Spokane River PCB and Source Survey August 2000

April 2001

Publication No. 01-03-016

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Spokane River PCB and Source Survey August 2000

by
Steven Golding

Environmental Assessment Program
Olympia, Washington 98504-7710

April 2001

Waterbody No. WA-57-1010

Publication No. 01-03-016
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Abstract

The Washington State Department of Ecology sampled the Spokane River upstream and downstream of Kaiser Aluminum and Chemical Corporation, Trentwood Works (Kaiser). The samples were analyzed for PCB Aroclors and congeners to determine concentrations and possible sources of PCBs to the river. Kaiser outfall 001 was also sampled for PCB Aroclors and congeners. Results were incomplete as a result of laboratory PCB-1254 and 1260 contamination. A single grab sample of river water downstream of Kaiser showed 1.1 pptr PCB-1248. Four other grab samples of river water downstream of Kaiser resulted in nondetected PCB Aroclors at detection limits between 0.9 and 1.0 pptr. Because river water concentrations of PCB-1248 were lower than expected, most samples yielded nondetectable results.

Results of samples from the Kaiser outfall were inconclusive. The four grab sample results were highly variable as a result of apparent non-homogeneity of the effluent. PCB-1248 was the only Aroclor detected in the effluent, with concentrations ranging from 53 pptr to nondetection at 0.9 pptr. A more precise measure of the PCBs in the Kaiser effluent will require a larger number of samples to be taken, or the production by Kaiser of a more homogeneous effluent.

Future characterizations of PCBs in Spokane River water may require ultra-low level detection methods or field sampling techniques that concentrate PCBs from the water.

Acknowledgements

The author would like to thank the following individuals for their help with this study:

- John Roland of the Ecology Eastern Regional Office Toxics Cleanup Program for leading the effort to sample the Spokane River.

- These staff with the Ecology Environmental Assessment Program:

  ◊ Dale Norton, Contaminant Studies Unit supervisor, for providing guidance and reviewing the quality assurance project plan and the study report.

  ◊ Art Johnson for reviewing the study report.

  ◊ Norm Glenn for assistance with sampling.

  ◊ Joan LeTourneau for formatting and editing the final report.

Introduction

The primary objective of this survey, conducted August 13-15, 2000, was to assess polychlorinated biphenyls (PCBs) concentrations in water from an eight-mile stretch of the Spokane River between Barker Road and the vicinity of Argonne Road (Figures 1 and 2). Another objective was to attempt to determine if contaminated groundwater from the Kaiser Aluminum and Chemical Corporation, Trentwood Works (Kaiser) might be a source of PCBs to the river during periods of low river flow and high groundwater inflow to the river.

River water samples were also collected for PCB analyses downstream of the Plante Ferry site in the Upriver Dam Reservoir downstream of the Argonne Road bridge (Figure 2). The results of this survey were intended to give an indication of whether PCB contaminated groundwater or outfall effluent are entering this section of the Spokane River. Groundwater recharge to the river provides a larger share of total flow during the summer season. Recent advances in analytical techniques that should allow water samples to be analyzed to a practical quantitation limit (PQL) of one part per trillion or below were used. Samples of the Kaiser 001 outfall effluent were also analyzed for PCBs.

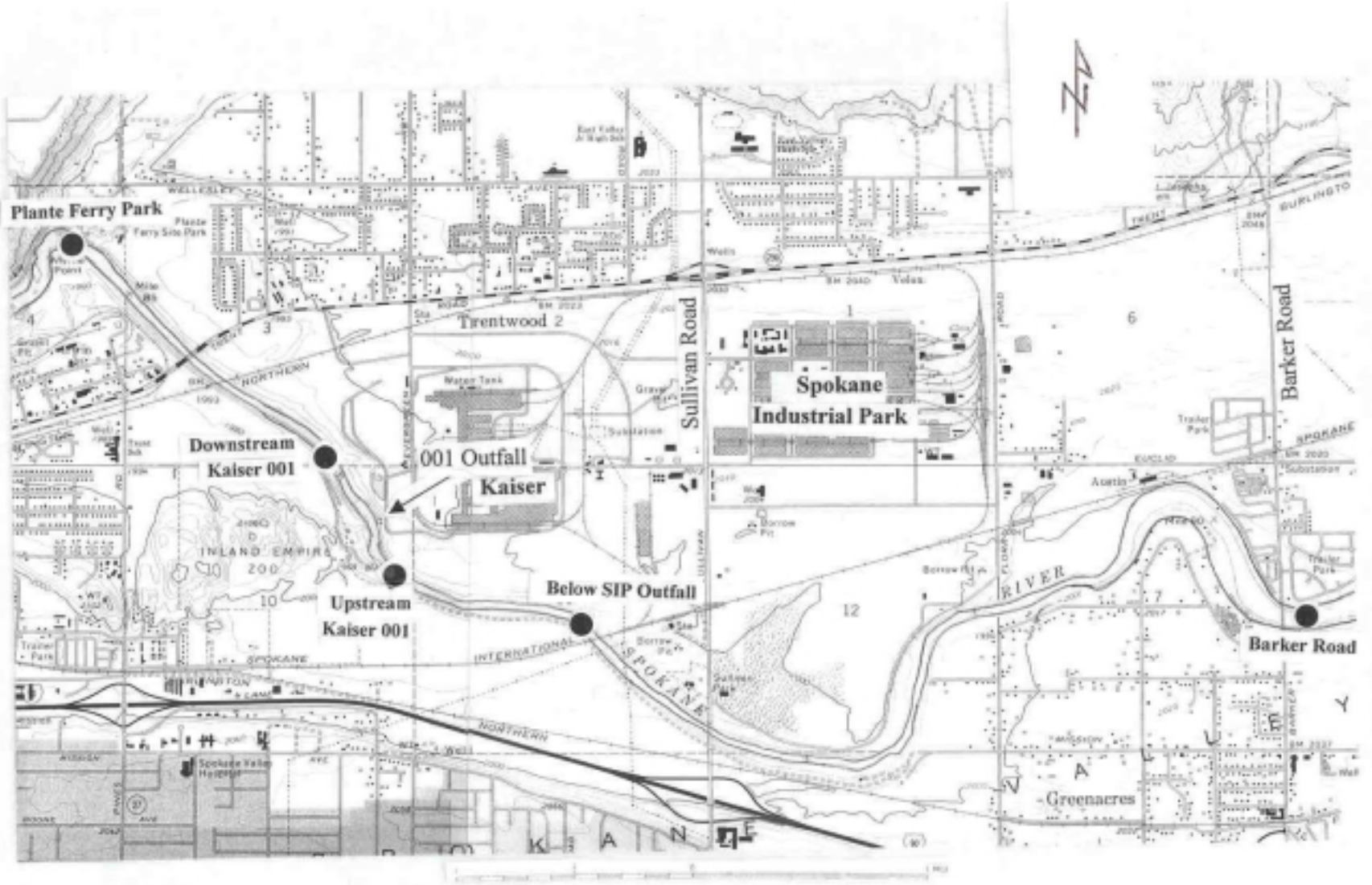

Figure 1 – Location Map

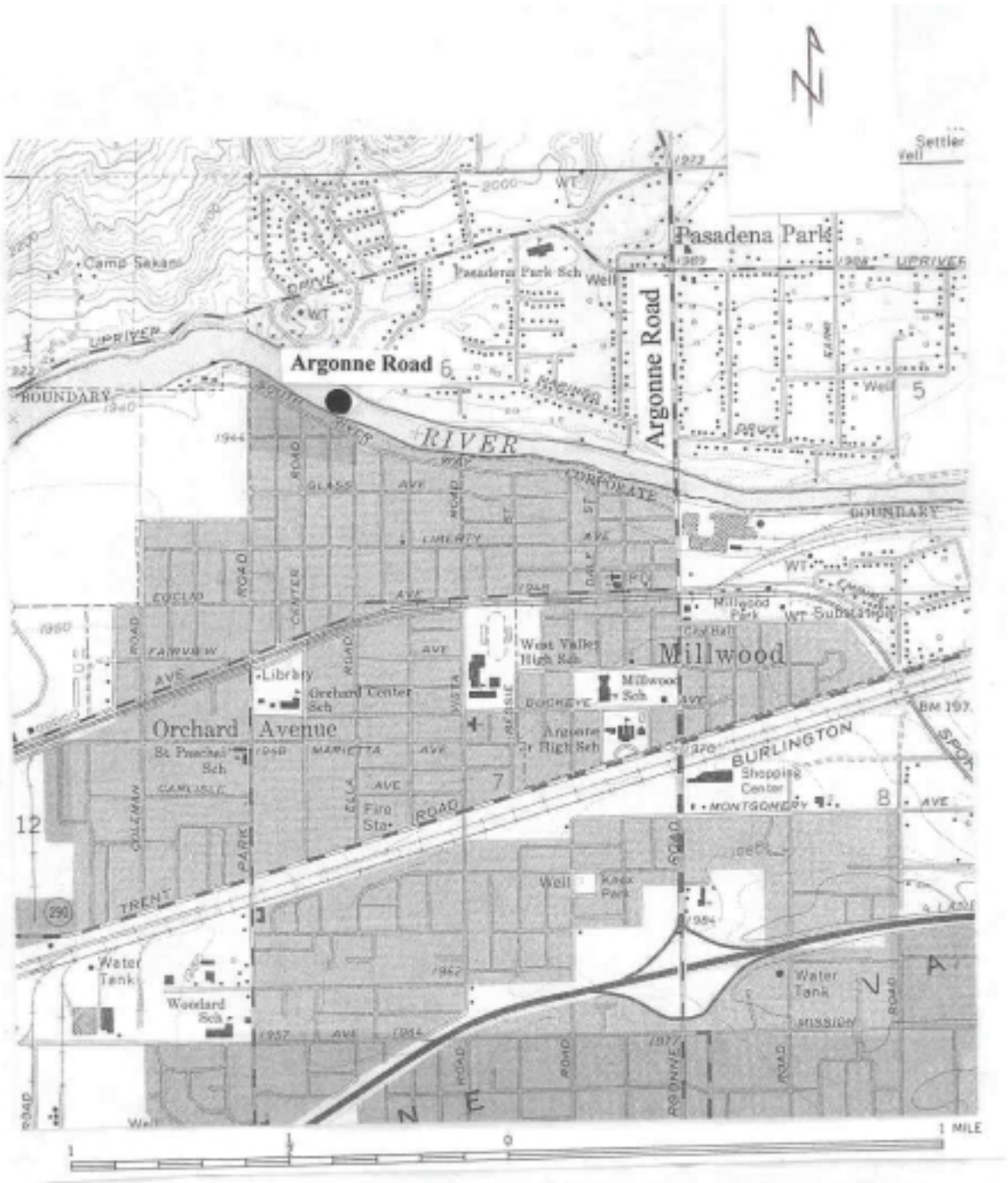

Figure 2 – Location Map, Downstream of Plante Ferry Park

PCB Terminology

PCB mixtures having a range of physical/chemical properties were formulated for commercial use and designated by a numbering system based on chlorine content. Historically, the PCBs detected in the Spokane River most closely resemble the commercial mixtures PCB-1248, PCB-1254, and PCB-1260. The last two digits are the average chlorine content by weight (e.g., PCB-1254 averages 54% chlorine) while the first two refer to the number of carbon atoms in biphenyl. In the United States, PCBs were produced under the trade name Aroclor (e.g., Aroclor-1254). (TIS, 1995)

PCBs can be analyzed as Aroclors or as congeners, the individual compounds forming the Aroclors. Once released to the environment, PCBs undergo alterations due to volatilization, uptake by biota, biodegradation, and mixing with PCBs from other sources. Because a single environmental sample may contain many of the 209 PCB congeners, and because of overlap in congeners between different commercial mixtures, PCB analysis is complex. (TIS, 1995)

Background

Fish and sediment samples collected from the Spokane River by Ecology in 1992-93 showed unusually high concentrations of PCBs (Johnson et al,1994; Serdar et al, 1994). Results from later fish and sediment samples did not indicate important sources of PCBs above Post Falls, Idaho (TIS, 1995).

A broad study of the Spokane River in the Spokane area, that included sampling of river water east of Spokane in 1994, was unable to detect PCBs at the Barker Road sampling station located upstream of the Spokane Industrial Park (SIP) and Kaiser. Kaiser discharges treated industrial wastewater to the Spokane River. The SIP discharged treated industrial wastewater to the river until December 1993. PCBs were found in sludge from an inactive SIP oxidation ditch in 1994 (TIS, 1995). PCBs were found in centrifuged solids at detectable levels at Plante Ferry, downstream of the Kaiser and SIP outfalls (TIS, 1995). Total suspended solids (TSS) concentrations were lower at Plante Ferry than at Barker Road, indicating that the PCBs in the water downstream came from a source other than sediment entrained in the water column.

Based on semi-permeable membrane (lipid tube) results, the 1995 report estimated concentrations of dissolved PCB-1248 at Plante Ferry of 1.0 to 1.9 pptr. The estimate at State Line was 0.8 pptr PCB-1248. The same study found significant concentrations of PCB-1248 in Kaiser lagoon sediments and skimmings (TIS, 1995). A study by Hart Crowser for Kaiser reported dissolved PCB concentration estimates from lipid tube data of 0.8 and less than 0.2 pptr upriver of Kaiser and 1.8 pptr, 1.5 pptr, and 1.3 pptr downriver (Hart Crowser, 1995). There is uncertainty in relating lipid tube data to dissolved concentrations of PCBs in the Spokane River. The 1995 Ecology study recommended that data on the final effluent from the Kaiser outfall be obtained by Ecology to determine if the effort by Kaiser to cleanup PCBs was successful.

The Kaiser outfall is between Barker Road and Plante Ferry, as was the former outfall from the SIP Wastewater Treatment Plant (WWTP). A follow-up study in 1995 confirmed the finding of measurable concentrations of PCB-1248 in the Kaiser effluent 25 – 34 pptr (Golding, 1996). With the relative large discharge rate from the outfall (17.9 –18.1MGD), PCB loading to the Spokane River during the study period was estimated to be 1.7 – 2.3 g/day total PCBs (Golding, 1996). The 1994 and 1995 studies identified other potential sources of PCBs to the Spokane River: decomissioned SIP WWTP, the City of Spokane WWTP, the Liberty Lake WWTP, and the Post Falls WWTP. SIP wastewater has been routed to the City of Spokane sewer system since 1993 (TIS, 1995). PCB contamination of soils at the Kaiser facility was discovered in 1991 (TIS, 1995). It is not known whether the contaminated soils are a potential source of contaminated groundwater entering the Spokane River.

Study Design

This project was not intended to be a thorough investigation of potential sources of PCBs to the Spokane River in the vicinity of Spokane. PCB analyses were intended to obtain the lowest possible Practical Quantitation Limits (PQLs). It was anticipated that PQLs as low as 1 pptr or lower might be achieved. Since previous studies had estimated that PCB concentrations in portions of the Spokane River may be approximately 1 pptr or somewhat higher (TIS, 1995), it was decided that a quantification limit of 1 pptr may be sufficiently low to detect PCBs in river water samples. It was recognized that source controls by Kaiser and the diversion of wastewater from the SIP to the city of Spokane sewage collection system may have caused river water PCB congeners to fall below a detectable level of 1 pptr. State water quality standards aquatic life criteria for total PCBs are 2 µg/L (2,000 pptr) acute, and 14 pptr chronic (WAC 173-201A). EPA National Toxics Rule Human Health Standards are 0.17 pptr for water from which there is water or fish ingestion (EPA, 1999). With current laboratory methods at the Ecology Manchester laboratory, a PQL of 0.17 pptr cannot be obtained from a whole water sample. In summary, in order to meet the objectives of this study, to screen a section of the Spokane River for PCBs and to compare the results with other studies, a PQL for PCBs of 1pptr or lower was desired.

In this study, PCBs were analyzed as both Aroclors and congeners. The 20 congeners on the standard NOAA list were analyzed (Lauenstein and Cantillo, 1993).

Site Descriptions

Water samples were collected from six points along the Spokane River listed below (Figures 1 and 2).

1. Barker Road bridge
2. Downstream of Spokane Industrial Park (SIP) historic outfall
3. Just upstream of Kaiser outfall
4. Downstream of Kaiser outfall (just upstream of railroad crossing)
5. Plante Ferry Site Park pedestrian bridge
6. Downstream of Argonne Road bridge in the Upriver Dam Reservoir (approximately 2 ½ miles downstream of Plant Ferry Site Park sampling site)

Samples were collected upstream of the Kaiser and historic SIP outfall (Barker Road bridge) and downstream of both facilities (Plante Ferry Site Park Centennial Trail pedestrian bridge and further downstream near Argonne Road). These samples were collected from mid-river in a well-mixed area of strong current, so as to be representative samples of the river water at these points. The Barker Road sample represented a background sample upstream of both Kaiser and the historic SIP discharge points. Sampling also took place at three points along the river

between these sampling locations. These three locations were along the north bank, where potential contaminated groundwater discharging to the river from industrial facilities north of the river may have an impact on river water PCB concentrations.

Sampling Methods

Latitude and longitude for each sampling location were determined with a GPS receiver and recorded.

River samples were collected as single grab samples. Two samples were collected at each river location, the second sample serving as a field replicate. Samples of river water were collected by hand from a boat. One-gallon jars were dipped directly into the river, placed upstream of the boat and with the jar mouth pointed upstream. The collection jars were organic-free glass jars with Teflon-lined lid, each supplied with a Certificate of Analysis. Nitrile disposable gloves were worn by personnel during sampling. Sample containers were placed in ice chests, and chain-of-custody procedures were followed to ensure security of the samples.

Samples from the Kaiser outfall were collected directly into the gallon jars. The jars were dipped by hand into the treatment lagoon just upstream of and directly in front of the overflow weir leading to the outfall box and discharge line to the river.

Table 1 shows the samples were collected for the parameters listed.

Table 1 – Samples Collected and Water Quality Parameters

Location	Date	Sample	Field Parameters	Lab Parameters
Barker Road (mid-river)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Below SIP Outfall (near north bank)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Upstream Kaiser (near north bank)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Downstream Kaiser (near north bank)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Plante Ferry Park (mid-river)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Argonne Rd (mid-river)	08/13/00	Grab sample	Temp., Conductivity	PCB, TSS, TDS
		Field replicate		PCB
Kaiser Outfall	08/14/00	Grab sample	Temp., Cond., Flow	PCB, TSS, TDS
		Field replicate		PCB
		Transfer Blank		PCB
	08/15/00	Grab sample	Temp., Cond., Flow	PCB, TSS, TDS
		Field replicate		PCB
		Transfer Blank		PCB

Analytical Procedures and Methods

Samples were analyzed for seven PCB Aroclors and nineteen PCB congeners. The Aroclor analysis is intended to provide comparison data to past studies. The congener analysis is intended to provide a detailed description/signature of the PCB Aroclors identified in the samples.

The analyses were performed by Manchester Environmental Laboratory using EPA SW-846, Methods 3510B and 8082A. Four initial demonstrations of capability (IDC) samples were prepared by the laboratory prior to sample analysis. The IDC samples showed no contamination. Unfortunately, after the IDC samples were collected and before the project samples were analyzed, contamination of the extraction equipment with PCB-1254 took place.

Two spike and two spike duplicate samples were analyzed in the laboratory to determine the extent of any matrix interference, affecting results. Laboratory duplicates were performed to provide an estimate of precision.

One field replicate PCB sample was collected for each river sample. The sample and field replicate were collected within minutes of each other at the same location. Samples and field replicate samples from the Kaiser outfall were collected within five minutes of each other.

Data Quality

Laboratory contamination of the samples with PCB-1254 and -1260 caused 17 of the 18 PCB-1254 and 7 of the PCB-1260 results to be rejected (Tables 2 and 3). Extraction of samples high in PCB-1254 from an unrelated project prior to the extractions for this project and the inability to achieve a complete cleanup of laboratory equipment were responsible for the contamination. The results reported for PCB-1248, -1242, -1232, -1221, and -1016 were not affected by the PCB-1254 and -1260 contamination.

Laboratory contamination resulted in the rejection of congeners 101, 118, 153, 105, 138 for some samples (Tables 2 and 3).

PCB-1242 and -1260 spiked at 5 pptr resulted in 78% and 96% recovery, respectively. PCB congeners spiked at 0.2 pptr resulted in 66% to 111% recovery, with an average recovery of 83%.

Transfer blanks were prepared as a check for PCB contamination during sampling. One transfer blank was prepared at the Kaiser sampling site each of the two days of sampling. Other than rejected PCB-1254 and -1260 results and two rejected congeners, the transfer blanks showed no detectable Aroclors or congeners.

Differences in results between each sample and its field replicate sample reflect environmental variability as well as variability in analysis. Variability in river water samples could not be well characterized because most samples had nondetected PCBs. Kaiser sample/field replicate pairs showed high variability, with one undetected result and one significant result for each of the two days of sampling.

A laboratory Quality Assurance and Quality Control case narrative appears in Appendix A.

Results

Spokane River PCB Results

Results of PCB analyses for grab samples of Spokane River water appear in Table 2. No results could be obtained for Aroclors and congeners shown in Table 2 as rejected, due to laboratory contamination.

Of the 12 river samples collected from six sites along the Spokane River, one sample showed the presence of a PCB Aroclor. PCB-1248 was detected downstream of Argonne Road in the Upriver Dam Reservoir at a concentration of 1.1 pptr. The 1.1 pptr concentration found is consistent with past estimates of 1 pptr or higher PCB in the Spokane River near Spokane (TIS, 1995).

No PCB Aroclors were found in the field replicate sample for the downstream Argonne Road sampling site. This may be the result of the closeness of the 1.1 pptr found to the 0.9 pptr detection limit.

Four river water samples from locations downstream of Kaiser with total PCB-1248 undetectable at 1 pptr or below indicate lower concentrations of PCBs than estimated from 1994 lipid tube data, but comparisons between the data sets are uncertain. Past estimates of concentrations of dissolved PCBs from lipid tube data ranged from 1.0 to 1.9 pptr (TIS, 1995; Hart Crowser, 1995). The lipid tube data represented dissolved rather than total PCBs. Estimates of dissolved PCB concentrations in water from lipid tube data are uncertain since lipid tubes do not measure PCB concentrations directly. Lipid tubes accumulate dissolved PCBs, typically over a period of a month or more. The PCBs pass through a membrane, accumulating in lipids inside the tubes. The membrane is subject to fowling with attached growths of biological matter. Other environmental conditions, in addition to the actual water concentration of dissolved PCBs, affect the extent of PCB absorption by the tubes.

Another factor in river PCB concentrations is river flow. The 1994 Ecology lipid tube data were collected from August to September, with river flow at Plante Ferry at 426 cfs. River flow was somewhat higher during the August 2000 monitoring event (583 cfs at Barker Road, increasing downstream toward Plante Ferry). As a result, there may have been more dilution of PCBs during the 2000 Ecology study than during the 1994 study. River flow during the 2000 monitoring is described in more detail below.

No PCB congeners were found in the river water samples, with the exception of several congeners found in one field replicate collected near Barker Road. These reported congeners may be an artifact of PCB contamination in the lab, although the results were not qualified by the lab as rejected. This is supported by that sample having rejected PCB-1254 and -1260 results. Also, the reported congeners were of unusually high congener numbers.

Table 2 - Spokane River Water Sample Results - p. 1

Location:	Barker	Barker-D	SIP	SIP-D	KUp	KUp-D
Type:	grab	grab	grab	grab	grab	grab
Date:	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00
Time:	0650	0650	0800	0800	0930	0930
Lab Log:	338098	338099	338100	338101	338102	338103
PCB Aroclors						
PCB - 1016 (ng/L)	0.9 UJ	0.9 UJ	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1221 (ng/L)	0.9 UJ	0.9 UJ	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1232 (ng/l)	0.9 UJ	0.9 UJ	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1242 (ng/L)	0.9 UJ	0.9 UJ	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1248 (ng/L)	0.9 UJ	0.9 UJ	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1254 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
PCB - 1260 (ng/L)	0.9 UJ	REJ	REJ	0.9 U	0.9 U	0.9 U
TSS (mg/L)	2		2		1	
TDS (mg/L)	39		70		106	
Conductivity (umhos/cm)	53.5		124		186	

1 ng/L = 1 part per trillion (pptr)

D - Replicate sample
Barker - Spokane River at Barker Bridge
SIP - Spokane River at Spokane Industrial Park historic outfall
K - Kaiser Trentwood
Up- Spokane River upstream of Kaiser Trentwood

U - Analyte was not detected at or above the reported value.
UJ - Analyte was not detected at or above the reported estimated value.
REJ - Data are unusable for all purposes.

Table 2 - Spokane River Water Sample Results - p. 2

Location:	Barker	Barker-D	SIP	SIP-D	KUp	KUp-D
Type:	grab	grab	grab	grab	grab	grab
Date:	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00
Time:	0650	0650	0800	0800	0930	0930
Lab Log:	338098	338099	338100	338101	338102	338103
PCB Congeners						
congener 8 (ng/L)	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 18 (ng/L)	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 28 (ng/L)	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 44 (ng/L)	0.2 UJ	0.2 U	0.2 UJ	0.2 U	0.2 U	0.2 U
congener 52 (ng/L)	0.2 UJ	0.2 U	0.4 REJ	0.2 U	0.2 U	0.2 U
congener 66 (ng/L)	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 101 (ng/L)	0.4 REJ	0.9 REJ	1.4 REJ	0.4 REJ	0.2 REJ	0.2 REJ
congener 110 (ng/L)						
congener 77 (ng/L)	0.2 UJ	1.3 UJ	0.2 U	0.2 U	0.2 U	0.2 U
congener 118 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
congener 153 (ng/L)	REJ	REJ	REJ	REJ	REJ	0.2 U
congener 105 (ng/L)	0.2 UJ	REJ	REJ	REJ	0.2 U	0.2 U
congener 138 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
congener 126 (ng/L)	0.2 UJ	1.2	0.2 U	0.2 U	0.2 U	0.2 U
congener 128 (ng/L)	0.2 UJ	REJ	REJ	0.2 U	0.2 U	0.2 U
congener 180 (ng/L)	0.2 UJ	2.0	REJ	0.2 U	0.2 U	0.2 U
congener 170 (ng/L)	0.2 UJ	1.3	0.2 U	0.2 U	0.2 U	0.2 U
congener 187 (ng/L)	0.2 UJ	1.1	0.2 U	0.2 U	0.2 U	0.2 U
congener 195 (ng/L)	0.2 UJ	0.2	0.2 U	0.2 U	0.2 U	0.2 U
congener 206 (ng/L)	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U

1 ng/L = 1 part per trillion (pptr)

D - Replicate sample

Barker - Spokane River at Barker Bridge

SIP - Spokane River at Spokane Industrial Park historic outfall

K - Kaiser Trentwood

Up- Spokane River upstream of Kaiser Trentwood

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

UJ - Analyte was not detected at or above the reported estimated value

REJ - Data are unusable for all purposes.

[ ] - Analyte detected

Table 2 - Spokane River Water Sample Results - p. 3

Location:	Kdown	Kdown-D	Plante	Plante-D	Argonne	Argonne-D
Type:	grab	grab	grab	grab	grab	grab
Date:	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00
Time:	1005	1005	1100	1100	1205	1205
Lab Log:	338104	338105	338090	338091	338088	338089
PCB Aroclors						
PCB - 1016 (ng/L)	1.0 U	0.9 U	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1221 (ng/L)	1.0 U	0.9 U	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1232 (ng/l)	1.0 U	0.9 U	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1242 (ng/L)	1.0 U	0.9 U	1.0 U	0.9 U	0.9 U	0.9 U
PCB - 1248 (ng/L)	1.0 U	0.9 U	2.6 UJ	0.9 U	1.1	0.9 U
PCB - 1254 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
PCB - 1260 (ng/L)	1.0 U	0.9 U	REJ	REJ	0.9 U	0.9 U
TSS (mg/L)	1		<1		<1	
TDS (mg/L)	115		107		112	
Conductivity (umhos/cm)	190		188		195	

1 ng/L = 1 part per trillion (pptr)

D - Replicate sample
K - Kaiser Trentwood
Down - Spokane River downstream of Kaiser Trentwood
Plante - Spokane River at Plante Ferry Park
Argonne - Spokane River downstream of Argonne Road
Up- Spokane River upstream of Kaiser Trentwood

U - Analyte was not detected at or above the reported value.
UJ - Analyte was not detected at or above the reported estimated value.
REJ - Data are unusable for all purposes.
[ ] - Analyte detected

Table 2 - Spokane River Water Sample Results - p. 4

Location:	Kdown	Kdown-D	Plante	Plante-D	Argonne	Argonne-D
Type:	grab	grab	grab	grab	grab	grab
Date:	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00	8/13/00
Time:	1005	1005	1100	1100	1205	1205
Lab Log:	338104	338105	338090	338091	338088	338089
PCB Congeners						
congener 8 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.5 UJ	0.2 U
congener 18 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 28 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 44 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 52 (ng/L)	0.2 U	0.2 UJ	0.2 U	0.2 U	0.2 U	0.2 U
congener 66 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 101 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
congener 110 (ng/L)						
congener 77 (ng/L)	0.2 U	0.2 U	0.9 UJ	0.2 U	0.2 U	0.2 U
congener 118 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	REJ
congener 153 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	REJ
congener 105 (ng/L)	0.2 U	0.2 U	0.2 U	REJ	0.2 U	0.2 U
congener 138 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
congener 126 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 128 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 180 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 170 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 187 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 195 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U
congener 206 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U

1 ng/L = 1 part per trillion (pptr)

D - Replicate sample
K - Kaiser Trentwood
Down - Spokane River downstream of Kaiser Trentwood
Plante - Spokane River at Plante Ferry Park
Argonne - Spokane River downstream of Argonne Road
Up- Spokane River upstream of Kaiser Trentwood

U - Analyte was not detected at or above the reported value.
UJ - Analyte was not detected at or above the reported estimated value.
REJ - Data are unusable for all purposes.

Kaiser Outfall PCB Results

The results of general chemistry and PCB analyses for Kaiser outfall appear in Table 3, with congener analyses following Aroclor analyses. Some analyses produced no results, but are reported as rejected Aroclors and congeners in Table 3.

The August 14 grab sample of Kaiser effluent had a PCB-1248 concentration of 53 pptr. Five PCB congeners were found in the sample in concentrations of up to 3.1 pptr (congener 66). The field replicate for that sample had no detected PCB Aroclors at a detection limit of 0.9 pptr. The August 15 grab sample of Kaiser effluent had no detected PCB Aroclors at a detection limit of 0.9 pptr. PCB-1248 was detected in the field replicate for that sample at an estimated concentration of 25 pptr. No congeners were detected in this sample.

That the results were highly variable suggests the effluent was not homogeneous with respect to PCBs. Because analyses were in the pptr range, the chance inclusion or exclusion of a small number of particles in any sample may affect results significantly. It may be that particles were not evenly distributed in the effluent, at least not on the scale of the one-gallon sampling that was conducted.

The conclusion that PCB-1248 in two of the samples represented actual PCB concentrations in the effluent is supported by the results of analyses on transfer blanks prepared on site at the time of sampling. On both days the transfer blanks showed no detectable PCB-1248 at a detection limit of 0.9 pptr.

Pat Blau of Kaiser performed the actual collection of the samples on August 14, while Steven Golding of Ecology observed. Several months later Pat Blau stated that he believed his hands may have been contaminated with PCBs, affecting the results (Blau, 2000). On August 15, Steven Golding collected the samples, wearing power-free nitrile gloves. On that day, PCB-1248 was detected in one of the effluent samples at an estimated concentration of 25 pptr. Since Pat Blau collected both samples on the 14th in the same manner, and one of those samples showed no detectable PCB 1248 at a detection limit of 0.9 pptr, it can be concluded that none of the samples were contaminated during collection. Although each sample collected appears to be valid, it is difficult to characterize the effluent with respect to PCB-1248 given the non-homogeneous nature of the effluent. The PCB-1248 concentration is difficult to characterize based on the current, highly variable results and the limited number of samples taken; the mean of the four samples is 19.5 pptr (est.).

The congener analysis for the sample showing 53 pptr PCB-1248 showed five PCB congeners. It is possible to relate, in an approximate way, patterns of congeners with particular Aroclors. Table 4 shows how the congeners found in the sample compare with congeners typically associated with PCB-1248 (Frame, 1996).

Table 3 - Kaiser Outfall 001 Effluent Sample Results - p. 1

Location:	K-001A	KD-001A	K-001B	KD-001B	TRN001A	TRN001B
Type:	grab	grab	grab	grab	grab	grab
Date:	8/14/00	8/14/00	8/15/00	8/15/00	8/14/00	8/15/00
Time:	1120	1125	1330	1335	1120	1330
Lab Log:	338080	338081	338085	338086	338084	338087
PCB Aroclors						
PCB - 1016 (ng/L)*	0.9 U	0.9 U	0.9 U	0.9 UJ	0.9 U	0.9 U
PCB - 1221 (ng/L)	0.9 U	0.9 U	0.9 U	0.9 UJ	0.9 U	0.9 U
PCB - 1232 (ng/l)	0.9 U	0.9 U	0.9 U	0.9 UJ	0.9 U	0.9 U
PCB - 1242 (ng/L)	0.9 U	0.9 U	0.9 U	0.9 UJ	0.9 U	0.9 U
PCB - 1248 (ng/L)	53	0.9 U	0.9 U	25 NJ	0.9 U	0.9 U
PCB - 1254 (ng/L)	REJ	REJ	REJ	REJ	REJ	0.9 U
PCB - 1260 (ng/L)	REJ	REJ	U	0.9 UJ	0.9 U	REJ
TSS (mg/L)	1.0		1 U			
TDS (mg/L)	177		184			
Conductivity (umhos/cm)	294		304			

1 ng/L = 1 part per trillion (pptr)

001 flow reported by Kaiser as 25.4 MGD from 7 AM 8/14/00 to 7 AM 8/15/00

001 - Kaiser Trentwood 001 effluent sample
K - Kaiser Trentwood
D - Replicate sample
TRN - Transfer blank of distilled water collected before samples collected.
A - sample A
B - sample B

U - Analyte was not detected at or above the reported value.
UJ - The analyte was not detected at or above the reported estimated value.
NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
REJ - Data are unusable for all purposes.
[ ] - Analyte detected

Table 3 - Kaiser Outfall 001 Effluent Sample Results - p. 2

Location:	K-001A	KD-001A	K-001B	KD-001B	TRN001A	TRN001B
Type:	grab	grab	grab	grab	grab	grab
Date:	8/14/00	8/14/00	8/15/00	8/15/00	8/14/00	8/15/00
Time:	1120	1125	1330	1335	1120	1330
Lab Log:	338080	338081	338085	338086	338084	338087
PCB Congeners						
congener 8 (ng/L)	1.0 UJ	1.9 UJ	2.5 UJ	0.2 UJ	0.2 U	0.2 U
congener 18 (ng/L)	1.5 NJ	2.2 UJ	0.6 UJ	1.1 UJ	0.2 U	0.2 U
congener 28 (ng/L)	1.8 NJ	2.8 UJ	0.9 UJ	1.3 UJ	0.2 U	0.2 U
congener 44 (ng/L)	0.3 NJ	3.1 UJ	1.0 UJ	1.3 UJ	0.2 U	0.2 U
congener 52 (ng/L)	2 UJ	REJ	REJ	1.5 UJ	0.2 U	0.2 U
congener 66 (ng/L)	3.1	3.4 UJ	1.1 UJ	1.1 UJ	0.2 U	0.2 U
congener 101 (ng/L)	REJ	REJ	REJ	REJ	REJ	REJ
congener 110 (ng/L)					0.2 U	
congener 77 (ng/L)	0.9 NJ	1.4 UJ	0.8 UJ	0.5 UJ	0.2 U	0.2 U
congener 118 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	REJ
congener 153 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	0.2 U
congener 105 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	0.2 U
congener 138 (ng/L)	REJ	REJ	REJ	REJ	0.2 U	0.2 U
congener 126 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 128 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 180 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 170 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 187 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 195 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U
congener 206 (ng/L)	0.2 U	0.2 U	0.2 U	0.2 UJ	0.2 U	0.2 U

1 ng/L = 1 part per trillion (pptr)

001 - Kaiser Trentwood 001 effluent sample
K - Kaiser Trentwood
D - Replicate sample
TRN - Transfer blank of distilled water collected before samples collected.
A - sample A
B - sample B

U - Analyte was not detected at or above the reported value.
UJ - Analyte was not detected at or above the reported estimated value.
NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.
REJ - Data are unusable for all purposes.
[ ] - Analyte detected

Table 4 – Percentages of Congeners in PCB-1248 and in Sample

Congener	Typical Found in PCB-1248	Found in Sample
18	3.8%	2.8%
28	4.6%	3.4%
44	5.7%	0.6%
52	6.2%	<3.8%
66	6.5%	5.8%
77	0.5%	1.7%

The congeners found are consistent with a pattern representing PCB-1248. Uncertainty in congener/Aroclor matching allows for the possibility of the presence of PCBs-1232 or -1242 (Olson, 2001), but Aroclor analyses have not resulted in their being identified in the Kaiser outfall.

Comparison with 1995 Ecology Data

PCB-1248 was the only Aroclor found in either the December1995 sampling event or the August 2000 sampling event of the Kaiser outfall (TIS, 1995). Table 5 shows the 1995 and 2000 results:

Table 5 – Comparison of 1995 and 2000 Results – Kaiser Outfall

Sampling Event	Aroclor 1248 Concentrations (pptr) (individual grab sample results)			
December 1995	29	34	25	29
August 2000	53	<0.9	<0.9	25 (estimated)

In 1995 Ecology identified PCB-1248 in all four grab samples of Kaiser outfall effluent in concentrations ranging from 25 to 34 pptr. The 19.5 pptr (est.) mean of the August 2000 samples is lower than that of the 1995 mean of 29 pptr. Two of the August 2000 samples showed no detectable PCBs at a detection limit of 0.9 pptr; this seems to indicate a considerable reduction in the background level of PCBs. These results are consistent with Kaiser indicating that it has spent considerable resources in an effort to reduce the concentration of PCBs discharged. However, the presence of PCB-1248 in the other two samples suggests that Kaiser may not have been completely successful in reducing the discharge of PCBs from outfall to the Spokane River.

Flow Rates and PCB Loadings to the Spokane River

Instantaneous discharge measurements were obtained for Ecology by the U.S. Geological Survey Spokane field office between 1100 and 1300 on August 4, 2000. The flow in the Spokane River was measured to be 583 cfs at Barker Road, upstream of Kaiser. The flow in the river was 1,090 cfs at Centennial Trail bridge, downstream of Kaiser (Roland, 2000). These measurements were rated "fair" (+/- 8% accuracy) and "good" (+/- 5% accuracy) respectively. The discharge

from the Kaiser outfall during the period was reported to be 25.4 MGD (39.3 cfs). The remaining gain in flow in the river between Barker Road and Centennial Trail bridge is attributed to groundwater inflow over a river length of approximately 6.5 miles (Roland, 2000).

A mass balance can be performed to estimate the concentration of PCB-1248 in the Spokane River downstream of Kaiser due to the outfall. Assuming complete mixing of the discharge with the river and steady state conditions, 19.5 pptr PCB-1248 at 39.3 cfs from outfall accounts for 0.7 pptr PCB-1248 in the Spokane River at the Centennial Trail bridge, downstream of Kaiser. Because of the high variability in measured PCB levels in the Kaiser effluent, the loading to the Spokane River and resulting concentration in the river is a rough estimate only.

A comparison can be made of the 1995 and 2000 loadings of PCB-1248 to the Spokane River from Kaiser outfall. With a discharge rate of 25.4 MGD in August 2000 and an estimated PCB-1248 concentration of 19.5 pptr, the Kaiser outfall contributed an estimated loading of 1.88 grams per day PCB-1248 to the Spokane River. This estimate is based on considerable uncertainty in the estimated concentration of PCB-1248 in the effluent. There was close agreement in the effluent PCB-1248 concentrations determined by analyses of the December 1995 samples. A reliable estimate of PCB-1248 loading at that time from the Kaiser outfall can be made. The results of the four samples of effluent at that time showed PCB-1248 ranging from 25 to 34 pptr in the effluent, with an average effluent PCB-1248 concentration of 29.3 pptr. With a discharge rate of 18.0 MGD, the corresponding loading to the Spokane River was 2.00 grams per day PCB-1248 at the time of the 1995 sampling.

At the quantitation limits of the analyses for this project, and the incompleteness of the data set as a result of laboratory contamination, the potential influence of any groundwater contribution to the PCB load in the Spokane River in the study area could not be determined.

Conclusions

The results of PCB analyses of Kaiser effluent in August 2000 yielded an average of 19.7 pptr PCB-1248, but the mean is highly uncertain since the results of the four grab samples were highly variable. The finding of two samples with nondetected PCB Aroclors at a detection limit of 0.9 pptr supports the conclusion that background levels of PCBs from the outfall have been substantially reduced since Ecology's 1995 sampling of Kaiser. However, the finding of PCB-1248 in two of the August 2000 samples indicates that the outfall may still have been releasing substantial levels of PCB-1248 at the time of the sampling. The apparent lack of homogeneity in the 2000 discharge and laboratory analytical errors did not allow for a full characterization of PCBs in the effluent from the four grab samples taken.

Of the 12 river samples, only one had detectable PCB Aroclors. The finding of 1.1 pptr of PCB-1248 in the sample taken downstream of Argonne Road, with other samples having no detectable PCBs at or below 1 pptr, suggests that PCBs in the Spokane River study area were at or below approximately 1 pptr. This is lower than previous estimates of dissolved PCBs in the Spokane River downstream of Kaiser of 1.0 to 1.9 pptr. Those previous estimates are uncertain because they are calculated from lipid tube data. It is uncertain whether the apparent decline in river water PCB concentrations in 2000 is the result of a reduction in PCB sources or of higher river flow and increased dilution in 2000 as compared with conditions during the study period of the 1995 TIS report.

Recommendations

Results from the Spokane River water and Kaiser effluent analyses were both inconclusive. The Kaiser grab sample results were highly variable as a result of apparent non-homogeneity of the effluent. A more precise measure of the PCBs in the Kaiser effluent will require a larger number of samples to be taken, or the production by Kaiser of a more homogeneous effluent.

The river sample results were incomplete as a result of laboratory PCB-1254 and -1260 contamination. Concentrations of PCB-1248 were lower than expected, causing most samples to yield nondetectable results. Future characterizations of PCBs in Spokane River water may require ultra-low level detection methods. Several private laboratories are now able to provide detection of a full range of PCB congeners at a method detection limit of 5 to 20 parts per quadrillion and an estimate of associated Aroclor concentrations (Magoon, 2001). This is approximately ten times lower than the sensitivity obtained in this study.

Since the August 2000 sampling, it has been reported that Kaiser has begun using a coagulant to settle solids in the effluent (Blau, 2001). Until it is determined that the Kaiser treatment system is being operated in a steady state – with planned-for, consistent, long-term operating conditions – a re-sampling of Kaiser may provide results that provide only a unrepresentative snapshot in time. Because solids in the Kaiser effluent may be related to growth in the treatment ponds, warm weather conditions are recommended for any re-sampling.

Sampling of wastewater treatment plants discharging to the Spokane River, in the Spokane vicinity, for PCBs is planned for May 2001.

References

Blau, Pat. 2000. Personal communication. Kaiser Aluminum and Chemical Corporation, Trentwood Works, Spokane, Washington. December 5.

Blau, Pat. 2001. Personal communication (letter). Kaiser Aluminum and Chemical Corporation, Trentwood Works, Spokane, Washington. January 17.

Ecology. 2000. Manchester Environmental Laboratory Lab Users Manual, Fifth Edition, Washington Department of Ecology, Manchester, Washington.

EPA. 1999. National Recommended Water Quality Criteria – Correction. EPA 822-Z-99-001, April.

Frame, George M.; Jack W.Cochran; and Soren S. Bowadt. 1996. *Complete PCB Congener Distributions for 17 Aroclor Mixtures Determined by 3 HRGC Systems Optimized for Comprehensive, Quantitative, Congener-Specific Analysis*. Journal of High Resolution Chromatography. Volume 19, December.

Golding, Steven. 1996. Spokane River PCB Source Monitoring Follow-up Study November and December 1995. Pub. No. 96-331. Washington Department of Ecology, Olympia, Washington.

Hart Crowser. 1995. Final Report: Supplemental 1994 Spokane River Investigations Kaiser Aluminum and Chemical Corporation, Trentwood Works, Spokane, Washington.

Johnson, Art. 1994. "PCB and Lead Results for 1994 Spokane River Fish Samples." Memorandum to G. Patrick. Washington Department of Ecology, Olympia, Washington.

Lauenstein, G.G. and A.Y. Cantillo, editors. 1993. Sampling and analytical methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch projects. 1984-1992. NOAA Tech. Memo. NOS ORCA 71. National Oceanic and Atmospheric Administration, Silver Spring, Maryland.

Magoon, Stuart. 2001. Personal communication. Manchester Environmental Laboratory, Washington Department of Ecology, Manchester, Washington. March 19.

Olson, Norman. 2001. Personal communication (E-mail). Manchester Environmental Laboratory, Washington Department of Ecology, Manchester, Washington. March 13.

Roland, John. 2000. Personal communication (E-mail). Toxics Cleanup Program, Eastern Regional Office, Washington Department of Ecology, Spokane, Washington. December 8.

Serdar, Dave, Art Johnson, and Dale Davis. 1994. Survey of Chemical Contaminants in Ten Washington Lakes. Pub. No. 95-154. Washington Department of Ecology, Olympia, Washington.

TIS. 1995. Department of Ecology 1993-94 Investigation of PCBs in the Spokane River. Pub. No. 95-310. Toxics Investigations Section, Environmental Investigations and Laboratory Services Program, Washington Department of Ecology, Olympia, Washington.

Appendix – Manchester Environmental Laboratory Quality Assurance and Quality Control Case Narrative

PCB Analyses

These samples were analyzed using a novel technique employing the Gerstel large volume injection system coupled to a gas chromatograph with electron capture detector (ECD). The system was evaluated by performing an initial demonstration of capability (IDC) for all the PCB congeners and Aroclors 1242 and 1260.

Aroclor 1242	spiked at 5 ng/Liter	78% Recovery
Aroclor 1260	spiked at 5 ng/Liter	96% Recovery
PCB Congeners	spiked at 0.2 ng/Liter	83% Recovery 66% - 111%

The practical quantitation limit (PQL) for the congeners is reported as 0.2 ng/Liter. The PQL reported for the Aroclors is 0.9 ng/Liter. There are no Aroclors or congeners detected above the PQL in any of the blanks prepared with the IDC study.

After the IDC study was completed but before the analysis of the Spokane River samples, a set of samples containing high levels of Aroclor 1254 were processed in the laboratory. Blanks extracted with the Spokane River samples were found to be contaminated with Aroclor 1254 at levels up to 7 ng/µL. It is protocol to qualify all results of a contaminating analyte up to ten times the level found in the highest blank. Although the values detected are shown on the report for the 1254 Aroclor and its congeners, the data have been qualified as REJ, indicating that it has been rejected. Since any additional native Aroclor 1254 would have added to this value, the data for Aroclor 1254 and its congeners should be considered the maximum amount of these analytes that are present in the samples.

Aroclor 1260 was also found in the blanks at the level of about 1 ng/Liter. And similarly, all 1260 results less than 11 ng/Liter are rejected. Results for the 1260 congeners are rejected unless they exceed ten times the level found in the highest blank.

The results for Aroclor 1248 are not affected by the 1254 and 1260 contamination and are reported unqualified.

METHODS

The water samples were extracted into methylene chloride. A 30 µL injection was introduced into the GC-ECD using the Gerstel Large Volume Injection (LVI) system.

These methods are modifications of EPA SW-846 methods 3510, and 8081/82.

BLANKS

Aroclors 1254, 1260 and thus their respective congeners were detected in the blanks. As a result of this, most of the sample results for these analytes had to be rejected.

SURROGATES

All samples and blanks were spiked with decachlorobiphenyl (DCB) prior to extraction. The surrogate recoveries are within the acceptable range 50% - 150% of the reference value, with the exception of samples 00338086 and 00338098. All results for these samples have been qualified as estimates.

SPIKED SAMPLES AND SPIKED SAMPLE DUPLICATES

Sample 00338080 were prepared in triplicate. Two replicates of each sample were spiked with Aroclors 1242 and 1260. The recoveries for Aroclor 1242 could not be calculated (NC) due to the interference of native Aroclor 1248 present in this sample. The recoveries of Aroclor 1260 are 84% and 183%. Five replicates of sample 00338104 were prepared. Two replicates were spiked with Aroclors 1242 and 1260. Two replicates were spiked with the 20 PCB congeners of interest.

Sample 00338104	Recovery 1	Recovery 2	Precision
1242	98	107	2.4%
1260	93	73	7.8%
Congeners (Most)	65%-145%		<50%

The congeners found in Aroclor 1254 had poor recoveries and precision due to contamination. Congener 77 recovery and precision are out of control due to interference from congener 110.

HOLDING TIMES

The samples were extracted and analyzed within the recommended holding times.

DATA QUALIFIERS

Code	Definition
E	Reported result is an estimate because it exceeds the calibration.
J	The analyte was positively identified. The associated numerical result is an estimate.
N	There is evidence the analyte is present in this sample.
NJ	There is evidence that the analyte is present. The associated numerical result is an estimate
NAF	Not analyzed for.
NC	Not calculated.
REJ	The data are unusable for all purposes.
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.

General Chemistry Analyses

SUMMARY

The data generated by the analyses of these samples are acceptable for use.

SAMPLE INFORMATION

These samples were received by Manchester Laboratory on 8/16/2000 in good condition.

HOLDING TIMES

The samples were analyzed within the EPA holding times for all parameters.

ANALYSIS PERFORMANCE

Instrument Calibration

All balances are professionally calibrated yearly with calibration verification occurring monthly and internal calibration occurring daily. Oven temperatures are recorded before and after analysis to ensure control. Other instrumentation is calibrated as needed and a documented calibration check is used for verification.

Laboratory Control Sample

Accuracy is evaluated through the use of laboratory control standards. All were within the acceptance windows.

Precision Data

Results from duplicate analysis were used to evaluate precision. All duplicates were within the acceptance window of +/- 20% RPD.

Method Blanks

Method blanks associated with these samples showed no analytically significant levels of analytes.

Other Quality Assurance Measures and Issues

The “U” qualification indicates that the analyte was not detected at or above the reporting limit.