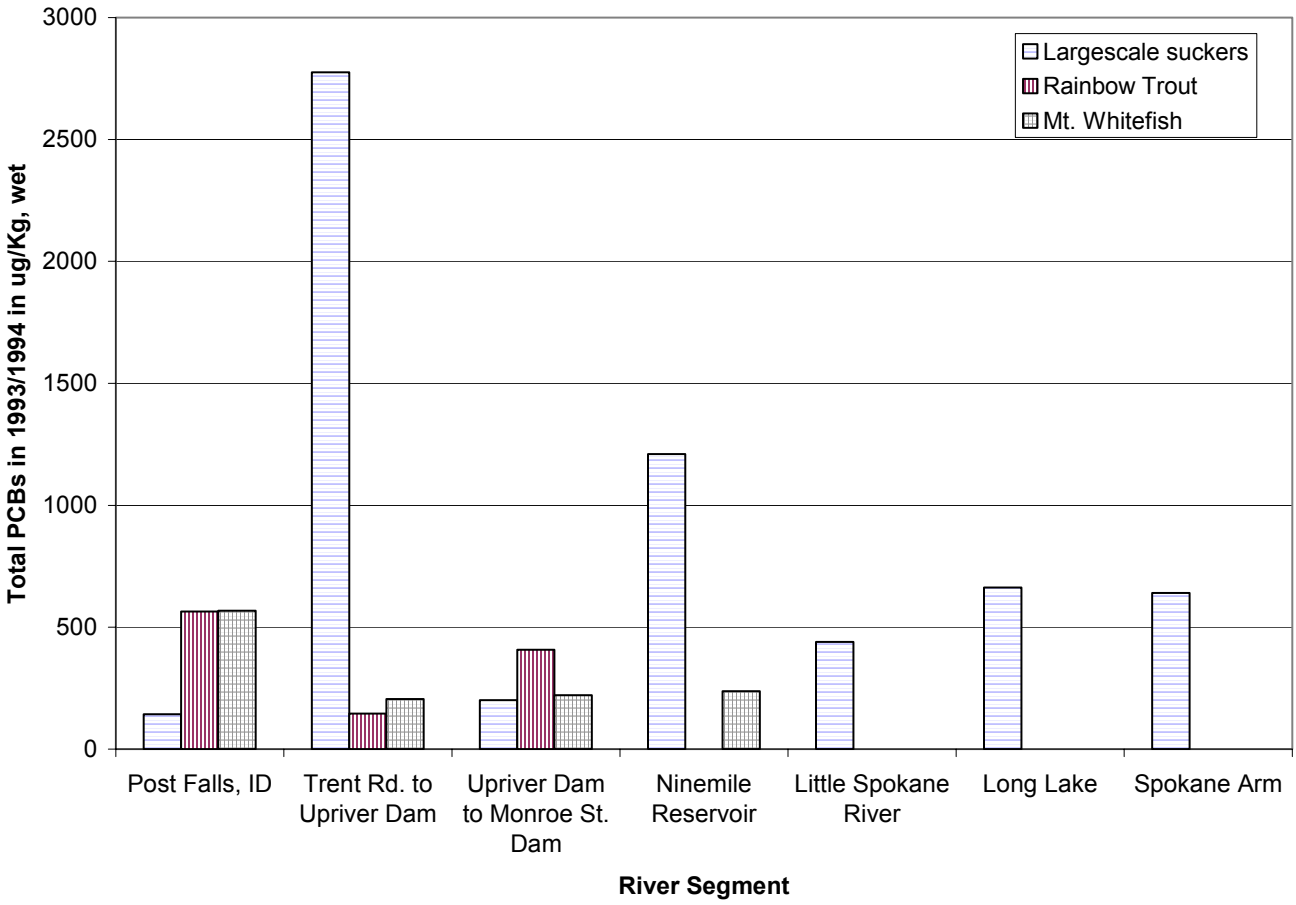

Figure 4. Total PCB concentrations in whole largescale sucker, rainbow trout fillet, and mountain whitefish fillet collected in 1993 and 1994 from the Spokane River by Ecology.

In July 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 piscivorous wildlife criterion of 110 µg/Kg. Concentrations in five-fish composites of whole suckers were between 120 and 700 µg/Kg 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 1600 µg/Kg for both species. Figure 5 shows mean PCB concentrations (Aroclors) in edible rainbow trout and mountain whitefish tissue and whole largescale suckers collected from four reaches during 1999.

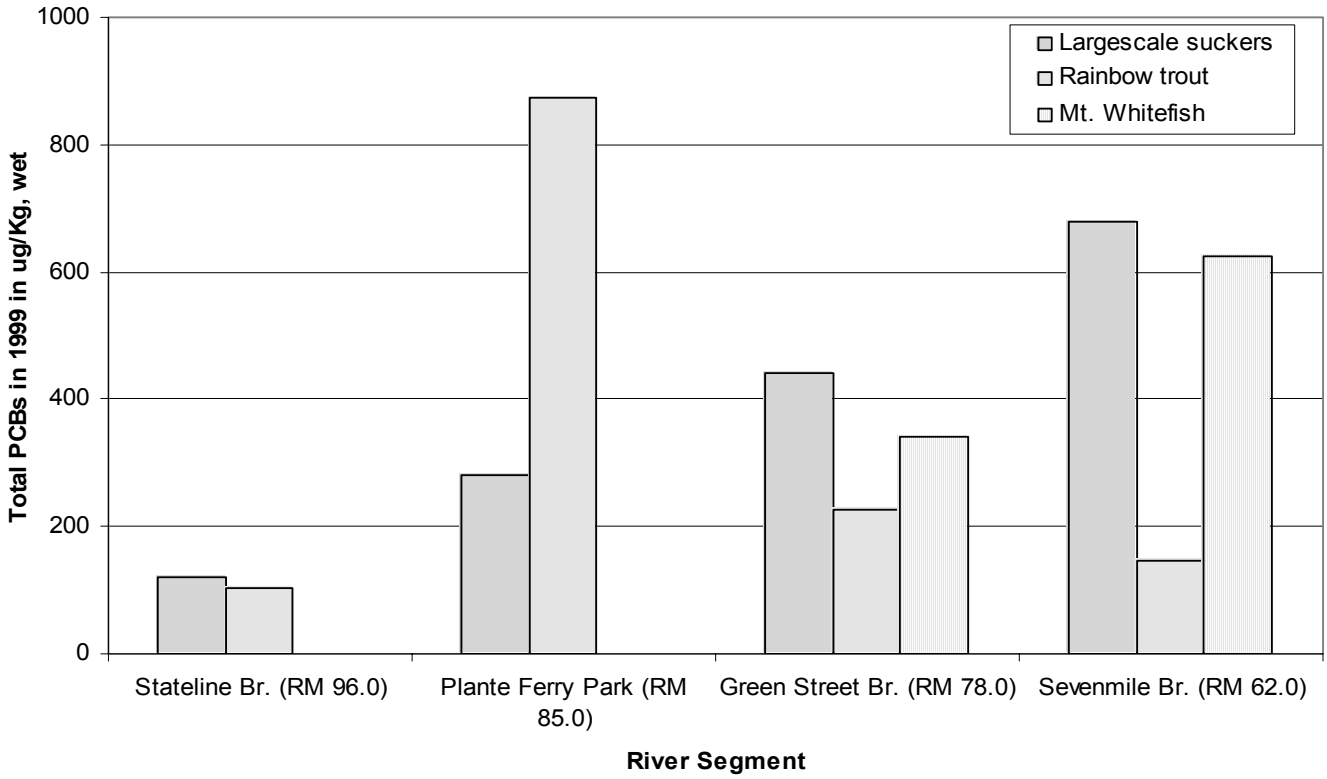

Figure 5. Total PCB concentrations in whole largescale sucker, rainbow trout fillet, and mountain whitefish fillet collected in 1999 from the Spokane River by USGS.

Recent Fish Tissue concentrations

In 2001, Ecology, the Washington State Department of Health, and the Washington Department of Fish and Wildlife 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 µg/Kg, while mountain whitefish fillets ranged from 60 to 89 µg/Kg. 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).

Historic fish tissue concentrations from the 1990s were used as a basis for setting the fish consumption advisory for the Upper Spokane River (Spokane Regional Health District and Washington State Department of Health, 2003) and for documenting the degree to which fish tissues exceed the regulatory limits derived from the NTR.

Historic Effluent PCB Concentrations

Some effluents discharging to the Spokane River have been monitored for PCB concentrations in the past. Ecology (1995), Golding (1996), Golding (2001), and Golding (2002) provide historic concentration data from July 1994 through May 2001. 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.

Table 4. Summary of historic Spokane area PCB point source data for effluent/wastewater samples.

Source	Date	Method	Total PCBs (pg/L)	Identified Aroclor	Effluent Flow (MGD)	Load to River (g/day)
Kaiser Trentwood	05/01/01	congener	**10,174 NJ**	NA	16.4	0.63
"	05/02/01	"	**5,165 NJ**	NA	"	0.32
"	08/14/00	Aroclor	**53,000**	PCB-1248	25.4	5.1
"	"	"	900 U	NA	"	0
"	08/15/00	Aroclor	900 U	NA	"	0
"	"	"	**25,000**	PCB-1248	"	2.4
"	12/05/95	Aroclor	**29,000**	PCB-1248	17.9	1.97
"	"	"	**34,000**	PCB-1248	"	2.30
"	12/06/95	Aroclor	**25,000**	PCB-1248	18.1	1.71
"	"	"	**29,000**	PCB-1248	"	1.99
"	08/01/94	Aroclor	**21,000**	PCB-1248	28.8	2.29
Spokane WWTP	05/01/01	congener	**1,813 NJ**	NA	37.6	0.26
"	05/02/01	"	**1,767 NJ**	NA	"	0.25
Liberty Lake WWTP	05/01/01	congener	**1,917 NJ**	NA	0.649	0.0047
"	05/02/01	"	**1,543 NJ**	NA	"	0.0038
Inland Empire Paper	05/01/01	congener	**2,436 NJ**	NA	4.3	0.040
Inland Empire Paper	06/05/02–a.m.	congener	**5,484**	NA	5.293	0.11
"	06/05/02–p.m.	"	**4,305**	NA	4.752	0.078
Spok. Industrial Park	05/01/01	congener	**9,371 NJ**	NA	*	*
"	05/02/01	"	**7,108 NJ**	NA	*	*
"	07/31/94	Aroclor	9,000 U	NA	*	*
"	08/04/94	"	31,000 U	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
MGD – million gallons per day
* Currently discharges to Spokane WWTP, former discharge to Spokane River.

Historic Surface Water PCB Concentrations

PCBs are difficult to measure in surface waters due to their high K_{ow}s and low solubility. Until recently, analytical techniques were not developed enough to directly detect ng/L (parts per trillion) or pg/L (parts per quadrillion) concentrations of PCBs. In 1994, Ecology separated particulate matter from Spokane River water via a centrifuge and analyzed for PCBs as Aroclor

equivalents (Ecology, 1995). PCBs were not detected in particulate samples upstream from Kaiser-Trentwood (RM 90.5, <67 µg/Kg dry weight) and were found at 220 µg/Kg, dry downstream of Kaiser-Trentwood (RM 84.7, Plante Ferry). Based on the total suspended solids ~0.5 mg/L measured at the time, the latter concentration equals 0.11 ng/L Aroclor equivalents.

In the same study, estimates of soluble PCB concentrations were obtained by deploying semi-permeable membrane devices (SPMDs) near the state line and at Plante Ferry during August 9 – September 14, 1994. SPMDs are passive samplers that take up PCBs by diffusion through a polyethylene membrane filled with a synthetic lipid (triolein). PCB concentrations in the ambient water are estimated from temperature-dependent PCB uptake rates determined in the laboratory.

Results of analyzing the SPMDs showed estimated PCB-1248 concentrations of 0.8 ng/L upstream (State line) and 1.0 – 1.9 ng/L downstream (Plante Ferry). A SPMD study conducted at the same time by Kaiser reported no PCBs detectable above their outfall (<0.2 ng/L) and 1.3 – 1.8 ng/L PCB-1248 below the outfall (Hart Crowser, 1995).

More recently, Kaiser (Anchor Environmental, 2000) deployed SPMDs at five locations in the Spokane River between Harvard Road (RM 93.0) and Riverside State Park (RM 67.0). The sampling devices were left in the river from late July to early September 2000, the low-flow period. Thirty-five of the 209 PCB congeners were analyzed.

Kaiser's results are summarized in Table 5. Kaiser calculated a total PCB concentration based on a correlation developed by the NOAA Status & Trends Program. Estimated total dissolved PCB concentrations in the Spokane River were reported to be <0.1 ng/L above the Kaiser outfall, 0.70 ng/L below the outfall, and 0.33 – 1.25 ng/L downstream of the outfall.

Table 5. Total detected congeners and estimated total PCBs from SPMDs deployed in the Spokane River during 2000 by Anchor Environmental.

	Below Harvard Rd. (RM 93.0)	Above Kaiser Intake (RM 86.2)	Trent Road Bridge (RM 85.5)	Trent Road (duplicate)	Above Greene St. (RM 79.7)	Riverside St. Park (RM 67.0)
Total detected congeners	**0.05 J**	0.1 U	**0.35 J**	**0.22 J**	**0.16 J**	**0.63 J**
Total PCBs*	**0.09 J**	0.1 U	**0.70 J**	**0.44 J**	**0.33 J**	**1.25 J**

Bold – analyte detected
U = analyte was not detected above the method reporting limit
J = analyte was detected in the sample and associated QA/QC samples at similar concentrations.
*estimated from NOAA Status & Trends Program correlation

Historic Sediment PCB Concentrations

Sediments were sampled as part of the Johnson et al. (1994) screening survey of PCBs in the Spokane River. Sediments were also analyzed for PCBs as part of Ecology's (1995) investigation of PCBs in the Spokane River. Sediment PCB concentrations in these investigations were measured as Aroclor equivalents.

The highest concentrations of total PCBs in both investigations were found at RM 80.5, immediately upstream from Upriver Dam. These highly organic sediments (11% total organic carbon) had total PCB concentrations between 2,453 and 4,500 µg/Kg. Sediments further upstream from Upriver Dam (~RM 75) had intermediate total PCB concentrations between 210 and 390 µg/Kg. Sediments furthest upstream and those in Idaho (RM 99.0) had concentrations of less than 15 µg/Kg. Concentrations in Long Lake were relatively low, between 21 and 53 µg/Kg. The lowest concentrations were found in Nine Mile reservoir and the Spokane Arm of Lake Roosevelt, 9.1 to 35 µg/Kg, respectively.

Comparison to Regulatory Thresholds and Bioaccumulation

The relevant regulatory thresholds for water quality impacts to freshwaters from PCBs are specified in the National Toxics Rule (NTR). The NTR applies in states, like Washington, which have not adopted sufficient chemical-specific numeric criteria for toxic pollutants necessary to comply with the federal Clean Water Act. The most recent revisions to the NTR applicable to PCBs were effective December 9, 1999 (40 CFR Part 131).

The NTR specifies an allowable concentration of PCBs in water based on a single bioconcentration factor (BCF) of 31,200 L/Kg which was derived from 21 studies of different Aroclors. This BCF represents an average for freshwater fish and shellfish and considers the uptake of PCBs by these organisms from water only. Using this BCF and average fish consumption data for the United States, USEPA developed a protective water concentration. This water quality criterion is 0.17 ng/L. This criterion is for the human consumption of water and organisms (fish + shellfish). The criterion for the consumption of fish only is also 0.17 ng/L. Because of the large BCF used, the consumption of relatively small water volumes (2 L/day) of water does not influence the criterion and thus they are both the same.

Using the BCF and the water quality criterion, fish tissue concentrations can be derived from the NTR. The derived concentration is 5.3 µg/Kg total PCBs. This tissue concentration assumes 6.5 gms of fish consumption per day and is considered protective of human consumption at the $1x10^{-6}$ cancer risk incidence level. It is the exceedances of NTR fish tissue concentrations which lead to the 303(d) listing of the Spokane River and the Little Spokane River. Recent water quality criteria guidance (USEPA, 2002) uses upwardly revised consumption rates. If and when these consumption rates are adopted into rule, the TMDL will be revised to reflect the new tissue target concentrations.

In 1999, the Seven Mile Bridge area (RM 61.9) had some of the higher PCB fish tissue concentrations. In this reach, whole largescale suckers exceeded the NTR criteria by 128 times. Mountain whitefish fillets exceeded criteria by up to 300 times. Farther downstream, whole largescale suckers in upper Long Lake exceeded the regulatory limits derived from the NTR by about 27 times (Jack and Roose, 2002). While the Long Lake exceedances are lower than found in the reaches upstream from Upriver Dam and Ninemile Dam, largescale suckers and mountain whitefish have been shown to generally represent the two available worst-case species throughout the Spokane River system.

As discussed previously and as recognized by USEPA, fish may accumulate PCBs from a variety of media, including suspended and bottom sediments, prey, and the water column. USEPA has not yet promulgated a bioaccumulation factor (BAF) to describe the multimedia transfer of PCBs to fish tissues.

Table 6 lists the NTR water column criterion and some historic water column measurements. Also shown in Table 6 are the NTR fish tissue standard and historic, worst-case fish tissue concentrations for a similar river reach. The BAFs give some indication of the source of the tissue concentrations. When the BAF is near the BCF (assumed to be 31,200), water column uptake is responsible for most of the tissue accumulation. When the BAF is greater then the BCF, other sources are predominantly responsible for the fish tissue concentration.

Table 6. BAFs calculated from fish tissue and water column PCB concentrations.

LRS Tissue Conc.(µg/Kg)	Water Conc. (ng/L)	BAF	Percent explained by BCF
5.3 (Criteria)	0.17 ng/L (Criteria)	31,200 (BCF)	100%
201(a)	~1.5 (b)	134,000	23%
1210 (a)	1.25 (c)	968,000	3%

LRS=Largescale Sucker
BAF=Bioaccumulation Factor
BCF=Bioconcentration Factor
(a) Total apparent Aroclors (Ecology, 1995)
(b) Estimated from SPMDs (Ecology, 1995)
(c) Estimated from SPMDs (Anchor Environmental, 2000)

Table 6 illustrates that the degree to which water quality standards are impaired as measured by SPMDs does not necessarily reflect the degree to which fish tissue concentrations exceed values derived from the NTR. This is probably due to variability surrounding the average BCF used by USEPA in the NTR, the presence of uptake pathways for PCBs to fish other than water column exposures, and the persistence of PCBs in fish tissues which reflects their current and historic exposures. Hart-Crowser concluded similarly in 1995 that current surface water discharges may explain less than 10% of the fish tissue concentrations.

The BAFs in Table 6 illustrate that current water column concentrations may only explain one-quarter or less of the current fish tissue concentrations. Sediment, for some river reaches, may be responsible for much of the fish tissue PCB concentrations. Sediment to biota bioaccumulation may vary considerably on a site-specific basis. Mathematically, a biota-sediment accumulation factor (BSAF) is simply a tissue concentration divided by a sediment concentration. Data for BSAFs may be either lipid/organic carbon normalized or in dry or wet weight basis.

Ranges of BSAFs are available in a metadata analysis conducted by PTI (1995). It is unclear whether these BSAFs were derived from total organic carbon (TOC) and lipid normalized data; however, subsequent calculations using these BSAFs have used lipid TOC/lipid normalized data. Both high end and low range BSAFs have been incorporated into Table 7, which illustrates the degree to which sediment may contribute to fish tissue concentrations in a Long Lake example.

Table 7. Potential range of mean sediment to high and low estimated fish bioaccumulation in Long Lake (data from Ecology, 1995).

BASF range (PTI, 1995) (a)	Mean Sediment Concentration µg/Kg TOC (b)	Expected Tissue Concentration (a*b=c)	Actual LRS Tissue Concentrations (d)	Percent Difference (d/c=e)
0.1	1,992 µg/Kg, TOC	199 µg/Kg, lipid	17,826 µg/Kg, lipid	8949%
90	1,992 µg/Kg, TOC	179,000 µg/Kg, lipid	24,118 µg/Kg, lipid	13%

LRS=Whole Largescale Sucker

This range of potential sediment influences is about three orders of magnitude. Using the mean whole fish and mean sediment concentrations from Ecology's (1995) data, a lipid/TOC normalized BSAF of 10.9 may be derived. But as Table 7 illustrates, this value may vary by orders of magnitude. A site-specific BAF/BSAF model which incorporates paired data of effluent, water column, sediment, and fish would reduce the uncertainty surrounding the proportional contributions of water and sediment to fish tissue PCB concentrations in selected reaches.

This QA Project Plan describes the collection of paired effluent, surface water, sediment, and fish data to develop a site-specific conceptual bioaccumulation model. The sections below will detail the media to be sampled and further rationale for their selection. The preparation methods and analytical methods for each media will also be described.

Responsibilities

Clients – Ken Merrill (509/329-3515) and John Roland (509/329-3581)

Project Lead – Dave Serdar (360/407-6772)

Sample Collection and Preparation – Dave Serdar and Steve Golding (360/407-6701)

Toxic Studies Unit Supervisor – Dale Norton (360/407-6765)

Watershed Ecology Section Manager – Will Kendra (360/407-6698)

Quality Assurance Manager – Cliff Kirchmer (360/407-6455)

Manchester Laboratory Director – Stuart Magoon (360/871-8801)

Contract Laboratory Manager at Manchester – Karin Feddersen (360/871-8829)

Schedule

Draft QA Project Plan – February 2003
Internal review – February-March 2003
External Review – July-September 2003
Final QA Project Plan – October 2003
Sampling – September 2003 – May 2004
Laboratory Processing ongoing after sampling – June 2004 (performed at Ecology HQ)
Chemical Analysis Complete – August 2004
Draft Ecology Report – December 2004
Data entered in EIM and/or SedQual – February 2005
Final Ecology Report – May 2005

Measurement Quality Objectives

Accuracy, Bias, and Precision

In an effort to minimize bias, Puget Sound Estuary Program (PSEP; USEPA, 1997) guidelines for collecting, preserving, transporting, and storing sediment and tissue samples will be followed. Acceptable accuracy will vary depending on the analyte (Table 8), while goals will principally be evaluated through the analysis of matrix spikes and laboratory control samples. The goal for precision will be from 10 to 20% RSD. The precision goals are subject to some discretion, depending upon the results relative to the detection limits. Table 8 summarizes the analytical accuracy, bias, and precision goals for the project, while Table 9 shows the necessary reporting limits.

Table 8. Analytical goals for the Spokane River PCB TMDL analysis.

Parameter	Accuracy (% Deviation from True Value)	Bias	Precision (RSD)
PCB congeners	30%	±5%	15%
PCB Aroclors	50%	±10%	20%
% lipids	[a]	[a]	20%
Total Organic Carbon (104 C)	[a]	[a]	20%
Grain Size	20%	-	10%
Cs-137	20%	-	10%
Pb-210	20%	-	10%

RSD = Relative Standard Deviation
[a] = Evaluated Qualitatively

Table 9. Necessary reporting limits by media for the Spokane River PCB TMDL analysis

Matrix	Analyte	Required Reporting Limit (Maximum)
Effluents, Stormwater, and Whole Water	Total PCB Homologs	0.4 ng/L
	PCB Congeners	0.4 ng/L each
	TSS	1 mg/L
Surface Waters (via SPMD extractions)	Total PCB Homologs	0.01 ng/Kg SPMD triolein
	PCB Congeners	0.1 ng/L each
	DOC	1 mg/L
	TOC	1 mg/L
	TSS	1 mg/L
Sediment and Suspended Particles	Total PCB Homologs	0.4 µg/Kg
	PCB Congeners	0.4 µg/Kg each
	PCB Aroclors	50 µg/Kg each
	Grain Size	±0.5% for each fraction
	TOC	0.5%
	Cs-137	-
	Pb-210	1 dpm/g
Fish Tissues and Gut Contents	Total PCB Homologs	0.4 µg/Kg
	PCB Congeners	0.4 µg/Kg each
	% lipids	±0.1 %

dpm = disintegrations per minute

Project Design and Field Methods

The absence of a close relationship between water and tissue concentrations and the variability between river reaches described in the synoptic data shown in Figure 4 is likely a function of several variables. These variables will be considered further in the planning of the PCB TMDL sampling:

- Sources in Idaho
- Atmospheric deposition across the entire watershed
- Point sources within the city of Spokane
- Sediment deposition areas
- Contaminated sediment source areas
- Clean sediment sources which may bury and/or dilute contaminated sediment
- Fish species differences
- Fish age
- Fish sex, with females having the potential to excrete PCBs during egg laying
- Temporal lags between media, with water having the most temporally variable data, and fish the least. Potential temporal changes in sediment concentrations are unknown.

The lack of agreement between the BCF and PCB concentrations in water and fish tissue has been recognized by USEPA (2000), and BSAFs have been recommended for hydrophobic contaminants. Additionally differences in reservoir productivity probably influence particulate and dissolved organic carbon concentrations and may further influence the solubility of PCBs in water or their partitioning between abiotic and biotic contaminant pools.

Because of the variability and lack of proportionality between media and NTR standards, this TMDL proposes to synoptically sample a variety of media for PCB congeners and Aroclors. This analysis will be used to derive a site-specific BAF/BSAF for PCBs for the most vulnerable river reaches. To assist with the use of historical data, some Aroclor equivalent analyses will also be conducted.

Aside from sediment sampling at the request of the Spokane Tribe, the Spokane Arm of Lake Roosevelt will not be sampled. The Spokane Arm is predominantly part of the Lake Roosevelt impoundment, which was formed by the damming of the Columbia River. The Spokane Arm is 303(d) listed for PCBs. This study will not directly monitor or estimate the concentrations of PCBs in the Spokane Arm. However, because this reach is downstream from the principle PCB sources within the city of Spokane and Long Lake, attainment of water quality and fish tissue criteria in the upstream reaches should allow attainment of water quality and fish tissue criteria below Long Lake. This includes those portions of the Spokane River within Spokane Tribe jurisdiction and downstream into the Spokane Arm.

Representativeness

The objective of the study is to describe the prominent pathways of PCB transfer through water and sediment into fish tissues, and, to the extent possible, to predict the level of PCBs in water and sediment that will lead to fish tissue concentrations below NTR standards.

Water samples will be collected to represent both long-term average surface water concentrations of PCBs and to represent average effluent and stormwater concentrations. Fish samples will represent different size classes of largescale suckers and rainbow trout. Male and female fish will be segregated. Samples of fish gut contents will represent PCBs in fish diet. Surface (2cm) sediment collections will represent current sediment deposits and current largescale sucker exposures. Suspended particles will be collected to represent particle-bound transport of PCBs in the water column. Sediment cores will be collected to represent temporal sediment trends. Water, fish, and sediment concentrations are only intended to represent conditions in the Spokane River system, although any BAF/BSAF derived may be useful for other PCB studies in Washington.

Comparability

Sampling methods will be consistent with PSEP protocols (USEPA, 1997) and prior fish sampling in the upper Spokane River. Thus, results from this study should be comparable with previous studies on the upper Spokane River and Long Lake. Some composites will be different from those used in previous studies. The composites, stratified by sex and size class, will allow

for greater accuracy and precision in estimating the mean tissue concentrations in different size/age classes of the selected fish species.

Prior studies on the Spokane River have not always analyzed for PCB congeners. However, the proposed congener analytical methods are industry standards, and the 209-congener list is consistent with prior Environmental Assessment Program studies and is the most comprehensive. Some congeners co-elute in this analysis; however, there is no known way to distinguish these compounds analytically.

NPDES Effluents, CSOs, and Storm Drainage

Only selected NPDES dischargers will be directly sampled for PCBs based on historic sampling results, the type of industry, and their potential for PCB use and/or disposal (Table 10). Land applied or groundwater NPDES discharges will not be sampled, unless they are PCB generators and have the potential to be PCB sources via groundwater migration to the Spokane River.

Table 10. Proposed industrial and municipal WWTPs for grab-composite PCB sampling.

Facility	Permit Number	River Mile	Flow as measured by Golding (2002)
City of Spokane WWTP	WA0024473B	64.4	37.6 MGD
Inland Empire Paper	WA0000825B	82.5	4.3 MGD
Kaiser Trentwood	WA0000892B	86.0	16.4 MGD
Liberty Lake Sewer District WWTP	WA0045144B	92.7	0.649 MGD

CSOs and storm drains will be selected for sampling based on their potential for PCB discharges, with type of land use in the service area as the primary consideration since there is little or no history of PCBs being detected in Spokane CSO or storm drains. A total of five CSO and/or storm drains will be sampled during two storm events. Selection of sampling locations will be made during October 2003.

For Kaiser Trentwood, samples will be collected from the final effluent as well as upstream of the settling pond to assess the effectiveness of particle removal on PCB concentrations. Two-day grab composites will be collected from the NPDES facilities listed in Table 10. The sampling of NPDES effluents will occur during the same week to allow for comparisons between the waste loads. The sampling events will be spaced throughout a calendar year to capture variation in flows induced by infiltration into the stormwater and sewer system, and variations in the quantity of water entering the facilities. Thus, effluent sampling will occur during April, October, and December-January. These time periods are paired with the SPMD sampling described below.

NPDES effluents, CSOs, and storm drainage will be sampled by dipping a precleaned glass quart container into the waste stream, either by hand or with a stainless steel pole. These quarts will be combined into a single gallon container. The compositing will occur at the time of the final day's collection, and the jars will only be opened for compositing at the collection site. Two-day

grabs will include two quart grabs per day at approximately the same time. CSO and storm drain samples will be composited over the course of several hours.

The gallon container represents a grab-composite concentration and will be analyzed for PCB congeners. Aroclor equivalents will be derived by the analytical laboratory using the congener patterns of Frame et al. (1996). Flow at the time of each subsampling event will be recorded, and the arithmetic average flow will be used in subsequent loading calculations. In addition, TSS will be measured in effluents at the time of each subsampling event and during the storm events for stormwater sampling.

Some of the other facilities listed in Table A1 were eliminated from effluent testing because they only discharge to groundwater ("ST" permits), or they have permits for activities which are unlikely to discharge PCBs. For instance, the Avista Corporate Headquarters uses river water for cooling and is permitted to discharge warmer waters back to the Spokane River. Newman Lake Flood Control District has a NPDES permit to inject alum into Newman Lake for phosphorus removal.

Sampling days will not be announced to the facilities prior to arrival. Sampling at each of the four facilities will occur during business hours only.

Surface Water

Surface waters will be sampled using semipermeable membrane devices (SPMDs), whole water, and suspended particles. SPMDs use a polyethylene membrane filled with a synthetic lipid to mimic biological uptake of organic compounds. The devices proposed for the current study were developed by the U.S. Geological Survey, Columbia Research Center. They are now a patented, standardized design, and commercially available through Environmental Sampling Technologies (EST), St. Joseph, Missouri (http://www.spmds.com). Ecology previously had limited but successful experience using SPMDs to sample PCBs in the Spokane River (Ecology, 1995) and is currently using them in studies of the Walla Walla River and Lake Chelan.

The SPMD is a thin-walled flat polyethylene tube filled with triolein, the major neutral lipid in fish. When placed in water, dissolved lipophilic organic compounds diffuse through the membrane and are concentrated over time. The typical deployment period is 20-30 days. SPMDs are then extracted and analyzed for chemicals of interest.

Semipermeable membrane devices will be deployed for 25 to 30 days during three river flow seasons. This approach will physically average surface water concentrations and provide a year's worth of data to match effluent concentrations. The SPMD deployments are timed to provide representative data over the range of flow, runoff, and temperature conditions typically occurring in the mainstem of the Spokane and in the lower Little Spokane River.

Two SPMDs will be deployed in each of the five river reaches in Table 11. The seasons for deployment include spring high water in April, warm low-flow condition in September-October, and cold moderate-flow conditions in December-January. The flow periods chosen are not the yearly flow minima and maxima, as these months are intended to represent the entire seasonal period, not only the annual variability. Literature suggests that the accumulation of PCBs takes

more than a month to reach steady state (Fisk et al., 1998), depending on log K_{ow}. This suggests that short-term flow variation and/or low-flow conditions are not likely to produce a critical condition.

Table 11. River Reaches for SPMD Sampling

Location	Upstream river mile	Downstream river mile
State line	RM 96.1 (ID border)	RM 93.0 (0.3 mile upstream from Liberty Lake WWTP)
Upriver Dam	RM 82.5 (Downstream of Inland Empire and Kaiser discharges)	RM 80.2 (Dam)
Monroe St./Upper Falls Dam	RM 75.5 (1 mile upstream from Upper Falls Dam)	RM 74.5 (Dam)
Nine Mile Dam	RM 62.9 (Downstream from Spokane River WWTP)	RM 58.1 (Dam)
Lower Long Lake	RM 39 (5 miles upstream from Dam)	RM 33.9 (Dam)
Little Spokane River	RM 8 (8 miles upstream from mouth)	RM 1

The exact SPMD positions have not been specified to allow for some field discretion to minimize the potential for vandalism. Generally each season's SPMD deployment will include the use of two SPMD canisters near mid-column within each selected river reach. The dual canisters will minimize the risks of loss or vandalism. Reaches with minimal apparent risk of loss will have only one SPMD with three membranes deployed.

SPMDs will be deployed at two locations in the Upriver Dam reach; one deployment near mid-column and the other within one meter of the bottom to determine if proximity to highly contaminated sediments results in differences of PCB uptake.

Within each canister, three membranes will be deployed to ensure sufficient residue for analysis. If both canisters are successfully recovered, the triolein within the sox membranes will be combined for extraction. During each deployment period, one of the SPMD pairs will be analyzed separately as a field duplicate.

One additional SPMD will be deployed in the lower two miles of Deep Creek. The Deep Creek watershed includes facilities such as Fairchild Air Force Base and the City of Medical Lake WWTP. The SPMD station in lower Deep Creek will be able to integrate these varied sources and determine their aggregate relative contribution of PCBs.

During the deployments, temperature will be monitored at half-hour intervals throughout the deployment using a Tidbit® temperature logger adjacent to the SPMD canister. At the beginning, middle, and end of the deployment period, total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) will be analyzed. When measurable concentrations of TOC are present, the total (dissolved + particulate) PCB concentration in water will be estimated using the procedures outlined in Meadows et al. (1998). These corrections are required because SPMDs only directly measure the dissolved fraction of contaminants in the water column.

Whole water and suspended particles will be analyzed at several locations to assess water column PCB concentrations downstream of the major known point sources (Table 12). Suspended particles are a useful surrogate for whole water sampling because organic hydrophobic chemicals such as PCBs preferentially sorb to particulate matter.

Table 12. River reaches for whole water and suspended particle sampling.

Location	Upstream river mile	Downstream river mile
Harvard Rd.	RM 92.7	RM 92.0
Plante Ferry	RM 84.8 (Downstream from Kaiser)	RM 84.6 (Myrtle Pt.)
Nine Mile Dam	RM 62.9 (Downstream from Spokane WWTP)	RM 58.1 (Dam)

Suspended particles will be collected using a Sedisamp II continuous-flow centrifuge (model 101IL) in a manner described by Serdar et al. (1997) and previously used to collect particle in the Spokane River (Ecology, 1995). Water will be pumped from an intake situated in the middle of the water column. All tubing will be composed of Teflon® unless a peristaltic pump is required, in which case Silastic® tubing will be used on the pump head. Centrifuge bowl parts are constructed of high quality stainless steel.

Collection will occur over a period of several days, depending on TSS concentrations. Sampling will be done in mid-October to coincide with the intial deployment of SPMDs. Particulate matter accumulated by the centrifuge will be scraped from the centrifuge bowl and placed into appropriate sample containers.

Water samples will be collected from centrifuge intake and outlet water to measure particle removal efficiency, which has been measured at nearly 100% using this model centrifuge in previous work. Whole intake water will also be collected periodically during the course of centrifugation to yield a composite whole water sample. Whole water samples will be analyzed to test agreement between PCB water concentrations calculated from the particulate fractions. Whole water will be collected in a manner similar to that previously described for sampling NPDES effluent samples. Ancillary analysis will include TSS and TOC in water, and TOC in suspended particles.

Sediment

Surficial Deposits

Surface sediment samples will be collected from an Ecology boat using a 0.1 m^2 stainless steel van Veen or a 0.01 m^2 Petite Ponar grab sampler. Sampling sites will be field located using GPS and upland landmarks within the river reaches shown in Table 13. The reach between the state line (RM 96.1) and Upriver Dam (RM 80.2) will not be sampled for sediment because this river reach is predominantly composed of cobble and large rocks, except for the heavily contaminated sediments near the forebay of Upriver Dam which are being extensively examined. Sediments just upstream of Monroe St. Dam will be sampled because there are few data on sediments in this reach and they will complement other sampling in this reach. In Long Lake, previous

investigations have concluded that a PCB concentration gradient exists in sediment (Johnson and Norton, 2001). The gradient may be due to inputs of cleaner sediment from Latah Creek and the Little Spokane River. Because of the potential for a gradient in the 23 mile long reservoir, additional surface sediment composites will be conducted in this portion of the river. Long Lake will be divided into three reaches, each five miles long.

Table 13. River reaches for surficial sediment sampling

Location	Upstream river mile	Downstream river mile
Monroe St./Upper Falls Dam	RM 76.0 (upstream of Trent Ave.)	RM 75.3 (downstream of Trent Ave.)
"	RM 73.2 (1 mile upstream from Dam)	RM 74.2 (Dam)
Long Lake	RM 39 (5 miles upstream from Dam)	RM 33.9 (Dam)
"	RM 46	RM 41
"	RM 54	RM 49
Little Falls Pool	RM 33.9	RM 29.3
Spokane Arm	RM 29	RM 25
"	RM 23	RM 21
"	RM 21	RM 19
"	RM18	RM 16
Little Spokane River	RM 8 (8 miles upstream from mouth)	RM 1

Target coordinates for each station will be generated prior to the field collection, although a paucity of sediment in some river reaches will likely necessitate field selection of the sediment stations. A field log will be maintained during sampling. See Appendix B for a sample log book page.

Grabs will be considered acceptable if the sampler is not overfull, overlying water is present and not significantly turbid, the sediment/water interface is relatively flat, and at least 5 cm of sediment depth is present. Not all locations in the river have sufficient fine sediment for collection with a grab sampler. Sample collection locations will be positioned between the river mile locations and considered representative of the available fine sediment for the entire river reach. To the extent practicable, five grabs will be taken over a 300 yard longitudinal reach within the segments shown in Table 13. The multiple grabs will serve to physically average surface sediment concentrations over a reasonable area and provide enough material for analysis. Only the top 2 cm of sediment will be collected for analysis, representing the ongoing fish exposure medium.

Sediment Cores

Two sediment cores will be collected from Long Lake to describe trends in historic PCB deposition. Core data will also be used to estimate sediment recovery rates. The cores will be collected using a stainless steel box corer from two Long Lake locations, one about RM 35 and RM 51. The box corer has a 13 cm by 13 cm opening (0.017 m^2) and a 50 cm length. Yake (2001) has reviewed other sediment coring efforts in Washington State and reports that

sedimentation rates vary from 0.18 to 0.45 cm/yr. Long Lake is likely at the high end or exceeds this range based on the episodic discharges of highly turbid water from Latah Creek (SCCD, 2002). Therefore, the 50 cm core length should retrieve approximately the previous 80-100 years of sediment deposition. This time period can be dated using the lead and cesium methods proposed below, and it is relevant for describing the deposition of PCBs, which were first produced in the U.S. in 1929.

The box corer will use a precleaned acrylic liner dedicated to each station. The cores will be extruded from the liner in the field, and the outer layers of sediment will be removed with a precleaned stainless steel spatula. This will prevent any outer smeared portion of the core from influencing the stratigraphy.

The sediment cores will only be partially radiodated if the cores exhibit varves or distinct stratigraphic layers corresponding to events of a known time horizon (e.g., ash from the Mt. St. Helens eruption of 1980). This will be used to confirm the time periods determined from any sediment layers. If no distinct layers are visible, radiodating will be more comprehensive. Both cesium-137, a relic of atmospheric atomic testing, and naturally occurring lead-210 will be analyzed in the cored sediments. The combination of both dating methods are suitable for dating back to the time of initial (1929) and peak (1950s) United States PCB production. The Long Lake Dam was constructed in 1914.

Regardless of the method used to establish chronology, the cores will be sectioned in 1 cm increments. Ten of these increments will be analyzed for PCB Aroclors, and the remainder will be archived for possible future analysis. Aroclors will provide an estimate of temporal PCB trends without the high cost of congener analysis. Later project budgets have used the ten section estimate for costs. Core sections will be placed into precleaned glass jars and held frozen pending radiodating results.

Following the radiodating, representative time periods (sections) within the core will be submitted for PCB Aroclor analysis. The selection of time periods will emphasize the past 50 years to describe changes in PCB sediment burdens and provide estimates of sediment recovery rates. The delay in analyzing the sediment for PCBs should not bias the results, as PCB holding times are one year. To provide matching TOC values, the core sediments will need to be frozen to provide a 6-month holding time.

Fish Collection

Fish will be collected using electrofishing, gill, and possibly fyke netting techniques. Depending on field success and fishing conditions, non-lethal collection methods will be used to the extent possible. The non-lethal methods will allow for the lowest possible by-catch. Two species will be collected, largescale suckers and rainbow trout. Whole largescale suckers have exhibited some of the highest concentrations of PCBs throughout the upper portions of the Spokane (USGS, 1999), and also in Long Lake (Jack and Roose, 2002). They are also consumed by some minority populations in the Spokane area. Rainbow trout are present throughout the Spokane River and are considered one of the premier game fishes in many reaches. They too have exhibited consistently elevated PCB concentrations in some reaches (Ecology, 1995; Johnson, 2000).

Largescale suckers predominantly feed on benthos and periphyton (Dauble, 1986). They typically graze on the tops and sides of cobbles and have been observed to ingest sediment and expel it through the gills, as if straining food. These life history traits suggest that suckers are predominantly exposed to sediments. As such, largescale suckers should be considered an omnivorous herbivore. For comparison, rainbow trout predominantly consume immature aquatic insects such as mayflies, stoneflies, beetle larvae, and caddis flies. They may also eat amphipods, small fish, and fish eggs (Wydoski and Whitney, 1979). Rainbow trout are not reported to be herbivores and are considered to be a secondary consumer. The two different feeding habits of these species suggest that they may accumulate PCBs from the water column or sediment differently.

Both species are targets for the TMDL, although different tissues will be analyzed. Largescale suckers will be analyzed whole because PCBs concentrations are generally higher in whole fish than fillet. Surveys of local consumption patterns in the Spokane region have illustrated that certain minority populations consume more than just fillet tissue (Spokane Regional Health District, 1998). Rainbow trout will only have their muscle (fillet) tissue analyzed. Skin-on fillets will be analyzed, which reflects a typical angler preparation method.

In addition to tissues, gut contents will be analyzed from both species to assess the potential for PCB exposure through diet. Gut contents from adult suckers and rainbow trout will be sampled from fish collected in the Plante Ferry and Long Lake reaches using standard operating procedures (SOPs) developed by the Washington Department of Fish and Wildlife. Each sample will be a composite of gut contents from 10 specimens of each species at each site. Specimens used to obtain gut contents will not be those used for tissue analysis.

Largescale Suckers

Fish length will be measured in the field, and two subpopulations will be segregated: between 250 and 350mm fish, and <200mm fish. While the exact fish ages within these sizes classes will not be known until after processing, the two size classes are intended to represent the intermediate and youngest segments of the largescale sucker population. As shown in Figure 6, fish less than 200mm should be second year fish, representing ongoing PCB exposures. Fish between 250 and 350 mm will be 3- to 5-year-old fish. Their PCB body burdens will reflect a combination of current and relatively recent exposures (within five years). These size ranges of fish are younger than have been sampled by Ecology in the past. The rationale for this choice is the longevity of largescale suckers and the potential for certain congeners to be highly resistant to metabolic action/excretion. Literature suggests that ortho- and meta-chlorinated PCBs half-lives are lower in smaller fish (Niimi and Oliver, 1983; Coristine et al., 1996) and range up to about 130 days. Thus, these smaller fish are more likely to be in equilibrium with current PCB sources. Jack and Roose (2002) found elevated levels of particularly metabolically resistant congeners in largescale suckers from Long Lake.

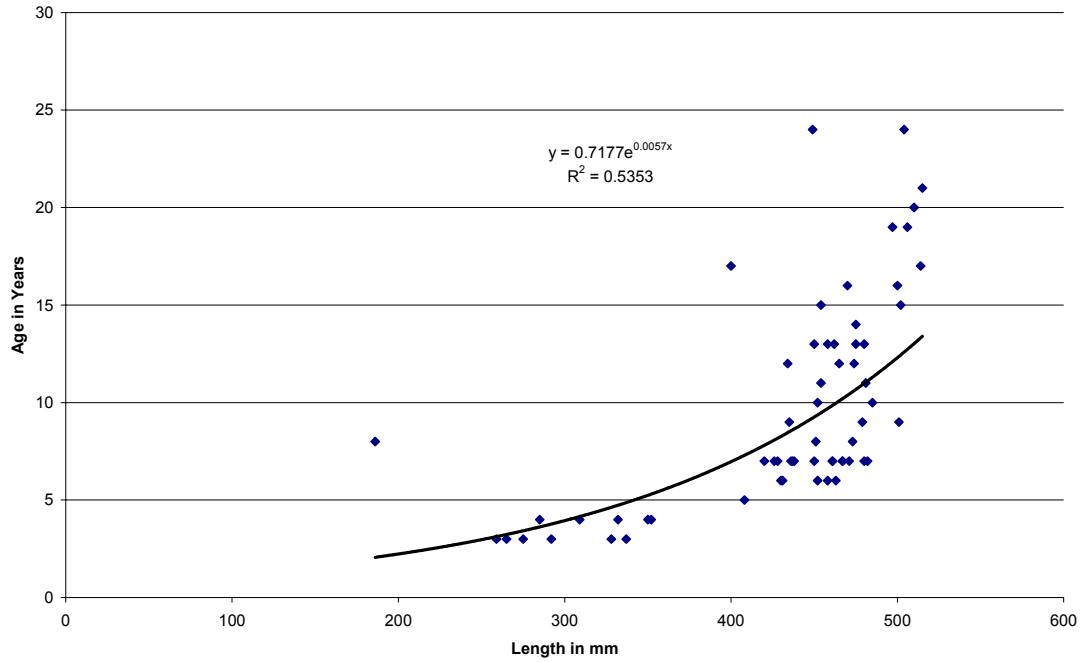

Figure 6. Largescale sucker length vs. age relationship for Long Lake. Data from Jack and Roose (2002) combined upper and lower Long Lake largescale sucker population.

The two different size/age classes will assist with evaluating the potential for the presence of growth dilution. Growth dilution occurs when a fish grows faster than the accumulation rate of the contaminant of concern. Largescale sucker growth rates from published literature may be used to evaluate this concern if warranted.

The size classes will be collected from four locations within the Spokane River system, and five fish will be in each size/sex class. Thus, a minimum of 80 largescale suckers will require harvesting. Fish will be collected in the fall of 2003. Table 14 describes the sampling locations and numbers of fish in each composite. The < 200 mm fish will be immature and will not have had the opportunity to depurate PCBs via spawning (Wydoski and Whitney, 1979) so they will not be sexually segregated. For historical comparability, locations are similar to the extent practicable to those used by Ecology (1995) and Johnson (2000).

Table 14. Largescale sucker composite size and classes by locations.

Location (river reach)	250-350mm 3-5 years	<200mm <2 years	Total by Location
State line	5 male, 5 female combined into one composite	10 fish, as one composite	20 fish
Upriver Dam (Plante Ferry)	5 male, 5 female combined into one composite	10 fish, as one composite	20 fish
Nine Mile Dam	5 male, 5 female combined into one composite	10 fish, as one composite	20 fish
Long Lake	5 male, 5 female combined into one composite	10 fish, as one composite	20 fish

Realistically, additional fish may need to be collected because fish sex cannot be determined until after euthanasia and dissection. Additional fish will also need to be collected for a field duplicate. To minimize the number of fish needed, fish will be euthanized in the field and immediately opened to verify their sex. Sampling will continue until five individuals have been collected from each sex. It is also recognized that largescale suckers <200 mm have not been typically seen in large numbers in the Spokane River, and therefore capturing enough to meet sample size requirements may require extraordinary effort.

Rainbow Trout

For wild rainbow trout, Johnson (2000) found a poor correlation between total lengths and age in a sample of 19 fish from Greene St. (RM 77.0) and at Seven Mile (RM 63.0). All fish were ≥ 250 mm and from one to three years in age. Some of the one-year-old fish had spawning checks on the scales indicating reproductive maturity. Although rainbow trout typically reach maturity at three years, one to five years is considered the range according to Wydoski and Whitney (1979). Therefore, rainbow trout ≥ 250 mm will be considered suitable for pooling into composite samples.

Table 15 shows the river reaches proposed for rainbow trout sampling. Thus these samples have been segregated by sex to ensure that sex-specific depuration of PCBs from their tissues does not bias the results. Future trend monitoring will potentially be able to determine differences between samples more easily, due to the size and sex stratification of fish samples. This strategy has been recommended by other investigators to minimize the covariability associated with size and contaminant concentrations (Evans et al., 1993).

Table 15. Rainbow trout composite size and classes by locations.

Location	≥ 250 mm	Total by Location
State line	10 male, 10 female, two composites	20 fish
Upriver Dam (Plante Ferry)	10 male, 10 female, two composites	20 fish
Nine Mile Dam	10 male, 10 female, two composites	20 fish
Long Lake	10 male, 10 female, two composites	20 fish

After sexing each fish, the entire fish will be double wrapped in aluminum foil and transported on ice to Ecology headquarters in polyethylene bags. Fish will be frozen at -18º C upon arrival. When ready for processing, fish will be partially thawed, and scales, opercles, and/or otoliths will be removed for aging based on the recommendations of the Washington Department of Fish and Wildlife biologists. Fish structures will be aged by Fish and Wildlife.

Rainbow trout will have their fillet tissue removed and equal mass aliquots of tissue will be used in each composite. For largescale suckers, all fish will be processed whole in a Hobart commercial meat grinder, and equal aliquots of tissue will be combined to form the composites.

Exact fish collection locations will not identified in the field, but fish will be assigned to river reaches. To facilitate tissue data entry into Ecology databases, the approximate midpoint of the sampled river reach will be determined using maps or Arcview. All fish collected within a reach will be assigned this location point.

Table 16 shows a summary of sampling discussed in the previous sections.

Table 16. Summary of the types, numbers, and locations of samples to be collected for the Spokane River PCB TMDL.

Location	River mile	SPMDs	Effluent	Stormwater/CSO	Whole water	Suspended particulate matter	Sediment core	Surficial sediments	Largescale sucker	Rainbow trout	Gut contents
State line	96.1 – 93.0	3							2	2	
Harvard Rd. – Trent Rd.	93.0 – 85.3		6		1	1					
Plante Ferry	84.7		3		1	1			2	2	2
Behind Upriver Dam	82.5 – 80.2	6									
Monroe St. Dam	74.5 – 75.5	3	3	10[a]				2			
Ninemile Dam	62.9 – 58.1	3			1	1			2	2	
Long Lake	58.1 – 33.9	3					2	3	2	2	2
Little Falls Pool	33.9 – 29.3							1			
Upper Spokane Arm	29.3 – 16.0							4			
Little Spokane R.		3						1			
Deep Creek		3									

a – locations not yet determined

Sample Equipment Preparation

Prior to sampling, all stainless steel sampling implements including the van Veen and the box corer will be cleaned by sequentially:

1. Wash in Liquinox detergent and hot tap water
2. Rinse with hot tap water
3. Rinse with deionized water
4. Rinse with pesticide grade acetone
5. Air-dry
6. Rinse with pesticide grade hexane
7. Air dry

After drying, equipment will be wrapped in aluminum foil until used in the field. Sampling equipment will be dedicated to the station and will only be used at subsequent stations following cleaning per the above procedures.

All sample containers will be precleaned to USEPA (1990) QA/QC specifications. Sample for PCB analysis will be in glass jars with Teflon lined lids. All samples will be cooled to 4º C immediately after collection and transported under chain-of-custody protocols.

Semipermeable membrane devices will be stored frozen in an argon atmosphere prior to deployment. The membrane canisters will be cleaned as described above, and the membranes will be inserted into the canisters in the field. A trip/field blank will be used during each SPMD deployment.

Tissue Preparation

Preparation of tissue samples will follow USEPA (1997, 2000) guidance. The techniques described below will be used to minimize the potential for sample contamination and cross-contamination.

All resection and homogenizing will use only non-corrosive stainless steel implements. Persons preparing samples will wear non-talc polyethylene or nitrile gloves and work on aluminum foil or a polyethylene cutting board. Gloves and foil will be changed between samples. The cutting board and knives will be cleaned using Liquinox® detergent and hot tap water, followed by rinses with deionized water, pesticide grade acetone, and pesticide grade hexane. Implements will be air dried in a fume hood before use.

Fish will be thawed only enough to remove their aluminum foil wrapping and aging structures. Fish will then be rinsed with deionized water and ground whole in a Hobart commercial meat grinder including all scales, bones, slime, and associated liquids. All composite samples, by species, will contain equal numbers of fish. Each composite sample will contain at least 100 grams of tissue, comprised of an equal mass from each fish.

The meat grinder will be cleaned between samples with Liquinox®, acetone, and hexane using the same procedures described above for cutting boards and knives. Each sample will be divided

into sample jars to facilitate laboratory handling and extraction. The minimum mass per container and holding time will be as shown in Table 17.

Table 17. Containers and holding times by parameter for Spokane River PCB 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 Particles	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)
"	Cs-137	-	Provided by contract lab	-
"	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)

TSS = total suspended solids
SPMD = semi-permeable membrane devices
TOC = total organic carbon
DOC = dissolved organic carbon

Analytical Methods

Percent lipids, Aroclors, and TOC in sediments, organic carbon, and solids in surface waters will all be analyzed at Manchester Laboratory. The 209 PCB congeners, Pb-210, Cs-137, and grain size will be analyzed at a commercial laboratory. Analytical methods are suggested in Table 18. Other methods may be used at the discretion of Manchester or the contract laboratory after consulting with the project lead.

Table 18. Preparation methods, analytical methods, and required reporting limits for the Spokane River PCB TMDL investigation.

Media	Parameter	Preparation method	Analytical method	Required reporting limit
Effluent, Stormwater	PCB Congeners	-	GC/HRMS, EPA Method 1668A	0.1 ng/L per congener
"	TSS	-	EPA Method 160.3	1 mg/L
Surface Water	PCB Congeners	-	GC/HRMS, EPA Method 1668A	0.1 ng/L per congener
"	SPMD extract (PCB Congeners)	EST dialysis	GC/LRMS, EPA Method 8082/1668A, modified	0.4 ng/g SPMD, ~1-3 pg/L water
"	TOC	-	EPA Method 415.1	1 mg/L
"	DOC	-	EPA Method 415.1	1 mg/L
Suspended Particles	PCB Congeners	Soxhlet extraction	GC/LRMS, EPA Method 8082/1668A, modified	0.5 µg/Kg per congener
"	TOC (104 C)	-	Combustion	0.1%
Surface Sediment	PCB Congeners	Soxhlet extraction	GC/LRMS, EPA Method 8082/1668A, modified	0.5 µg/Kg per congener
"	Grain size	-	Sieve and Pipet	±0.5% for each fraction
"	TOC (104 C)	-	Combustion	0.1%
Sediment Core	PCB Aroclors	Soxhlet extraction	GC/ECD or ELCD, EPA Method 8082	2.5 - 50 µg/Kg
"	TOC (104 C)	-	Combustion	0.1%
"	Cs-137	-	Gamma detection	-
"	Pb-210	-	Gamma detection	-
Fish Tissue	PCB Congeners	Soxhlet extraction	GC/LRMS, EPA Method 8082/1668A, modified	1.0 – 0.50 µg/Kg per congener
"	% lipids	-	Gravimetric	0.1%
Gut Contents	PCB Congeners	Soxhlet extraction	GC/LRMS, EPA Method 8082/1668A, modified	1.0 – 0.50 µg/Kg per congener

Estimated costs for the required analysis are provided in Table 19. This estimate includes analysis of reference materials, as discussed below. Including a 25% contracting fee for all contract laboratory analyses, the total project cost is approximately $114,000. Costs for samples analyzed by Ecology's Manchester Laboratory include a 50% discount.

Table 19. Sample numbers and analytical costs for Spokane River TMDL samples.

Media	Parameter	Number Samples	QA samples	Total Number	Unit Cost	Amount
Fish Tissue	PCB Congeners*	16	2	18	$650	$11,700
"	% lipids	16	1	17	$31	$527
Gut Contents	PCB Congeners*	4	1	5	$650	$3,250
Surface Sediment and Suspended Particles	PCB Congeners*	9**	1	10	$650	$6,500
"	Grain size*	6**	1	7	$100	$700
"	TOC (104 C)	6**	1	7	$39	$273
Sediment Core	PCB Aroclors	20	2	22	$108	$2,376
"	TOC (104 C)	20	1	21	$39	$819
"	Cs-137*	12	-	12	$50	$600
"	Pb-210*	20	-	20	$75	$1,500
Surface water	SPMD membranes*	156	-	156	$40	$6,240
"	SPMD dialysis*	24	4	28	$112	$3,136
"	SPMD extract (PCB Congeners*)	24	4	28	$650	$18,200
"	TOC	24	3	27	$31	$837
"	DOC	24	3	27	$31	$837
Effluent, Stormwater, Whole Water	PCB Congeners*	25***	6	31	$1,100	$34,100
"	TSS	37***	9	46	$10	$460
					subtotal=	$92,055
			Contract analysis=		$85,926	
		Contracting fees, 25% of contract analyses=				$21,428
					Grand Total=	**$113,537**

*Contract analysis

**Does not include one sample from Little Falls Pool and four samples from the Spokane Arm to be paid from a separate funding source.

***Does not include pre-filter samples from Kaiser Trentwood (3 PCB congeners, 6 TSS) to be paid from a separate funding source.

Quality Control Procedures

Field and Processing Measures

To estimate sampling precision, at least one field duplicate is proposed for each sampling event and for all sampled media. The duplicates will not be identified to the laboratory. Table 20 documents the necessary field duplicates by media/analyte.

Table 20. Field duplicates required by analyte and media.

Media	Parameter	Field/Processing Duplicates	Blanks	Reference Samples	Total QA Samples
Fish Tissue	PCB Congeners	1	-	1	2
"	% lipids	1	-	-	1
Gut Contents	PCB Congeners	1	-	-	1
Surface Sediment and Suspended Particles	PCB Congeners	1	-	-	1
"	Grain size	1	-	-	1
"	TOC (104 C)	1	-	-	1
Sediment Core	PCB Aroclors	1	-	1	2
"	TOC (104 C)	1	-	-	1
"	Cs-137	-	-	-	0
"	Pb-210	-	-	-	0
Surface Water	SPMD extract (PCB Congeners)	1	3	-	4
"	TOC	3	-	-	6
"	DOC	3	-	-	6
Effluent, Stormwater, Whole Water	PCB Congeners	3	3	-	6
"	TSS	3	-	-	6

- = not applicable

Laboratory Measures

The quality control (QC) procedures routine to the methods cited in Table 17 will be satisfactory for this project. PCB congener methods proposed in this study add internal standards which contain isotopically labeled analogs of the target PCB compounds. Thus, additional matrix spiking to measure the congener extraction efficiency is not proposed.

For the SPMDs, a performance reference spiking solution (PRC) will be used to evaluate the uptake of PCBs from the triolein. This spiking solution will be developed by the contract laboratory based on previous congener specific wastewater (Golding, 2002) and fish tissue results (Jack and Roose, 2002). Four congeners which were not present or only present in very

small amounts in these previous analyses will be used for the spiking solution. The spikes will be mixed with the triolein during the manufacture of the SPMDs. The loss of these PCBs will be used to adjust the uptake rate from water for temperature, water velocity, and biofouling. The PRC data will be used to calculate a field exposure adjustment (FEA) factor to the laboratory determined sampling rates. Formulas for deriving FEAs are provided in Huckins et al. (2000).

Precision will be estimated in the laboratory using control samples and analytical duplicates. These will be conducted at a frequency of one per sample batch. Table 21 documents the necessary laboratory QC procedures.

Table 21. Laboratory quality control measures and frequency by parameter.

Parameter	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spike & Duplicate	Reference Materials
PCB Aroclors	10%	1 per batch	1 per batch	1 per batch	None
PCB Congeners	10%	1 per batch	1 per batch	1 per batch	1 per batch
TOC/DOC in Water	10%	1 per batch	1 per batch	1 per batch	None
Grain Size	None	None	1 per batch	None	None
TOC in Sediment	10%	1 per batch	1 per batch	None	None
Percent Lipids	None	None	1 per batch	None	None
Cs-137	1 per batch	1 per batch	1 per batch	None	None
Pb-210	1 per batch	1 per batch	1 per batch	None	None

Reference Materials

A certified reference material (tissue) of PCB congeners in cod liver oil will be analyzed. This certified reference tissue (SRM 1588a) will be obtained from the National Institute of Standards and Technology in Gaithersburg, MD. This tissue is not certified for all the congeners of interest in this study. However, the 29 congeners this material has been certified for cover a broad range of congener types, from 2,4,4'-trichlorobipheynl to 2,2',3,3',4,5',6,6'-octachlorinated biphenyl. These congeners will serve as effective surrogates for the spectrum of congeners analyzed. They also represent the toxic coplanar PCB forms as recognized by the World Health Organization (WHO). Bias in congener results will be estimated from the analysis of this reference material. The analytical objective is to be ± 35% of the reference material window(s) as specified by the supplier.

Certified reference materials are available for sediment; however, these CRMs do not quantify PCB Aroclors. Because of the biotic and abiotic weathering of PCBs, sediment concentrations rarely provide chromatographic patterns which exactly match Aroclor standards. Thus, PCB Aroclor methods, like those proposed for the sediment cores, must use hand matching to the most appropriate Aroclor pattern. This semi-quantitative approach cannot be used for comparisons with CRMs.

Several certified sediment reference materials are available for PCB congeners. The laboratory may use CRM 1944, New York New Jersey Waterway sediment from the National Institute of Standards & Technology, or they may use another commercially available CRM at their discretion and based on availability.

Data Review, Verification, and Validation

Data Review and Verification

Manchester Environmental Laboratory (MEL) will review the QA Project Plan and all of the sample and quality control data. Reviews will be sent to the project lead in the form of case narratives and will include an assessment of MEL's performance in meeting the conditions and requirements set for in this sampling plan. Case narratives will also include a comparison of QC results with method acceptance criteria, such as precision data, surrogate and spike recoveries, laboratory control sample analysis, and procedural blanks. QC checks on instrument performance such as initial and continuing calibrations will also be noted. Results of standard reference material analysis will be reported along with certified values in the case narratives. MEL will explain flags or qualifiers assigned to sample results.

Data Validation

The project lead will examine the complete data package in detail to determine whether the procedures in the methods, SOPs, and QA Project Plan were followed.

Precision will be assessed by calculating relative percent differences (RPDs) for the following data:

- Analytical duplicates
- Field duplicates

Laboratory duplicates will yield estimates of precision obtained at the laboratory. Field duplicates will indicate overall variability (environmental + sampling + laboratory).

Bias will be calculated as deviations of mean% recoveries of surrogate spike and laboratory control sample analyses. Consistently low or high recoveries may indicate the data are biased in that direction. Wide ranges in recovery values may indicate data are of questionable accuracy, but do not indicate bias in any particular direction. Matrix spike recoveries will indicate if bias is present due to matrix effects.

Completeness will be assessed through the following accounting:

- Number of samples collected compared to sampling plan
- Number of samples shipped and received at MEL and contract laboratories in good condition
- Ability of MEL and contract laboratories to produce usable results for each sample
- Acceptability of sample results by project lead

Data Quality Assessment

Data quality will be assessed to determine whether the project objectives can be met. The project lead will make this determination by examining the data and all of the associated quality control information. The project lead will be guided in this determination by the methods and procedures in this project plan. Chemists and other scientists familiar with this field may also be consulted. The project lead will continually assess field procedures and sampling conditions to assess subtle forms of bias. The project lead will review all field and laboratory data to uncover sources of bias which, if found, will be noted in the project report.

Audits and Reports

Audits

The project lead will periodically assess the field sampling procedures to ensure consistency with this sampling plan or make modifications if necessary. The project lead will review all field notes to ensure quality of the field data. Laboratory results will be reviewed by the project lead to check for reasonableness, and consistency with performance and completeness expectations. Any problems with the data will be discussed with chemists at MEL.

Reports

A draft data report will be prepared by the Environmental Assessment Program. Completion of the draft report is anticipated by December 2004. The report will include:

1. A map of the study area showing sampling areas.
2. Descriptions of field and laboratory methods.
3. Sample information including lengths, weights, and ages of fish sampled and composited.
4. Sediment core descriptions.
5. Surficial sediment concentrations and variability.
6. Surface water and effluent concentrations and variability.
7. Discussion of data quality and any significant analytical problems.
8. Summary tables of analytical data.
9. Comparisons of data with previous work on the Spokane River.
10. A conceptual model for PCB transfer to fish tissues including the proportional contribution of various pathways.
11. Discussion of seasonal variability and its potential influences.
12. A description of the ongoing and legacy/historic sources of PCBs to the Spokane system.
13. An uncertainty analysis.
14. A discussion of appropriate safety factors.
15. A proposal to proportion effluent load allocations to meet water quality standards.
16. A discussion of sediment reductions needed to meet fish tissue guidelines using literature and site-specific BSAFs.
17. An appendix of analytical case narratives.

Comparisons with previous analytical results will consider the estimates of accuracy, precision, and bias in available historic data. Concentrations of dissolved contaminants will be derived using the formula as published by the USGS and Huckins et al. (1993).

Project data will be entered in Ecology's Environmental Information Management (EIM) prior to completion of the final report.

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Appendix A

Table A1. Spokane River Basin NPDES Permits.

Facility Name	Fac Type	Permit Type	Per. Cnt	Permit Number	EXPIR DT	WRIA
Industrial Facilities						
NEWMAN LK FLOOD CONTROL ZONE DIST	Indust.	Minor	1	WA0045438A	10-Jun-99	57
B F GOODRICH	Indust.	POTW	1	ST0008068A	8-Feb-04	57
COLUMBIA LIGHTING INC	Indust.	POTW	2	ST0005222B	19-Feb-00	57
GROUP PHOTO	Indust.	POTW	3	ST0005378A	12-Oct-98	57
JOHNSON MATTHEY ELECTRONIC	Indust.	POTW	4	ST0005350B	4-Sep-03	57
NOVATION INC	Indust.	POTW	5	ST0005355B	1-Jan-01	57
INLAND EMPIRE PAPER COMPANY	Indust.	Major	6	WA0000825B	30-Jun-02	57
KAISER TRENTWOOD	Indust.	Major	7	WA0000892B	30-Jun-02	57
DAWN MINING COMPANY	Indust.	State	13	ST0005230C	30-Jun-02	54
AVISTA CORP HEADQUARTERS	Indust.	Minor	17	WA0045195B	31-Jul-02	57
JOHNSON MATTHEY CHENEY	Indust.	POTW	18	ST0008055A	18-Apr-03	56
KEY TRONIC CORP (SPOKANE)	Indust.	POTW	19	ST0005284B	7-Nov-01	57
OLYMPIC FOODS	Indust.	POTW	20	ST0008051A	30-Jun-02	57
SPOKANE CO UTIL.(MICA LANDFILL)	Indust.	POTW	21	ST0005356B	6-May-01	56
WILCOX FARMS INC.(MILK PLANT)	Indust.	POTW	22	ST0005399A	22-Jun-02	56
Municipal Facilities						
BADGER LAKE ESTATES	Munic.	State	5	ST0008057B	1-Jun-02	56
CLAYTON SEWER DISTRICT	Munic.	State	6	ST0005392A	5-Nov-01	55
FREEMAN SCHOOL DISTRICT #358	Munic.	Minor	7	WA0045403A	1-Nov-99	56
LIBERTY SCHOOL DISTRICT #362	Munic.	State	8	ST0005397A	11-Sep-01	56
MULLEN HILL TERRACE PROPERTIES	Munic.	State	9	ST0008041A	20-Oct-01	57
SNOWBLAZE CONDOMINIUMS	Munic.	State	10	ST0008039A	25-Aug-01	57
SPOKANE CO UTIL.(HANGMAN HILLS)	Munic.	State	11	ST0008045A	29-Jun-02	56
UPPER COLUMBIA ACADEMY	Munic.	State	12	ST0008034A	20-Oct-01	56
DEER PARK WWTP	Munic.	State	8	ST0008016B	30-Jun-02	55
DIAMOND LAKE WWTP	Munic.	State	9	ST0008029C	30-Jun-02	55
MEDICAL LAKE WWTP	Munic.	Minor	10	WA0021148A	30-Jun-82	54
LIBERTY LAKE SEWER DISTRICT #1	Munic.	Minor	8	WA0045144B	30-Jun-02	57
SPOKANE ADVANCED WWTP	Munic.	Major	9	WA0024473A	30-Apr-97	54
CHENEY WWTP	Munic.	Minor	16	WA0020842B	30-Jun-00	56
TEKOA WWTP	Munic.	Minor	17	WA0023141B	27-Jun-99	56
FAIRFIELD TOWN OF WWTP	Munic.	Minor	2	WA0045489B	30-Jun-02	56
ROCKFORD TOWN OF WWTP	Munic.	Minor	3	WA0044831B	21-Jan-00	56
SPANGLE TOWN OF WWTP	Munic.	Minor	4	WA0045471A	30-Jun-02	56

Appendix B

Sample Sediment Log

Site: _____

Station	Grab No.	Depth (ft)	Date	Time	Sediment Penetration (cm)	Sample Description

Recorder: _____