DEPARTMENT OF ECOLOGY

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TO: Carl Nuechterlein
Water Quality Program -- Eastern Regional Office

THROUGH: Larry Goldstein
EILS Program -- Toxics, Compliance, and Ground Water Investigations Section

FROM: Art Johnson
Toxics, Compliance, and Ground Water Investigations Section

SUBJECT: Planar PCBs in Spokane River Fish

BACKGROUND

Environmental Investigations and Laboratory Services' 1993 survey of the Spokane River found high concentrations of polychlorinated biphenyls (PCBs) in fish and sediments of the upper river (Johnson *et al.*, 1994). A subset of the fish tissue samples with the highest concentrations were selected to be analyzed for planar PCBs. These analyses were undertaken because the toxicity of planar PCBs has been recognized as an important consideration in assessing the human health and ecological implications of PCB mixtures. Planar PCBs are a recent direction of research on the toxicology of PCBs.

Planar PCBs are present at the parts per thousand level in commercial PCB mixtures. Their planar structure (other PCBs tend toward a right angle shape) with lateral substitution of chlorine is similar to other highly toxic planar chlorinated hydrocarbons (PCHs) which include but are not limited to dioxins, furans, naphthalenes, diphenyl ethers, diphenyl toluenes, and dibenzothiophenes. Evidence from animal studies suggest these compounds act by the same cellular mechanism as TCDD ("dioxin") and, at much higher doses, may elicit dioxin-like effects.

SAMPLE SELECTION AND ANALYSIS

The Spokane fish samples selected for planar PCB analysis are shown in Figure 1 and Table 2 in Johnson *et al.* (1994) - attached as Appendix A. Samples analyzed were: mountain whitefish fillets from upper Long Lake, fillets from the larger of two rainbow trout samples above Nine Mile Dam, and two rainbow trout fillet samples collected above Upriver Dam. A whole largescale sucker sample taken above Upriver Dam was also analyzed. All samples were composites of four-to-five individual fish. Concentrations of total PCBs in these samples ranged from 475 - 2,775 parts per billion (ppb).

There are 209 individual PCB compounds, 18 of which have a planar type configuration. The Spokane samples were analyzed for eight of the most toxic planars. Analysis was by high resolution GC/MS (EPA Method 8290) at Alta Analytical Laboratory, Inc., in El Dorado Hills, California. The quality of the data was evaluated by Stuart Magoon of the Ecology Manchester Environmental Laboratory (Appendix B). No significant problems were encountered in the analysis.

RESULTS

Results are shown in Table 1. Planar PCBs are identified by their IUPAC[1] number (e.g., PCB-77 is 3,3',4,4'-tetrachlorobiphenyl). All concentrations are in parts per billion on a wet (fresh) weight basis.

Concentrations of individual planar PCBs ranged from 0.031 to 70 ppb, with PCB-114 and -105 being present in the highest concentrations. One of the eight compounds analyzed, PCB-169, was not detected at detection limits of 0.0019 - 0.0044 ppb. This is consistent with other reports that PCB-169 is usually present at very low levels in the environment and not considered an important contaminant (EPA, 1991).

Table 1. Total and Planar PCBs in Spokane River Fish Samples (ug/Kg (ppb) wet weight)

		Sample	Total	Planar PCB Compounds							% Planar
Location	Species	Type	PCBs	77	81	114	118	105	126	156	PCBs
Upper Long Lake	Mountain Whitefish	Fillet	810	0.38	0.19	15	0.55	6.1	0.034	2.0	3.0 %
Above Nine Mile Dam	Rainbow Trout (lg)	Fillet	475	0.33	0.14	11	0.45	4.3	0.031	0.85	3.6 %
Above Upriver Dam	Rainbow Trout (sm)	Fillet	1000	0.46	0.38	24	1.0	12	0.060	1.0	3.9 %
	Rainbow Trout (lg)	Fillet	1124	0.45	0.48	23	1.2	11	0.068	1.0	3.3 %
	Rainbow Trout (lg)*	Fillet	-	0.47	0.44	23	1.2	12	0.069	0.99	3.4 %
	Largescale Sucker	Whole	2775	0.73	1.5	70	3.4	30	0.12	2.8	3.9 %

*duplicate analysis

The precision of the analysis can be gauged by the results of a duplicate analysis on rainbow trout fillets, shown near the bottom of Table 1. Duplicate measurements agreed within 8% or better for each of the planar PCBs detected. The sum of planars was consistently 3.0 - 3.9% of total PCBs across all samples.

[1]International Union of Pure and Applied Chemists

There are not enough data on the occurrence of these compounds in Washington State fishes to put these results in a local perspective. The only published data I am aware of is for the Willamette River where PCB-77, -105, -126, and -169 were analyzed in whole squawfish (Curtis *et al.*, 1993). In this study, only PCB-77 was consistently detected and no planar PCB was measured at a concentration exceeding 8 ppb. Some planar PCB analyses have also been conducted on Columbia River fish by the Oregon Department of Environmental Quality, but results are not available as of this writing.

The potential toxicity of planar PCBs is sometimes assessed using Toxic Equivalent Factors (TEFs). A TEF is a numeric estimate which relates the toxicity of a particular PCH to that of TCDD, which is believed to be the most toxic PCH.

If, for example, a planar PCB had 1/10th the toxicity of TCDD, its TEF would be 0.1. The product of the planar's concentration and TEF is its TCDD equivalent or TCDD-EQ. Assuming that the toxicities of different planar PCBs are additive, TCDD-EQs for individual planars can be summed to give the combined toxicity potential for the sample in question, usually expressed in units of parts per trillion (pptr).

The TEF approach is not universally accepted, and there is disagreement on what TEFs are appropriate. It is important to note that a conclusive link has not been established between effects seen with planar PCBs in the laboratory and effects in the environment. EPA considers TEFs "useful in assessing traditional measures of wildlife toxicity" but is currently re-evaluating dioxin-based TEFs for human health (EPA, 1991).

Table 2 shows three sets of TEFs that have been derived for planar PCBs and may be relevant to aquatic life and wildlife. TEFs have also been proposed to protect human health (Safe, 1990) but are not included here due to the above mentioned uncertainty about dioxin's toxicity to human beings.

Smith *et al.* (1990) developed their TEFs from a variety of studies and applied them to fish and birds of the Great Lakes region. The TEFs of Tillitt *et al.* (1993) were based on results of a rat liver cell bioassay. Walker and Peterson (1991) and Janz and Metcalfe (1991) have reported TEFs for PCB-126 and -77 in rainbow trout liver and eggs.

TCDD-EQs were calculated for the Spokane River samples using the data in Tables 1 and the TEFs of Smith *et al.* and Tillitt *et al.* (Table 3). The TEFs of Smith *et al.* were used in instances where none were provided by Tillitt. Smith-based TCDD-EQs are 19.1 - 44.3 pptr in rainbow and whitefish fillets and 89.8 pptr in the single whole fish sample analyzed. Much lower TCDD-EQs of 1.8 - 9.7 pptr result if Tillitt's TEFs are used. The disparate results reflect both lack of agreement in experimental data and the different endpoints for which the TEFs were intended.

Table 2. Planar PCB Toxic Equivalent Factors (TEFs) Relevant to Fish and Wildlife

Reference: Applied to or derived from:	Smith et al. (1990) Fish and birds of Great Lakes region	Tillitt et al. (1993) Rat liver bioassay	Walker & Peterson (1991), Janz & Metcalfe (1991) Toxicity tests on rainbow trout
PCB-126	0.40	0.022	0.005
PCB-169	0.0016	0.00047	-
PCB-77	0.0027	0.000018	0.002-0.00016
PCB-81	0.0000086	-	-
PCB-60*	0.0000085	-	-
PCB-118	0.0000083	-	-
PCB-105	0.0011	0.000008	-
PCB-123*	0.000024	-	-
PCB-114	0.000095	-	-
PCB-156	0.000046	-	-
PCB-157*	0.000135	-	-
PCB-167*	0.0000072	-	-
PCB-189*	0.0000085	-	-

*not analyzed in Spokane samples

Table 3. 2,3,7,8-TCDD Toxicity Equivalents in Spokane River Fish Samples (ng/Kg (pptr) wet weight)

			TCDD-EQs based on TEFs in:	
Location	Species	Sample Type	Smith et al. (1990)	Tillet et al. (1993)
Upper Long Lake	Mountain Whitefish	Fillet	22.9	2.3
Above Nine Mile Dam	Rainbow Trout (lg)	Fillet	19.1	1.8
Above Upriver Dam	Rainbow Trout (sm)	Fillet	40.8	3.8
	Rainbow Trout (lg)	Fillet	42.8	3.8
	Rainbow Trout (lg)*	Fillet	44.3	3.9
	Largescale Sucker	Whole	89.8	9.7

*duplicate analysis

By way of comparison, prior to improvements at pulp mills on the Columbia River, contamination of the river's fish by chlorinated dioxins and -furans resulted in TCDD-EQs of up to 7.4 and 25 pptr in Lake Roosevelt whole largescale suckers and sturgeon fillets, respectively (Johnson *et al.*, 1991). The highest TCDD-EQ recorded for the Columbia River in Washington was 88 pptr in a whole carp sample from Lake Wallula (McNary Pool) (EPA, 1992). The concentrations in the Spokane fish samples appear high relative to dioxin-based TCDD-EQs for Columbia River fish.

At present, it is not possible to say with any certainty what effects TCDD-EQs in this range may have on fish and wildlife of the Spokane River. It has been shown that planar PCBs are biomagnified in predatory fish and fish-eating birds. Jones *et al.* (1993), for example, reports biomagnification factors of 7 to 30 between TCDD-EQ levels in Great Lakes forage fish and their predators. Adverse effects to a number of wildlife species occur at TCDD-EQs in the approximate range of 10 - 500 pptr (Ludwig *et al.*, 1993). Therefore, even the relatively low Tillitt-based TCDD-EQs in Spokane River fish could lead to substantial accumulations at higher trophic levels where planar PCBs have been linked to reproductive failures (Ankley *et al.*, 1993).

Acknowledgement: The planar PCB analysis through Alta Analytical was arranged by Stuart Magoon of the Ecology Manchester Environmental Laboratory. His efforts are much appreciated.

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AJ:blt
Attachment

APPENDIX A.

Table 2. PCB Concentrations in Spokane River Fish (ug/Kg (ppb) wet weight)
[from Johnson et al., 1994]

Location	Species	Sample Type	% Lipid	PCB-1242	PCB-1254	PCB-1260	Total PCBs
Spokane Arm (FDR Lake)	Walleye	Fillet	0.4	8.8 U	15	8.8 U	15
	Smallmouth Bass	"	1.2	7.1 U	28	7.1 U	28
	Kokanee	"	4.4	10 U	70	22	92
	Largescale Sucker	Whole	5.1	190	250	190	630
Long Lake	Crayfish	Muscle	0.4	17 U	17 U	17 U	ND
	Yellow Perch	Fillet	0.2	6.8 U	9.4	6.8 U	9.4
	Largemouth Bass	"	0.6	15 U	74	23	97
	Mountain Whitefish	"	3.5	230	410	170	810
	Largescale Sucker	Whole	2.3	140	180	130	450
Above Nine Mile Dam	Rainbow Trout (sm)	Fillet	2.7	180	210	64	454
	Rainbow Trout (lg)	"	2.9	170	240	65	475
	Mountain Whitefish	"	2.7	200	280	42	522
	Largescale Sucker	Whole	5.6	360	600	210	1170
Above Upriver Dam	Rainbow Trout (sm)	Fillet	1.7	450	550	78 U	1000
	Rainbow Trout (lg)	"	1.9	440	610	74	1124
	Largescale Sucker	Whole	4.3	800	1800	175	2775
Above Post Falls (Idaho)	Largescale Sucker	Whole	7.2	28 U	55	41	96

samples analyzed for planar PCBs, subject of present report

U = not detected at or above reported value

ND = not detected

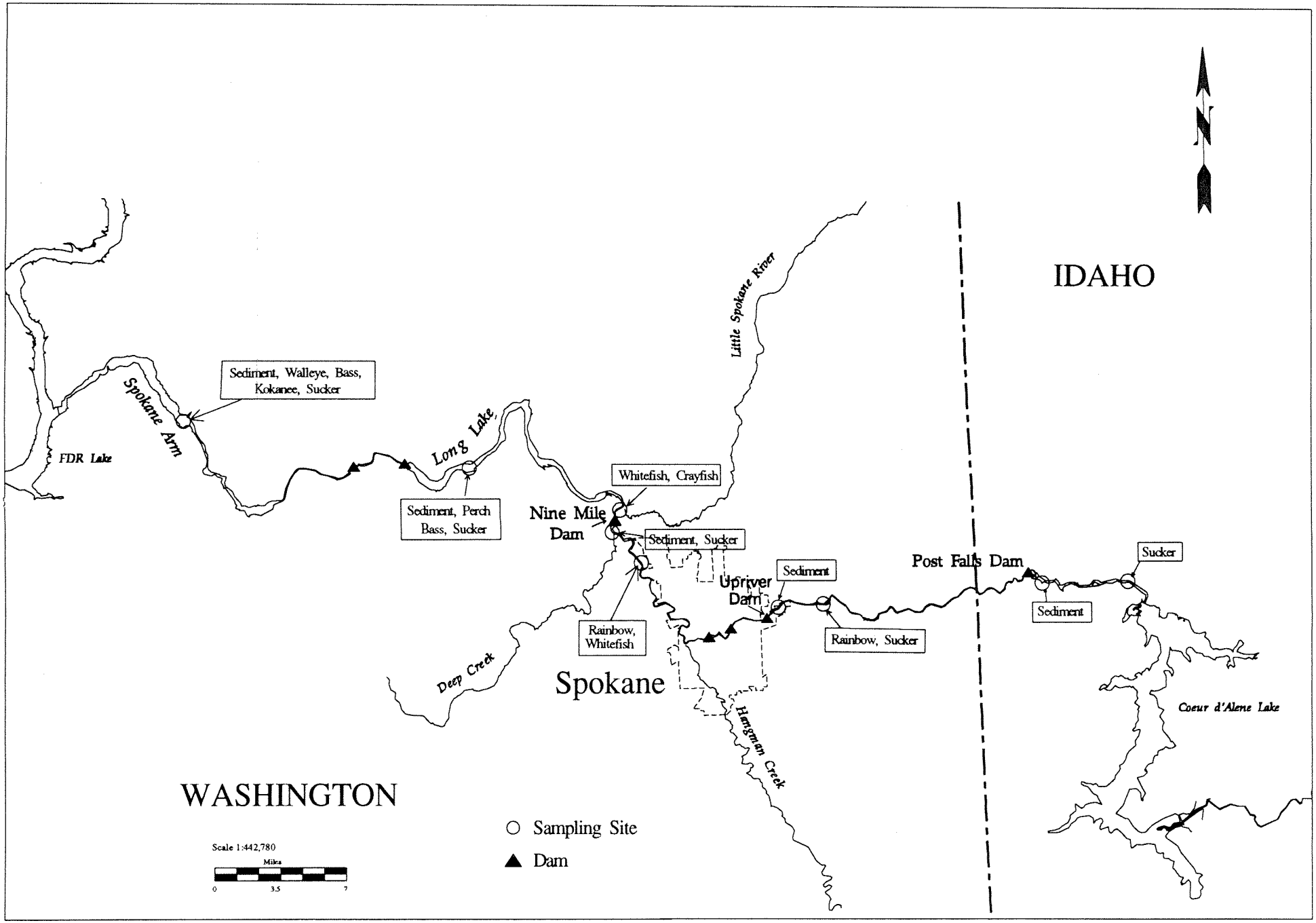

Figure 1. Location of Ecology 1993 Spokane River Sediment and Fish Samples [from Johnson et al., 1994]

APPENDIX B.

State of Washington Department of Ecology
Manchester Environmental Laboratory
7411 Beach Dr. East Port Orchard WA. 98366

Data Review
April 6, 1994

Project: **Spokane River PCBs**

Samples: 318243, 50, 52, 55, 56

Laboratory: Alta Analytical Laboratories Inc. 13219

By: Stuart Magoon

Case Summary
for Coplanar PCBs

Data from these analyses were reviewed for qualitative and quantitative accuracy, validity, and usefulness. These samples were prepared and analyzed according to a modification of EPA method 8290.

The results are reported in Pico grams per gram (pg/g) which is parts per trillion as received.

Results for the percent Non-polar Lipids and Extractable Lipids are not to be added to get a "total" lipid content. The percent Non-Polar Lipids are expressed in relation to the total tissue sample (wet weight) and the percent Extractable Lipids are also expressed in relation to the total tissue sample (wet weight).

There is a number reported for each analyte that appears in one of two columns. If the number appears in the column labeled "Conc." then this analyte has been detected at the level reported. If the number appears in the column labeled "D.L." then the analyte was not detected and the number is the detection limit at or above which the analyte was not detected (there should be an "ND", short for not detected, that appears in the "Conc." column).

Alta Laboratories has developed their own "Qualifiers". The definitions of these "Qualifiers" are described in Appendix A. Alta "Qualifiers" are to be considered separate from Manchester laboratory "data qualifiers".
the Alta qualifiers are added by the laboratory performing the analysis, usually the analyst. Data qualifiers are added by the data reviewer as part of addressing the usability of the data. Generally the laboratory (Alta in this case) qualifiers signal the reviewer to access the results and determine what to do about the fact that the laboratory qualifiers were added. For your reporting purposes the Alta "Qualifiers" should not be considered part of the final result. The data qualifiers, however, are to be considered part of the final result.

ANALYSIS

Holding times:

EPA method 8290 recommends holding times of thirty days (30) from the date of collection to the date of extraction and forty five (45) days total from collection to analysis. The method also states PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Section 6.4 may be as high as a year for certain matrices. Likewise PCB's are very stable.
Considering the environmental persistence of PCBs no data qualifiers have been added due to holding times.

Method Blank:

Trace amounts of PCB-77, PCB-114, and PCB-105 were detected in the method blank. The amount of PCBs detected in the method blank are insignificant compared to the amount of PCBs detected in each of these samples, therefore the "B" qualifier assigned by Alta can be ignored.

Continuing Calibration:

The continuing calibration standards were within the relative standard deviation (RSD) limit of 20% for the target analytes and 30% for the isotopically labeled compounds.
All the ion abundance ratios were within +/- 15% of the theoretical value.

Internal Standard Recoveries:

All internal standard recoveries were above the lower limit of 20%.

Isotopic abundance ratios:

Every PCB congener reported as detected met the isotopic abundance ratios criteria for positive identification.

Matrix Spikes (MS/MSD):

Spike recoveries are reasonable and acceptable for all the coplanar PCB congeners spiked. The RPD quality control limit specified by the method is 20.
The native amount of PCB-114 and PCB-105 in sample 318252 is large in comparison to the amount added as the spike. Often when this is the case the spike recoveries fall outside of QC limits. In this case however, recoveries for these two congeners is reasonable. Actually the recovery for PCB-114 is very good considering the amount of native PCB-114 is over 13 times the amount spiked.

Summary:

This data is acceptable for use. The "J" data qualifier was added to the three detected PCB congeners in the method blank because the amount detected fell below the calibration curve.