

CONTAMINANT TRENDS IN LAKE ROOSEVELT

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Contaminant Trends in Lake Roosevelt

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Abstract

During 1992 and 1993 the Washington State Department of Ecology (Ecology) monitored dioxin, furan, and trace metal concentrations in suspended particles and selected fish tissues collected from upper Lake Roosevelt. The primary objective of the monitoring was to provide information about temporal trends in concentrations of these pollutants. This monitoring was predicated on earlier Ecology studies of metals and dioxins/furans that described the extent and degree of contamination in Lake Roosevelt through 1990. This report presents new 1993 data and discusses this information in the context of previously reported 1990 and 1992 data.

The primary historical source of dioxins and furans (especially 2,3,7,8-TCDD and 2,3,7,8-TCDF) in Lake Roosevelt has been the Celgar pulp mill in Castlegar, British Columbia. The Cominco lead-zinc smelter in Trail, B.C. is largely responsible for elevated metals concentrations (especially zinc, lead, copper, arsenic, cadmium, and mercury).

Dioxin and furan concentrations in suspended particles, as well as lake whitefish muscle and eggs, found in 1993 generally confirm the decreases in contamination recorded between 1990 and 1992. While concentrations of some of the less toxic forms of dioxin and furan in suspended particles increased between 1992 and 1993, the overall toxicity of these compounds in particles and whitefish tissue remained much lower than it had been in 1990. The reduction in dioxin/furan levels reflects changes in pulp production and wastewater treatment methods at Celgar.

Loads of specific metals associated with suspended particles in 1993 were generally 13% to 46% lower than those found in 1992. None the less, concentrations in both particles and whole largescale suckers were still very high. Significant additional reductions in metals discharged from the Cominco facility will be necessary before concentrations in Lake Roosevelt fish and sediments begin to return to levels typical of unperturbed systems.

Summary

To track changes in pollutant loads to Lake Roosevelt over time, dioxin, furan and trace metal concentrations were monitored in suspended particle and fish tissue samples collected from the upper Columbia River (Canada Border to Kettle Falls). Samples were collected for this study during the early autumn, low-river-flow periods (September-October) of 1992 and 1993. This report focuses on the new 1993 data and interprets it in light of data collected during 1990 and 1992.

Flow-through centrifuges were used to collect the suspended particles from the river that were analyzed for a range of metals (zinc, lead, copper, arsenic, cadmium, and mercury) and 2,3,7,8-substituted dioxins and furans. Lake whitefish muscle and egg tissues were analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF. Analysis of muscle was subsequently expanded to the full range of 2,3,7,8-substituted congeners. Whole largescale suckers were analyzed for zinc, lead, copper, cadmium, and mercury.

2,3,7,8-TCDD (the most toxic of the dioxins) was not detected in suspended particles in 1993 (this was also true in 1990 and 1992). 2,3,7,8-TCDF (a furan with 1/10 the toxicity of 2,3,7,8-TCDD) in suspended particles fell from a concentration of 99 pg/g in 1990, to 6.2 pg/g in 1992, to 4.4 pg/g in 1993. Several less potent congeners that had not been detected in earlier years were detected in the 1993 particle sample. This caused the dioxin/furan-associated toxicity of particle samples to actually increase somewhat between 1992 and 1993. This toxicity as measured by toxic equivalents (TEQs) was approximately 10.8 pg/g in 1990; 1.1 pg/g in 1992; and 3.3 pg/g in 1993. At present it is unclear whether the 1992 to 1993 increase in TEQ represents "noise" associated with sampling and analyses, changes in detection limits between years, or changes in pollutant discharges upstream of Northport. In any case, the proportion of TEQ associated with 2,3,7,8-TCDF fell from 92% in 1990, to 56% in 1992, to 13% in 1993.

1993 was the first year Ecology analyzed dioxins and furans in the dissolved phase. Dissolved 2,3,7,8-TCDD was not detected while 2,3,7,8-TCDF was. About 75% of the Columbia River's 2,3,7,8-TCDF load was estimated to be in the dissolved phase. In 1993 the dissolved 2,3,7,8-TCDF load was about 4.0 mg/day while the particle-bound load was about 1.3 mg/day. This compares to particle-bound loads of 2,3,7,8-TCDF estimated to be 29.9 mg/day in 1990 and 2.0 mg/day in 1992.

In 1993 as in 1992, TEQs of lake whitefish muscle and egg tissue were well below values recorded in 1990. Lake whitefish muscle TEQ averaged 14 pg/g in 1990, 6.9 pg/g in 1992, and 3.8 pg/g in 1993. Whitefish egg TEQ was 87 pg/g in 1990, and averaged 7.6 pg/g in 1992 and 12.9 pg/g in 1993.

After results for suspended particles showed apparent increases for dioxins and furans other than 2,3,7,8-TCDD and 2,3,7,8-TCDF, analysis of three of the six composite lake whitefish muscle samples was expanded to include the full range of 2,3,7,8-substituted dioxins and furans. The results confirmed that 2,3,7,8-TCDD and 2,3,7,8-TCDF continued to be responsible for nearly all of the whitefish muscle TEQ.

Concentrations of metals in suspended particles were highest for zinc, followed in order by lead, copper, arsenic, cadmium, and mercury. Excepting mercury, concentrations of specific metals fell by 10-44% between 1992 and 1993. Similarly, particle-bound loads transported into Lake Roosevelt by the Columbia River were 13-46% lower. Mercury in the river was elevated in 1992 due to a spill from the Cominco smelter in Trail, B.C. 1993 mercury concentrations and loads were about 80% lower than those measured in 1992. Despite these decreases, metals concentrations in Columbia River particles remain very high.

Metals concentrations in whole fish (largescale suckers) from the upper Columbia River are very high in comparison to national averages. Except for mercury, all metals were found in Northport fish at higher concentrations than in Kettle Falls fish. Comparison of 1993 whole fish data with Ecology's 1986 data suggests no improvement over these seven years and should allow these data to serve as a representative "baseline" for judging future trends in metals contamination in the upper Columbia.

Acknowledgements

We are indebted to many individuals who helped with this project. We would especially like to thank Art Johnson (Ecology) for his work on previous Lake Roosevelt studies and for his thoughtful review of this report. We would also like to thank members of the Lake Roosevelt Water Quality Council's Technical Advisory Committee for reviewing the report and offering helpful feedback. We are also grateful to the following people for their support: Lee Daneker and Judith Leckrone (EPA) helped plan and review the work; Carol Jolly (Ecology) for moral support; Stuart Magoon, Dave Thomson, Bill Kammin, Aileen Smith, Kitty Bickle, Myrna McIntosh, Debbie Lacroix, and other staff of the Manchester Environmental Laboratory; Keith Seiders of Ecology (especially) for technical support in the field; Steve Cox (USGS) for technical assistance; Jim McLaren (Celgar Pulp Co.) and Graham Kenyon (Cominco Ltd.) for information about their respective industries; John Sneva (Washington State Department of Fisheries and Wildlife) for ageing fish scales; and many thanks to Kelly Carruth, who provided word processing support under somewhat stressful circumstances. This work was funded, in part, through a grant from the EPA Clean Lakes Program.

Introduction

In 1992, EPA provided a Clean Lakes Grant to the Washington State Department of Ecology (Ecology) to initiate contaminant monitoring in Lake Roosevelt during 1992-1993. The primary goal of the study was to document the effects of pollution controls being implemented by Canadian industries located on the Columbia River upstream of Lake Roosevelt. Major contaminants of concern are 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD; commonly referred to as dioxin), 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), and metals (zinc, lead, copper, arsenic, cadmium, and mercury). Sample collection was completed during October 1993 and results are reported here. Complete results and discussion of the 1992 sample collection are included in a separate report entitled *Interim Report on Monitoring Contaminant Trends in Lake Roosevelt* (Serdar et al., 1993).

Background on Chemical Contamination of Lake Roosevelt

The Celgar bleached kraft pulp mill in Castlegar, British Columbia, located approximately 35 river miles above the international border (Figure 1), is considered to be the major historical source of polychlorinated dioxins and furans (PCDDs/PCDFs) to Lake Roosevelt. During the past six years, Canadian investigators have found substantial concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sediment and fish collected below Celgar (Mah *et al.*, 1989; B.C. Ministry of Environment, 1990; Boyle *et al.*, 1992).

Ecology responded to initial reports from Canada by conducting a suite of investigations during 1990 to assess the degree of contamination in Lake Roosevelt. Results showed elevated levels of 2,3,7,8-TCDF and, to a lesser extent, 2,3,7,8-TCDD in several species of fish and in bottom sediments (Johnson *et al.*, 1991a and b). The amounts (loads) of dioxins and furans entering Lake Roosevelt were also estimated by analyzing a three-day composite sample of suspended particulate matter (particles) from the Columbia River near the border (Johnson *et al.*, 1991c).

Since Ecology conducted their initial investigations in 1990, Celgar has made a number of changes in bleaching and wastewater treatment processes that have improved the quality of their effluent (Table 1). Substituting chlorine dioxide for elemental chlorine bleaching was one of the major process changes intended to substantially reduce the formation of PCDDs/PCDFs. Celgar also added secondary (biological) treatment of wastewater during 1993. Previously, wastewater was discharged to the Columbia River untreated. These changes were made as Celgar doubled its pulp production and constructed a new bleach plant. Details of modifications at Celgar are discussed in their annual Environmental Performance Reports (Celgar Pulp Co., 1992, 1993, and 1994) and Ecology's previous trend monitoring report (Serdar *et al.*, 1993).

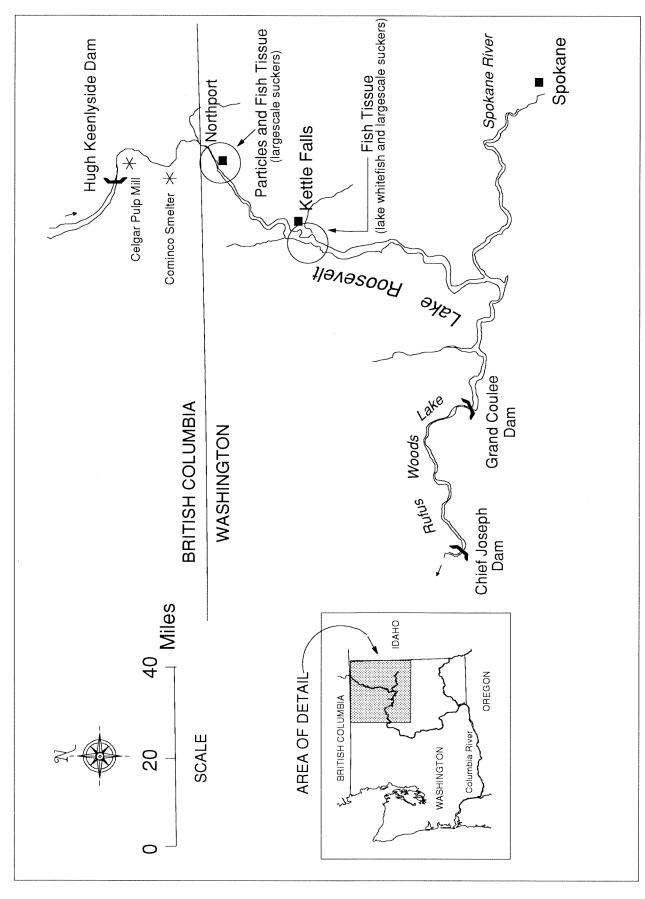


Figure 1. Sampling Sites for Ecology's 1992/1993 Contaminant Monitoring Program in Lake Roosevelt

Table 1. Summary of Process Changes Reported at Celgar.

Year	Process Change
1989	Terminated use of defoamers which contain PCDD/PCDF precursors.
	Began 20-40% chlorine dioxide substitution for chlorine in the bleaching process.
	Began using high shear mixers in the chlorination stages.
1991	Removed recovery boiler water, which contained dibenzofuran, from bleach plant.
	Utilized 40% chlorine dioxide substitution for chlorine in the bleaching process.
	Began using hydrogen peroxide in the delignification process.
1993	Old bleach plant off-line in May, 1993; New bleach plant on-line in mid-1993.
	Instituted 70 - 100% chlorine dioxide substitution for chlorine.
	Began secondary (biological) treatment of mill effluent.

Sources: Celgar Pulp Co. (1992 and 1993); J. McLaren (personal communication)

Contamination of Lake Roosevelt by zinc, lead, copper, arsenic, cadmium, and mercury was documented in the decade prior to concerns about dioxins and furans (Lowe *et al.*, 1985; Johnson *et al.*, 1988). The Cominco Ltd. lead-zinc smelter in Trail, B.C., located approximately 10 river miles above the international border, is the major source of these metals to Lake Roosevelt (B.C. Ministry of Environment, 1979; Smith, 1987). The Spokane River, contaminated by mining in the Coeur d'Alene drainage, is an additional metals source to the lower lake (Mink *et al.*, 1971; Yake, 1979; Johnson *et al.*, 1994).

Cominco Ltd. facilities have operated in Trail since the turn of the century and remain the world's largest integrated lead-zinc smelter and refiner. Cominco also operates a fertilizer plant adjacent to the smelter that uses residual sulfur from the metallurgical plant as feedstock. An average of 360 metric tons of slag per day are discharged directly to the Columbia as a result of smelting operations (Cominco, 1991a). Slag is a black sandy waste product of the smelting operation. This slag is subjected to a metals' recovery process called "fuming", and is then discharged to the Columbia River as a slurry. Chemical analysis of the slag shows it contains approximately 2.5% zinc, 0.5% copper, and less than 0.1% lead (Cominco, 1991a; Nener, 1992).

In addition to slag, Cominco discharges a significant quantity of metals to the Columbia River through four wastewater and storm sewers. Discharge of metals from a fifth outfall, sewer 07, was reduced during September 1993, just prior to Ecology's 1993 sampling event. Sewer 07 formerly received gas-cooling water from the lead sinter plant. It is reported to have discharged the greatest non-slag loads of lead and cadmium to the Columbia River.

Table 2. Historical and Projected Changes Reported at Cominco and Their Effects on Metals Loading to the Columbia River.

[Means Loading to the Common Myor.				
Year	Process Change	Effect on Metals Loadings to Columbia River			
1981	Addition of effluent treatment plant	Reduction in lead, zinc, arsenic, cadmium and mercury			
1981	Modernization of zinc plant	Reduction in zinc			
1981	Diversion of electrolyte purge to fertilizer operations	Reduction in zinc			
1990	Elimination of electrolyte stripping discharge	Reduction in zinc			
September 1993	Elimination of contact cooling water to sewer 07.	Reductions in zinc, lead, copper, arsenic, cadmium, and mercury			
May 1994	Change from ammonium phosphate to ammonium sulfate fertilizer production	Reductions in mercury and zinc			
Mid-Late 1994	Collection and treatment of storm water runoff, flow-equalization to waste water treatment.	Reductions in all metals, but primarily zinc			
1995	Elimination of slag discharge to the river	Reductions in zinc, copper, and lead			
1996	Replace lead smelter.	Undefined reductions.			

Source: Cominco (1991b); G. Kenyon (personal communication); C. Johnson (personal communication)

Table 2 shows changes made by Cominco in the past, and modifications designed to improve metals discharges in the future. In addition to improvements to sewer 07, Cominco forecasts a reduction in metals discharges to the Columbia River by:

 conversion from ammonium phosphate fertilizer to ammonium sulfate fertilizer production in May 1994;

- construction of an equalizing pond in September 1994 to control surface runoff around the zinc smelter; and
- completing a facility for land disposal of slag in 1995.

Objectives of Ecology's Monitoring Program

Objectives of the 1992/1993 trend monitoring effort were to:

(1) Determine if and how 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations are changing in Lake Roosevelt as a result of process modifications and effluent treatment at Celgar.

Data on suspended particles and lake whitefish (*Coregonus clupeaformis*) from Ecology's 1990 surveys form the basis for detecting trends in 2,3,7,8-TCDD and 2,3,7,8-TCDF contamination. Table 1 summarizes process changes affecting 2,3,7,8-TCDD and 2,3,7,8-TCDF discharges by Celgar immediately prior to and following the 1990 surveys.

Sampling sites and methods were consistent between 1990, 1992, and 1993. Figures 1 and 2 show where particle samples were collected during each year. In all cases, samples were three-day composites collected at Northport during the relatively low-river-flow period of September and October. Six composite samples of muscle from five whitefish each, and one or three composite sample(s) of eggs were analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF during each year. Whitefish were collected near Kettle Falls (Figure 1) in each case.

Particle samples (collected using flow-through centrifuges) were analyzed in preference to whole water samples because 2,3,7,8-TCDD and 2,3,7,8-TCDF have low solubility in water and high affinity for particulate matter. Anticipated concentrations in whole water were far below currently achievable detection limits. Previous estimates of 2,3,7,8-TCDF loads calculated from the 1990 and 1992 particle samples showed good agreement with 2,3,7,8-TCDF loads calculated for Celgar effluent in 1989 and 1992, respectively (CPPA, 1989; Johnson *et al.*, 1991c; Serdar *et al.*, 1993).

In 1993, analysis of dissolved dioxins and furans using resin columns was added to the survey. This effort was undertaken following a similar effort by the United States Geological Survey (USGS) during 1992 and in response to interest expressed by members of the Technical Advisory Committee of the Lake Roosevelt Water Quality Council. Preliminary results by USGS indicated that loads of dissolved polychlorinated dioxins and furans (PCDDs/PCDFs), including 2,3,7,8-TCDD and 2,3,7,8-TCDF, may be appreciable because of the large discharge and low concentration of suspended solids in the Columbia River at Northport (S. Cox, written communication). The additional data on dissolved phase PCDD/PCDF concentrations permit better estimates of loads to Lake Roosevelt than those based solely on particulate phase concentrations.

Lake whitefish were chosen for monitoring because, along with white sturgeon, they were the most contaminated of seven fish species analyzed in 1990 (Johnson *et al.*, 1991a and b).

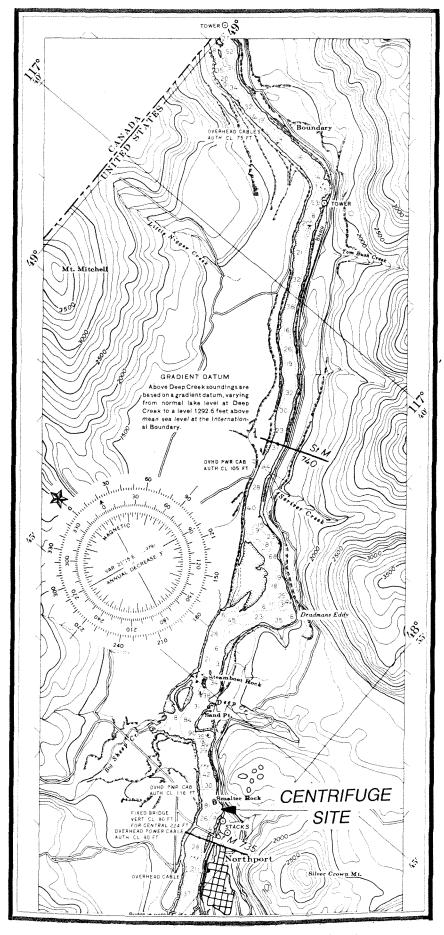


Figure 2. Sampling Site for Particulates

Analysis was initially limited to 2,3,7,8-TCDD and 2,3,7,8-TCDF because previous data showed other PCDDs/PCDFs were not substantial contributors to overall toxicity in Lake Roosevelt fish (as measured by 2,3,7,8-TCDD equivalents, or TEQs). In addition, whitefish eggs were analyzed because they are particularly high in lipid content (dioxins and furans are extremely lipophilic - they tend to be sequestered in fatty tissues) and because the single egg sample from 1990 had very high 2,3,7,8-TCDD and 2,3,7,8-TCDF levels. Eggs may be particularly useful for long-term monitoring if they continue to show high 2,3,7,8-TCDD and 2,3,7,8-TCDF residues after concentrations in muscle have fallen below detection limits.

(2) Establish a baseline on zinc, lead, copper, arsenic, cadmium, and mercury contamination of Lake Roosevelt to gauge impacts of future modifications at Cominco.

Potentially significant reductions in metals discharges by Cominco are expected during 1993-1995 (see Table 2). Historical data on metals contamination are not sufficient to establish a meaningful basis for trend monitoring. Therefore, a primary objective of the 1992/1993 trend monitoring effort for metals has been to establish a baseline to gauge the impacts of future improvements at Cominco.

Suspended particles were analyzed for zinc, lead, copper, arsenic, cadmium, and mercury in 1992 and 1993 to provide an estimate of metals concentrations in the particulate phase of Columbia River water. The 1990 particle sample was not analyzed for metals. Dissolved metals were not analyzed because Ecology already conducts bimonthly sampling of dissolved zinc, lead, copper, cadmium, and mercury at Northport (results of these samples are reported annually by Ecology's Ambient Monitoring Section).

Largescale suckers (Catostomus macrocheilus) were chosen for metals monitoring because previous surveys of Lake Roosevelt fish by U.S. Fish & Wildlife Service and Ecology have shown very high concentrations of zinc, copper, lead, and cadmium in whole fish samples of this species (Lowe et al., 1985; Johnson et al., 1988; Schmitt and Brumbaugh, 1990). Liver was analyzed in 1992 because of concern that potential nonhomogeneity of whole fish samples would add variability to sample results. Liver tissue was also expected to be a better indicator of mercury exposure than whole fish, and it has a potential to respond more quickly to changes in ambient metals concentrations. In 1993, liver samples were replaced by whole fish analysis because of the unexpectedly low metals concentrations found in the 1992 liver samples.

Methods

1993 Sampling and Laboratory Analysis

A complete description of sampling methods, chemical analysis, and data quality is presented in Appendix A. Briefly, suspended particle samples were collected at Northport (river mile 735) on October 5-7, 1993 using two Sedisamp II continuous-flow centrifuges (model 101IL). Northport is approximately 10 river miles below the international border, 20 mi. below

Cominco, and 45 miles below Celgar (see Figure 1). Particles were analyzed for PCDDs/PCDFs, metals, total organic carbon, and percent moisture. A portion of the centrifuged water was also pumped through XAD resin columns. The XAD resins were analyzed for PCDDs/PCDFs to estimate concentrations of these compounds in the dissolved phase.

Twenty-nine lake whitefish were collected by gill net on October 6, 1993 from Lake Roosevelt near Kettle Falls. Six composite samples of muscle from four or five fish each were analyzed for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and percent lipids. Electroshocking methods were used to collect largescale suckers from Lake Roosevelt near Kettle Falls and from the Columbia River in the vicinity of Northport. Fifteen specimens from each site were analyzed whole for zinc, lead, copper, cadmium, mercury, and percent moisture.

Results and Discussion

General Characteristics of Columbia River Water at Northport

Samples of Columbia River water entering the centrifuges were periodically collected for measurement of conventional parameters (Table 3). Specific conductance, temperature, and total suspended solids were similar during 1990-1993 and within ranges normally observed at Northport during September-October (USGS, 1980-1991). River flow during the sampling period was approximately 40% lower in 1993 than in 1992. However, flows for all years were within the range previously recorded during early autumn. Total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) all increased in concentration by about 50% compared to the 1992 measurements, possibly as a result of decreased dilution.

Table 3. Summary of Columbia River Water Quality at Northport, October 9-12, 1990, September 29 - October 2, 1992, and October 5-7, 1993 (mean \pm SD).

Variable	1990 (n=8)	1992 (n=7)	1993 (n=6)
Specific Conductance (umhos/cm)	148 ± 2	135 ± 2	150 ± 3
Temperature (C)	13.0 ± 0.6	14.7 ± 1.0	14.5 ± 1.0
Total Suspended Solids (mg/L)	2.0 ± 0.5	1.4 ± 0.5	2.2 ± 0.4
Total Organic Carbon (mg/L)	3.3 ± 0.1	1.3 ± 0	1.9 ± 0.2
Dissolved Organic Carbon (mg/L)	N/A	1.1 ± 0.1	1.9 ± 0.6
Average Flow at Border (m³/s)	1,745	2,662	1,628

N/A = Not Analyzed

Median pH measurements during 1990, 1992, and 1993 were 8.2, 7.2, and 6.9, respectively. A pH of 8.2 is more consistent with historical data obtained by USGS (USGS, 1980-1991). The lower pH observed during 1992 and 1993 is probably a result of the difference in the point of sampling from that of 1990. The sampling point for pH in 1990 was *in situ* (in the river), but was changed to the point where water entered the centrifuge during the following years. Pumping the water from the river to the centrifuge, approximately 200 feet horizontally and 20 feet vertically upward, appears to cause a change in pH. Although the reason for the change in pH is not certain, it may be a result of changes in dissolved gas concentrations caused by the pressure differential.

PCDDs/PCDFs in Suspended Particles

Characteristics of particle samples obtained using high-speed centrifugation during 1990, 1992, and 1993 are shown in Table 4. Aside from total organic carbon (TOC) content, characteristics of the particle sample were fairly consistent from 1990-1993. Table 5 and Figure 3 show concentrations of PCDDs/PCDFs analyzed in particles during 1990, 1992, and 1993. 2,3,7,8-TCDD, the most toxic of the seventeen PCDDs/PCDFs analyzed, was not detected during any year of sampling. The quantitation limit for 2,3,7,8-TCDD in the 1993 sample was 0.7 pg/g, the lowest achieved since suspended particle sampling began in 1990.

2,3,7,8-TCDF in suspended particles remains much lower than the 1990 level. This is probably due largely to changes which have occurred at the Celgar pulp mill since 1991 (see Table 1). The 1993 concentration of 2,3,7,8-TCDF in particles was about 70% of the 1992 concentration (4.4 vs. 6.2 pg/g) and less than 5% of the 1990 concentration (4.4 vs. 99 pg/g).

In addition to 2,3,7,8-TCDF, thirteen PCDD/PCDF congeners were detected in the 1993 particle sample (Table 5). Eight of these congeners were not detected in either 1990 or 1992. The congener patterns of 1990, 1992, and 1993 samples are shown in Figure 3. OCDD was detected at the highest concentration (482 pg/g), followed by 1,2,3,4,6,7,8-HpCDD (74 pg/g) and OCDF (24 pg/g). OCDD and 1,2,3,4,6,7,8-HpCDD were also the congeners found at the highest concentrations in the 1992 particle sample. Other congeners were detected at 8.5 pg/g or less.

OCDD, 1,2,3,4,6,7,8-HpCDD, and perhaps OCDF show a consistent and substantial increase in concentration from 1990 to 1993. The reason for this is unknown. For the remaining penta-, hexa-, and heptachlorinated compounds, the 1993 results are inconclusive due to: 1) differences in quantitation limits from year to year, and 2) the uncertainty of near quantitation limit values and estimated concentrations. As noted below, these compounds have little toxicological significance for human health or aquatic life at the concentrations so far reported for Lake Roosevelt.

Table 4. Characteristics of the Suspended Particle Samples Collected at Northport During 1990, 1992, and 1993.

Variable	1990	1992	1993
Volume of Water Centrifuged (L)	15,450	10,200	11,540
Amount of Particle Sample Obtained (g, wet)	90	68	81
% Total Organic Carbon	7.6	2.2	10.4
% Solids	26.2	21.2	16.4

Table 5. PCDD/PCDF Concentrations in Columbia River Suspended Particles at Northport During 1990, 1992, and 1993 (mean \pm range of duplicate analysis in pg/g, parts per trillion; dry weight basis).

Compound	TEF	1990	1992	1993
2,3,7,8-TCDD	1	U(0.8)	U(1.6)	U(0.7)
2,3,7,8-TCDF	0.1	99 ± 22	6.2 ± 0.4 J	4.4 ± 0.2
Other PCDDs/PCDFs:				
PCDDs				
1,2,3,7,8-PeCDD	0.5	U(0.5)	U(1.3)	0.5 EMPC
1,2,3,4,7,8-HxCDD	0.1	U(1.1)	U(2.5)	1.5
1,2,3,6,7,8-HxCDD	0.1	U(0.8)	U(3.2)	3.0
1,2,3,7,8,9-HxCDD	0.1	U(0.9)	U(2.7)	3.2 J
1,2,3,4,6,7,8-HpCDD	0.01	11 ± 1	31 ± 6 J	74
OCDD	0.001	79 ± 9	214 ± 30	482
PCDFs				
1,2,3,7,8-PeCDF	0.05	1.0 ± 0.1	U(1.8)	0.7 J
2,3,4,7,8-PeCDF	0.5	1.4 ± 0.2	U(2.6)	0.6 EMPC
1,2,3,4,7,8-HxCDF	0.1	U(0.3)	U(2.4)	1.3 EMPC
1,2,3,6,7,8-HxCDF	0.1	U(0.2)	U(2.5)	0.6
2,3,4,6,7,8-HxCDF	0.1	U(0.3)	U(2.4)	В
1,2,3,7,8,9-HxCDF	0.1	U(0.4)	U(2.5)	U(0.5)
1,2,3,4,6,7,8-HpCDF	0.01	U(1.4)	U(5.8)	8.5
1,2,3,4,7,8,9-HpCDF	0.01	U(0.5)	U(5.7)	0.9 EMPC
OCDF	0.001	4.6 ± 0.7	U(14)	23.6
	TEQ =	10.8	1.1 J	3.3 J

TEF=Toxic Equivalent Factor

U=Undetected at quantitation limits in parentheses

J=Estimate

EMPC=Estimated Maximum Possible Concentration

TEQ=Toxic Equivalents

B=Not reported due to blank contamination

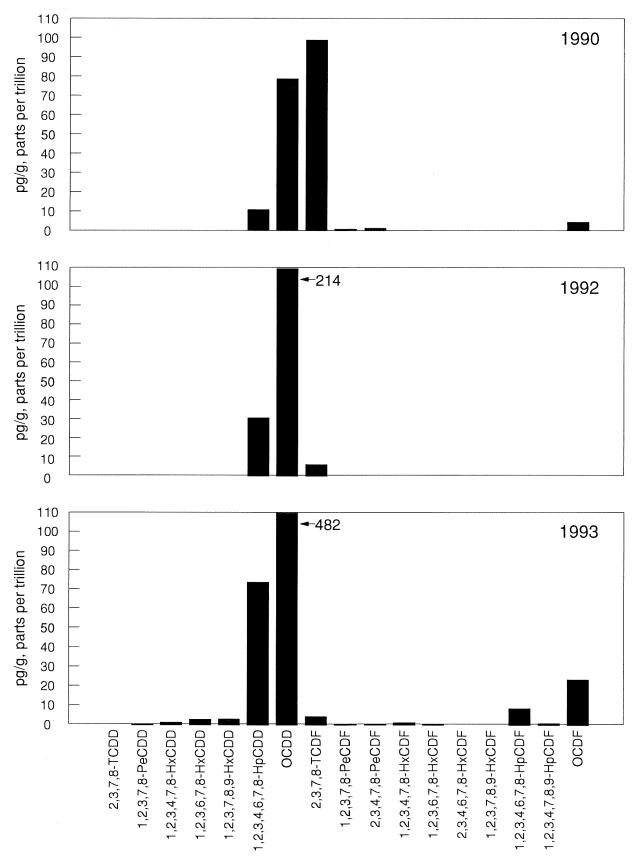


Figure 3. PCDD/PCDF Concentrations in Suspended Particles from the Columbia River at Northport During 1990, 1992, and 1993

Four of the PCDDs/PCDFs detected did not meet the method criteria (EPA 8290) for isotopic abundance ratios. This presented a problem in quantifying the actual amount of analyte present in the sample. As a result, some results are qualified as the estimated maximum possible concentration (EMPC).

Toxicity equivalents, or TEQs, may be used to translate the toxicity of a mixture of 2,3,7,8-substituted PCDDs/PCDFs into an equivalent concentration of 2,3,7,8-TCDD (Barnes et al., 1989). Toxicities of PCDDs/PCDFs relative to 2,3,7,8-TCDD, expressed as toxic equivalent factors (TEFs), are shown in Table 5. In general, congeners with greater chlorine substitution (e.g. octachlorodibenzofuran or OCDF) are considered less toxic than less chlorinated congeners (e.g. 2,3,7,8-TCDF).

The TEQ of the 1993 particle sample increased threefold from the 1992 sample (3.3 vs. 1.1 pg/g), mainly due to the detection of additional PCDDs/PCDFs. However, TEQ of suspended particles remained well below the 1990 level of 10.8 pg/g. It should be noted that only PCDDs/PCDFs with detectable concentrations were used to calculate TEQs. The reader should also be aware that PCDD/PCDF concentrations qualified as EMPC were used in calculating the TEQ, and the resulting TEQ is a maximum possible concentration.

As shown in Figure 4, 2,3,7,8-TCDF accounted for 92% of the TEQ in the 1990 particle sample. Contribution of 2,3,7,8-TCDF to the TEQ fell to 13% in 1993. As noted previously, 2,3,7,8-TCDF is a substantial contributor to TEQs in Lake Roosevelt fish.

PCDDs/PCDFs in the Dissolved Phase

Measuring dissolved PCDDs/PCDFs in Columbia River water was added in 1993 after the USGS detected two dioxin congeners in the dissolved phase during their 1992 study of Lake Roosevelt (S. Cox, written communication). USGS also theorized that 60-75% of 2,3,7,8-TCDD in the Columbia River at Northport was carried in the dissolved phase.

To follow up on this finding, Ecology used XAD resin columns to extract dissolved PCDDs/PCDFs during 1993. Although the attempt to measure dissolved PCDDs/PCDFs was met with limited success due to a pump failure, three PCDDs and seven PCDFs, including 2,3,7,8-TCDF, were detected (Table 6). 2,3,7,8-TCDF was detected at 0.029 pg/L (parts per quadrillion). 2,3,7,8-TCDD was not detected at a quantitation limit of 0.016 pg/L. Estimated maximum possible concentrations of five of these compounds are shown due to isotopic abundance ratios which did not meet method criteria. Concentrations qualified with a J are considered estimates because they were below the practical quantitation limit.

Table 6 and Figure 5 show dissolved PCDDs and PCDFs analyzed by USGS during 1992 and Ecology during 1993. OCDD and 1,2,3,4,6,7,8-HpCDD were detected at the highest

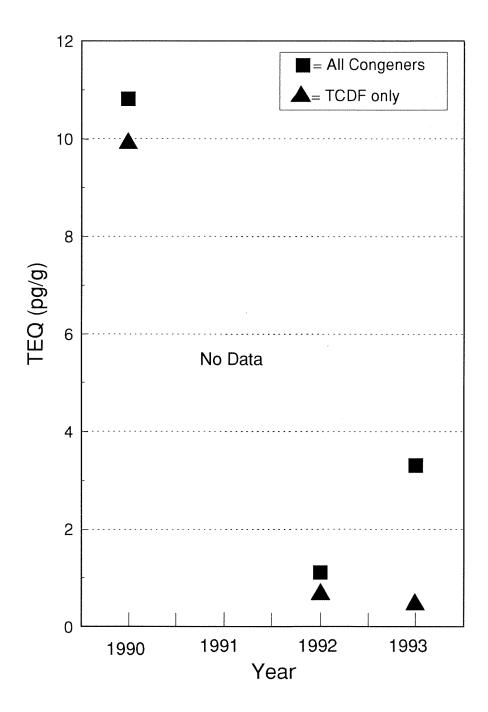


Figure 4. TEQ Concentrations in Suspended Particles from the Columbia River at Northport During 1990, 1992, and 1993

Table 6. Concentrations of PCDDs/PCDFs in the Dissolved Phase of Columbia River Water at Northport Analyzed by USGS During 1992 and Ecology During 1993 (pg/L, parts per quadrillion).

	USGS	Ecology
Compound	1992	1993
2,3,7,8-TCDD	U(0.01)	U(0.016)
2,3,7,8-TCDF	U(0.01)	0.029 J
Other PCDDs/PCDFs:		
PCDDs		
1,2,3,7,8-PeCDD	U(0.02)	U(0.020)
1,2,3,4,7,8-HxCDD	U(0.02)	U(0.027)
1,2,3,6,7,8-HxCDD	U(0.02)	0.020 EMPC
1,2,3,7,8,9-HxCDD	U(0.01)	U(0.023)
1,2,3,4,6,7,8-HpCDD	0.10	0.29 Ј
OCDD	0.78	0.49 J
PCDFs		
1,2,3,7,8-PeCDF	U(0.01)	U(0.016)
2,3,4,7,8-PeCDF	U(0.02)	0.005 J
1,2,3,4,7,8-HxCDF	U(0.01)	0.016 EMPC
1,2,3,6,7,8-HxCDF	U(0.01)	0.005 J
2,3,4,6,7,8-HxCDF	U(0.01)	В
1,2,3,7,8,9-HxCDF	U(0.01)	U(0.020)
1,2,3,4,6,7,8-HpCDF	U(0.01)	0.018 EMPC
1,2,3,4,7,8,9-HpCDF	U(0.01)	0.012 EMPC
OCDF	U(0.03)	0.015 EMPC

U=Undetected at quantitation limits in parentheses

J=Estimate

EMPC=Estimated Maximum Possible Concentration

B=Not reported due to blank contamination

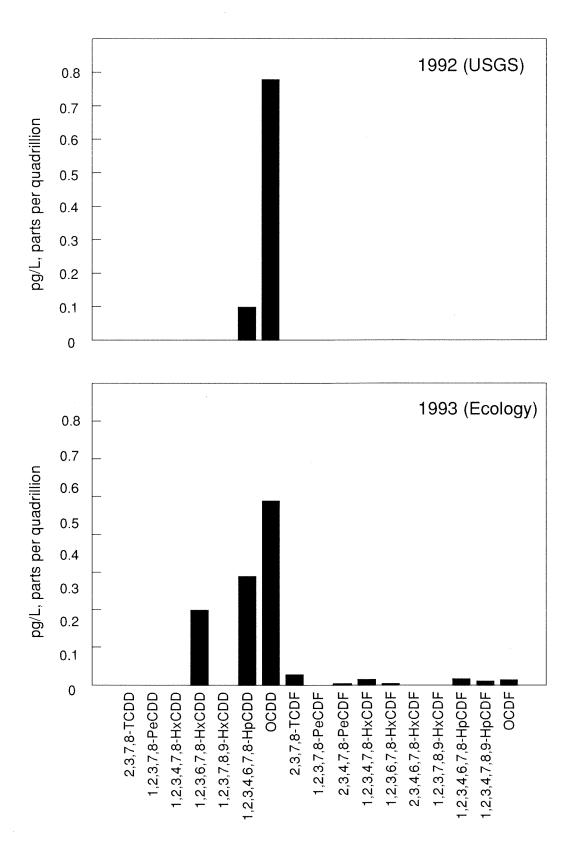


Figure 5. Dissolved PCDD/PCDF Concentrations in the Columbia River at Northport Analyzed by USGS During 1992 and Ecology During 1993

concentrations during both years. To some extent, the apparent change in the PCDD/PCDF congener pattern from 1992 to 1993 mirrors the pattern in suspended particles from 1992-1993 (see Figure 3).

2,3,7,8-TCDD and 2,3,7,8-TCDF Loads to Lake Roosevelt

Ecology's 1990-1993 data were used to estimate 2,3,7,8-TCDD and 2,3,7,8-TCDF loads to Lake Roosevelt. Table 7 shows 2,3,7,8-TCDD and 2,3,7,8-TCDF loads calculated for the particulate and dissolved phases. Total loads were derived by summing the loads from each phase.

Because 2,3,7,8-TCDD was not detected in any particulate or dissolved phase samples, method quantitation limits for 2,3,7,8-TCDD analysis were used to calculate the maximum possible loads to Lake Roosevelt. The same holds true for calculation of the total 2,3,7,8-TCDF load during 1992, when 2,3,7,8-TCDF was detected in the particulate phase but not in the dissolved phase. A range of possible values is shown for the total 1992 2,3,7,8-TCDF load.

Conclusions about 2,3,7,8-TCDD and 2,3,7,8-TCDF loads to Lake Roosevelt are limited due to the fact that 2,3,7,8-TCDD was not detected in any samples, and dissolved 2,3,7,8-TCDD and 2,3,7,8-TCDF were not measured during 1990. For instance, no conclusions can be made about 2,3,7,8-TCDD concentrations in these media from year-to-year. However, several inferences *can* be drawn based on these data:

- ♦ Particle-bound 2,3,7,8-TCDF loads during 1993 were approximately 70% of the 1992 level and 3% of the 1990 level.
- ♦ The total 2,3,7,8-TCDF load increased by at least 25% between 1992 and 1993. However, total 2,3,7,8-TCDF loads since 1990 have decreased by at least 80%.
- ♦ Approximately 75% of the 2,3,7,8-TCDF in the Columbia River entering Lake Roosevelt in 1993 was in the dissolved phase.
- ♦ The available data do not provide a means to determine 2,3,7,8-TCDD loads to Lake Roosevelt. However, the maximum possible load (based on 2,3,7,8-TCDD quantitation limits) during 1993 was 2.47 mg/day. This value approaches the Columbia River loading capacity of 2.30 mg 2,3,7,8-TCDD/day at the Canada border established by EPA to meet water quality standards (EPA, 1991).

2,3,7,8-TCDD and 2,3,7,8-TCDF Loading from the Celgar Pulp Mill

Celgar conducted effluent sampling of their pulp mill to compare to Columbia River load estimates obtained by Ecology. Loads from Celgar were calculated based on 24-hr composite effluent samples collected during Ecology's 1992 and 1993 sampling events (Table 8). Celgar

Table 7. Estimated Loads of Particulate and Dissolved 2,3,7,8-TCDD and 2,3,7,8-TCDF to Lake Roosevelt During 1990, 1992, and 1993 (mg/day).

	1990	1992	1993
2,3,7,8-TCDD			
Particulate Phase	< 0.24	< 0.52	< 0.22
Dissolved Phase	N/A	<u><2.3¹</u>	<2.25
TOTAL =	N/A	< 2.8	< 2.47
2,3,7,8-TCDF			
Particulate Phase	29.9	2.0	1.4
Dissolved Phase	N/A	<2.31	4.1
TOTAL =	>29.9	2.0 - 4.3	5.5

¹ Data provided by USGS

N/A = Not Analyzed

did not conduct concurrent sampling during 1990. Therefore, for the purpose of comparison, 1990 loading estimates obtained by Ecology are compared with Celgar effluent data collected by the Canadian Pulp & Paper Association during early 1989 (CPPA, 1989).

2,3,7,8-TCDF loading estimates obtained by Ecology (and USGS) sampling of Columbia River water at Northport agreed reasonably well with Celgar effluent data during 1990 and 1992. However, Ecology's 1993 2,3,7,8-TCDF loading estimate of 5.5 mg/day is at least an order of magnitude higher than loading from Celgar during the same period. There are several possible explanations for this: 1) The Celgar sample was based on a 24-hr composite collected within Ecology's sampling period which lasted 68 hours - it may not have been representative of the mill effluent during Ecology's sample collection period; 2) Previously contaminated bed sediments are being resuspended; and 3) There is an additional source of 2,3,7,8-TCDF to the Columbia River upstream of Northport.

There are currently no data to support the latter explanation. However, data from Canada's Columbia River Integrated Environmental Monitoring Program (CRIEMP), due to be released early-1995, may shed some light on this issue.

Table 8. 2,3,7,8-TCDD and 2,3,7,8-TCDF Loads in the Columbia River Compared to Loads from Celgar (mg/day).

	1990	1989	1992		1993	
	Columbia River	Celgar Effluent	Columbia River	Celgar Effluent	Columbia River	Celgar Effluent
2,3,7,8- TCDD	N/A	<1.35	<2.8	0.8	<2.47	< 0.2
2,3,7,8- TCDF	>29.9	30	2.0 - 4.3	2.0	5.5	< 0.2
Sample Dates	10/9- 10/12/90	early 1989	9/29- 10/2/92	9/29/92	10/5- 10/7/93	10/6/93
Data Source	Ecology	СРРА	Ecology and USGS	Celgar	Ecology	Celgar

N/A = Not Analyzed

2,3,7,8-TCDD and 2,3,7,8-TCDF in Fish Tissue

Concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in lake whitefish muscle are summarized in Table 9. Biological data on whitefish and complete analytical results are shown in Appendix B. 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in muscle tissue collected during 1993 continued to decrease from 1990 levels, and were about 60% of the 1992 levels. Results of nonparametric statistical tests for multiple comparisons (Zar, 1974) to test 2,3,7,8-TCDD, 2,3,7,8-TCDF, and TEQ concentrations between years show 1990±1992; 1990±1993; and 1992=1993 (p<0.05). As shown in Table 10, lipid-normalized 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in muscle are similar between 1992 and 1993, yet are an order of magnitude lower than 1990. This indicates that the differences in dioxin and furan residues between years are probably not due to lipid content alone. Normalizing data to lipid content is used to express contaminant concentrations in terms of pg per gram of lipid. It is sometimes useful in comparing concentrations of compounds which have a strong affinity to fatty tissues (such as 2,3,7,8-TCDD and 2,3,7,8-TCDF).

There does appear to be a positive correlation between age and 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in muscle tissue. This may account for some of the decreases in dioxin and furan residues since 1990. However, the bulk of the decrease can probably be attributable to decreased discharges from Celgar rather than differences in age. In addition, age data reported here are probably not reliable since: 1) scales were used rather than the

Table 9. 2,3,7,8-TCDD and 2,3,7,8-TCDF Muscle Concentrations, Lipid Content, and Size of Lake Whitefish Collected Near Kettle Falls During 1990, 1992, and 1993 (mean \pm SD in pg/g, parts per trillion; wet weight basis).

	Muscle		
Compound	1990 (n=6)	1992 (n=6)	1993 (n=6)
2,3,7,8-TCDD	1.9 ± 0.4	0.8 ± 0.6	0.5 ± 0.3
2,3,7,8-TCDF	126 ± 29	62 ± 53	33 ± 25
TEQ	14 ± 3.2	6.9 ± 5.9	3.8 ± 2.9
% Total Lipid	6.0 ± 2.9	12 ± 2	7.9 ± 2.4
% Non-Polar Lipid	N/A	9 ± 2	7.4 ± 2.3
Total Length (mm)	462 ± 18	497 ± 25	460 ± 21
Weight (g)	$1,168 \pm 133$	$1,682 \pm 354$	$1,290 \pm 181$
Age (yr)	4.2 ± 0.3	3.5 ± 1.0	2.7 ± 0.6

N/A=Not Analyzed

Table 10. 2,3,7,8-TCDD and 2,3,7,8-TCDF Concentrations in Lake Whitefish Muscle Normalized to Total Lipid and Non-Polar Lipid (mean \pm SD in pg per gram lipid, parts per trillion).

	Muscle		
Compound	1990 (n=6)	1992 (n=6)	1993 (n=6)
TOTAL LIPID:			
2,3,7,8-TCDD	49 ± 46	6.1 ± 3.3	6.9 ± 4.7
2,3,7,8-TCDF	$3,330 \pm 3,200$	480 ± 360	439 ± 395
NON-POLAR LIPID:			
2,3,7,8-TCDD	N/A	7.8 ± 4.2	7.7 ± 5.6
2,3,7,8-TCDF	N/A	611 ± 414	495 ± 469

N/A=Not Analyzed

preferred otoliths; 2) ages obtained from scales do not positively correlate with fish weight and length measurements; and 3) scales from 1990 fish and scales from 1992/1993 fish were aged by different biologists at different laboratories. The biologist that aged the 1992/1993 scales also gave results an average of 19% lower when asked to age a subset of the 1990 scales, suggesting that the ages of fish collected in 1990 may be closer to the ages of fish collected in 1992/1993 than originally reported.

Concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in eggs were approximately double the levels seen in the 1992 fish, yet well below the 1990 levels (Table 11). It appears that some of the difference between 1990 and 1992/1993 levels can be attributed to the substantial differences in lipid content of the egg samples. Total lipid-normalized concentrations of 2,3,7,8-TCDD in eggs do not indicate a clear trend among the three years of sampling (Table 12). 2,3,7,8-TCDF normalized to lipid suggests that it was substantially reduced from 1990 concentrations. The reader should note that the egg data are based on small sample size (n=1 for 1990; n=3 for 1992 and 1993).

Figure 6 show TEQs calculated from 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in muscle and eggs, respectively. The original study design did not call for tissues to be analyzed for other PCDD/PCDF congeners because previous studies have shown 2,3,7,8-TCDF, and to a lesser degree, 2,3,7,8-TCDD, to account for the bulk of toxicity associated with dioxins and furans in Columbia River fish (Mah *et al.*, 1989; Johnson *et al.*, 1991a). However, because of the apparent shift in congener patterns in Columbia River suspended particles, Ecology reanalyzed three whitefish muscle samples for the full complement of PCDDs/PCDFs (Appendix B). One sample had 0.95 pg/g 1,2,3,4,6,7,8-HpCDD and 4.4 pg/g OCDD. The second sample had 0.32 pg/g 2,3,4,7,8-PeCDF and 0.57 pg/g OCDD. No additional PCDDs/PCDFs were detected in the third sample. Therefore, it appears that 2,3,7,8-TCDF and 2,3,7,8-TCDD continue to be the major contributor to overall toxicity in whitefish muscle.

In summary, data on 2,3,7,8-TCDD and 2,3,7,8-TCDF in fish tissue analyzed during 1990, 1992, and 1993 indicate that:

- ♦ 2,3,7,8-TCDD, 2,3,7,8-TCDF, and overall toxicities (TEQs) of whitefish muscle and egg tissue continue to be well below values recorded in 1990. However, 2,3,7,8-TCDD, 2,3,7,8-TCDF and TEQ in egg tissue have increased from 1992 levels.
- ♦ The results confirmed that 2,3,7,8-TCDD and 2,3,7,8-TCDF continued to be responsible for nearly all of the whitefish muscle TEQ.

Table 11. 2,3,7,8-TCDD and 2,3,7,8-TCDF Concentrations in Eggs of Lake Whitefish Collected near Kettle Falls During 1990, 1992, and 1993 (mean ± SD in pg/g, parts per trillion; wet weight basis).

	Eggs		
Compound	1990 (n=1)	1992 (n=3)	1993 (n=3)
2,3,7,8-TCDD	8.5	0.9 ± 0.4	2.2 ± 0.1
2,3,7,8-TCDF	787	66 ± 28	113 ± 46
TEQ	87	7.6 ± 3.2	12.9 ± 5.9
% Total Lipid	45	12 ± 4	13.9 ± 0.5
% Non-Polar Lipid	N/A	8 ± 2	11.3 ± 2.3
Total Length (mm)	530	519 ± 7	541 ± 28
Weight (g)	1,858	$2,089 \pm 175$	$1,953 \pm 314$
Age (yr)	4.5	3.8 ± 0.6	4.7 ± 1.2

Table 12. 2,3,7,8-TCDD and 2,3,7,8-TCDF Concentrations in Lake Whitefish Eggs Normalized to Total Lipid and Non-Polar Lipid (mean ± SD in pg per gram lipid, parts per trillion).

	Eggs		
Compound	1990 (n=1)	1992 (n=3)	1993 (n=3)
TOTAL LIPID:			
2,3,7,8-TCDD	19	7.7 ± 2.2	16 ± 0.6
2,3,7,8-TCDF	1,750	540 ± 130	825 ± 348
NON-POLAR LIPID:			
2,3,7,8-TCDD	N/A	11 ± 3.2	20 ± 4.6
2,3,7,8-TCDF	N/A	776 ± 214	997 ± 294

N/A=Not Analyzed

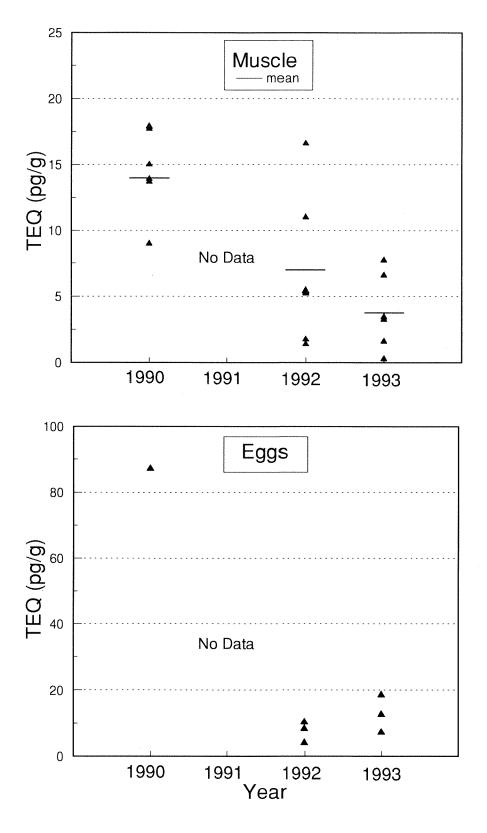


Figure 6. TEQ Concentrations in Lake Whitefish Muscle and Eggs

Metals in Suspended Particles

Concentrations of zinc, lead, copper, arsenic, cadmium, and mercury in particles are shown in Table 13. As in 1992, zinc, lead, and copper were present at the highest concentrations, followed by arsenic, cadmium, and mercury. Except for mercury, concentrations of metals in particles decreased by 10 to 44%. Mercury concentrations decreased by 82%. This is probably due to the unusually high 1992 concentrations resulting from the accidental discharge of mercury from Cominco on October 1, 1992 (Serdar *et al.*, 1993).

Deposition in Lake Roosevelt is one probable fate for suspended sediments entering from the Columbia River. USGS analyzed 32 Lake Roosevelt bottom sediment samples for metals during 1992 and reported median concentrations of 970 ug/g for zinc; 310 ug/g for lead; 85 ug/g for copper; 16 ug/g for arsenic; 6.2 ug/g for cadmium; and 1.3 ug/g for mercury (G. Bortelson, written communication). Except for copper, concentrations of metals in 1993 particles are 37-89% higher than the average Lake Roosevelt bottom sediments. Copper concentrations were 200% higher in particles. This indicates that the contribution of metals from the Columbia River continues to represent a metals problem in Lake Roosevelt.

There are currently no criteria or standards for metals in suspended sediments to protect aquatic life. Ecology is in the process of developing standards for freshwater bottom sediments. In the interim, Ecology has reviewed sediment quality criteria and guidelines developed by other government agencies and found those developed by the province of Ontario for managing contaminated sediments to be the best supported by *in situ* impacts (Bennett and Cubbage, 1991).

Figure 7 shows concentrations of zinc, lead, copper, arsenic, cadmium, and mercury found in Columbia River suspended particles during 1992 and 1993. These concentrations are compared to "severe effects levels" established by Ontario. "Severe effects levels" are concentrations at which pronounced impacts to benthic organisms are expected to occur (Persaud *et al.*, 1992).

Aside from arsenic concentrations in the 1993 particulate sample, all metals found in 1992 and 1993 exceed the Ontario guidelines. In most instances, concentrations of particulate-bound metals also exceeds the median and 90th percentile levels of sediments statewide (Figure 7). The statewide metals concentrations are derived from an Ecology database of synoptic data collected at potentially contaminated sites in Washington (excluding Lake Roosevelt).

Table 13. Concentrations of Metals in Columbia River Suspended Particles at Northport During 1992 and 1993 (mean ± range of duplicate analyses in ug/g, parts per million; dry weight basis).

Metal	1992	1993
Zinc	$1,478 \pm 8$	1,130
Lead	554 ± 4	498
Copper	352 ± 6	256
Arsenic	44.2 ± 0.5	24.8 ± 5.3
Cadmium	16.1 ± 0.2	10.3
Mercury	$13.7 \pm 0.2^{\circ}$	2.46 J
Manganese	$1,794 \pm 12$	N/A
Aluminum(%)	4.50 ± 0.37	N/A
Iron(%)	3.47 ± 0.1	N/A

J = Estimate

N/A=Not Analyzed

Particulate-Bound Metals Loading to Lake Roosevelt

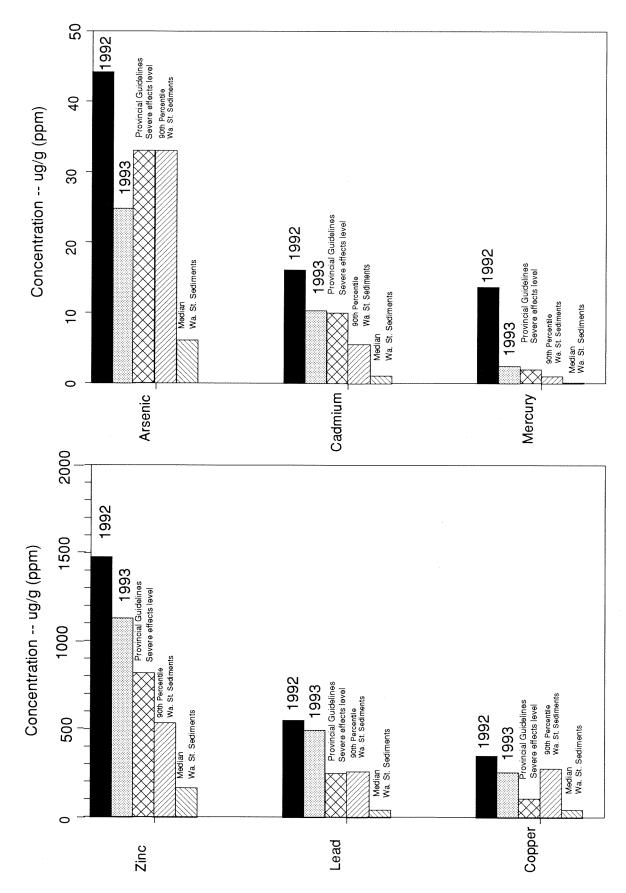
1993 particulate-bound metals loads to Lake Roosevelt were reduced by up to 46% in comparison to 1992 loads (Table 14). Mercury was reduced by 83%, due mainly to the elevated 1992 levels resulting from the October 1, 1992 mercury spill at Cominco.

Metal loads to Lake Roosevelt in the dissolved phase of Columbia River water are not discussed here. As mentioned previously, Ecology currently conducts bimonthly sampling of dissolved zinc, lead, copper, cadmium, and mercury at Northport. Results of this sampling will be reported separately by Ecology's Ambient Monitoring Section.

Data on metals loading to the Columbia River from Cominco's metallurgical and storm sewers concurrent with Ecology's sampling are shown in Table 15. Cominco data from 1992 were provided by Carl Johnson, B.C. Ministry of Environment; 1993 data were provided by Graham Kenyon, Cominco. Ltd.

Reductions in metals loadings were probably attributable, at least in part, to elimination of contact cooling water previously discharged through Cominco's sewer 07 (see Table 2). This is especially true for lead and cadmium. Discharges from sewer 07 accounted for 64% of total lead and 68% of total cadmium from Cominco's outfalls during September 29 - October 2,

¹Elevated levels due to mercury spill on October 1, 1992



Compared to Sediment Guidelines and Statewide Sediment Concentrations Figure 7. Metals Concentrations in Suspended Particles

1992. In contrast, sewer 07 accounted for 4% of the total lead and 6% of total cadmium discharged by Cominco's metallurgical and storm sewers during October 4-7, 1993.

Particulate-bound metals loads at Northport agreed reasonably well with loads discharged by Cominco during the 1993 sampling event. Lead concentrations in Columbia River particles do not appear to reflect the decreased discharges from Cominco's sewers. However, the Cominco data in Table 15 do not include contributions from slag discharges and do not differentiate between concentrations in dissolved and particulate-bound discharges.

Table 14. Estimated Loads of Particulate-Bound Metals at Northport During September 29 - October 2, 1992 and October 5-7, 1993 (Kg/day).

Metal	1992	1993	Change
Zinc	476	350	- 26%
Lead	178	154	- 13%
Copper	113	79	- 30%
Arsenic	14.2	7.7	- 46%
Cadmium	5.2	3.2	- 38%
Mercury	4.41	0.76	- 83%

¹Elevated levels due to mercury spill on October 1, 1992

Table 15. Loads of Metals Discharged to the Columbia River from Cominco's Metallurgical and Storm Sewers During September 29 - October 2, 1992 and October 4-7, 1993 (mean ± SD in Kg/day).

[<u> </u>		
Metal	1992 (n=3)	1993 (n=4)	Change
Zinc	330 ± 24	340 ± 29	+3%
Lead	160 ± 17	63 ± 17	-61%
Copper	7.0 ± 0.7	59 ± 100^{2}	+740%
Arsenic	8.2 ± 2.7	8.2 ± 4.3	0%
Cadmium	10.0 ± 3.0	2.4 ± 0.7	-76%
Mercury	21 ± 33 ¹	0.56 ± 0.22	-97%

¹Elevated levels due to mercury spill on October 1, 1992

²Elevated levels due to 207 Kg copper discharged from Outfall III on October 7, 1993

Metals in Whole Fish

As mentioned previously, whole largescale suckers were chosen for metals monitoring during 1993 because previous surveys of Lake Roosevelt fish by U.S. Fish & Wildlife Service and Ecology have shown very high concentrations of zinc, copper, lead, and cadmium in whole fish samples of this species (Lowe *et al.*, 1985; Johnson *et al.*, 1988; Schmitt and Brumbaugh, 1990). Results of Ecology's 1993 analysis of metals in whole largescale suckers from Northport and Kettle Falls are shown in Table 16.

Zinc, lead, and copper were much higher in Northport fish compared to those collected near Kettle Falls. However, mean cadmium concentrations in Northport fish were only 30% higher than Kettle Falls samples, and mercury concentrations in fish from Kettle Falls were 50% higher than Northport samples. Concentrations of zinc, lead, copper, cadmium, and mercury in whole fish demonstrate the same pattern seen in suspended particles, that is: zinc > lead > copper >> cadmium > mercury. This pattern has also been observed in fish analyzed during Ecology's 1986 survey of metals in Lake Roosevelt (Table 16; Gifford is approximately 25 river miles below Kettle Falls), and to a lesser extent, the pattern seen in bottom sediments from Northport and upper Lake Roosevelt (Johnson *et al.*, 1988; Bortelson, personal communication).

Concentrations of zinc, lead, copper, and cadmium in Northport and Kettle Falls suckers were very high compared to national averages, as shown in Table 16. National averages are geometric mean values reported during a 1984 U.S. Fish & Wildlife Service survey of whole fish from 110 sites nationwide. Average lead and cadmium concentrations in suckers from Northport are higher than any of the fish analyzed during the national survey.

The 1993 data on metals in whole suckers should provide a firm basis for detecting future changes. At a minimum, changes of 15% to 50% in mean metals concentrations should be detectable (at a power of 80% and $\alpha = 0.05$). It appears that this is a reasonable level of change given the elevations in metals concentrations over national averages in most cases. Comparisons to whole fish data from Ecology's 1986 survey suggest that concentrations in metals have not changed appreciably during the past seven years.

In summary, whole fish data indicate that:

- ♦ Concentrations of zinc, lead, and copper in whole largescale suckers from the Northport area were much higher than suckers from the Kettle Falls area. Cadmium concentrations in Northport fish were higher, but to a lesser degree.
- Mercury concentrations in whole suckers from the Kettle Falls area were 50% higher than suckers from Northport.
- ♦ Concentrations of zinc, lead, copper, and cadmium in Northport and Kettle Falls suckers were very high compared to national averages.

Table 16. Concentrations of Zinc, Lead, Copper, Cadmium, and Mercury in Whole Largescale Suckers from the Columbia River (mean \pm SD in ug/g, parts per million, wet. Range in parentheses).

				THE PERSON NAMED AND PASSED AND P				
	Zinc	Lead	Copper	Cadmium	Mercury	Total Length (mm)	Weight (g)	Percent Moisture
PRESENT SURVEY:								
Northport (n=15)	84.5 ± 26.5 $(43.9-136)$	12.0 ± 4.5 (6.4–23.3)	10.4 ± 4.5 $(4.6-20.1)$	0.48 ± 0.17 $(0.29-1.0)$	0.12 ± 0.07 $(0.07-0.35)$	514 ± 35 (452–580)	$1,539 \pm 288$ $(1,024-2,087)$	72%
Kettle Falls (n=15)	23.1 ± 6.1 $(15.5-40.1)$	3.0 ± 1.1 (1.71–6.01)	1.23 ± 0.37 $(0.74-1.78)$	0.35 ± 0.09 $(0.23-0.63)$	0.18 ± 0.03 $(0.14-0.22)$	541 ± 33 (485-592)	$1,771 \pm 273$ $(1,267-2,238)$	69%
1986 ECOLOGY SURVEY*:								
Northport (n=4)	59.5 ± 21.0 (40.0–86.7)	6.1 ± 1.3 $(4.6-7.3)$	4.8 ± 1.5 (2.8-6.4)	0.33 ± 0.07 (0.26-0.43)	0.11 ± 0.02 (0.08-0.14)	$468 \pm 26 \sim$ (442–503)	$1,481 \pm 316$ (1,287-1,954)	N/A
Gifford (n=4)	31.0 ± 8.5 (21.7-42.0)	2.0 ± 0.3 (1.5-2.3)	1.3 ± 0.6 $(0.7-1.9)$	0.38 ± 0.04 $(0.33-0.43)$	0.17 ± 0.05 $(0.13-0.25)$	$452 \pm 15 \sim$ (438-470)	$1,221 \pm 191$ (1,001–1,386)	N/A
U.S. Fish & Wildlife Service 1984 National Survey** (315 samples from 110 sites)	21.7 (9.6–118)	0.11	0.65	0.03 (<0.01-0.22)	0.10 (0.01-0.37)			

^{*} Johnson et al., 1988

N/A=Not Analyzed

^{**} Schmitt and Brumbaugh, 1990

[~] Fork Length

Conclusions

- 1. 2,3,7,8-TCDF in Columbia River suspended particles and 2,3,7,8-TCDD and 2,3,7,8-TCDF in lake whitefish muscle have decreased significantly since 1990. These reductions appear to be largely due to modifications at the Celgar pulp mill in British Columbia.
- 2. There is an apparent shift in the pattern of PCDDs and PCDFs in suspended particles entering Lake Roosevelt. Several congeners with 5 to 8 chlorine atoms are present at greater concentrations than during 1990 and, possibly, 1992. The reason for this shift in congener patterns is not known.
- 3. During the 1993 investigation, approximately 25% of the 2,3,7,8-TCDF in the Columbia River at Northport appeared to be associated with suspended particles. The remaining 75% appeared to be in the dissolved phase.
- 4. Loading of zinc, lead, copper, cadmium, mercury, and to a lesser degree arsenic, from upriver sources continues to represent a significant source of contamination to Lake Roosevelt. The Cominco smelter in Trail, B.C. is almost certainly the major source of these metals. 1993 data provided the first opportunity to look for trends in particulate contamination. Concentrations of all metals in the 1993 particle sample were lower than those in 1992. This is probably due, at least in part, to the elimination of a major sewer outfall at Cominco during 1993.
- 5. The degree of metals contamination of Lake Roosevelt water and sediment is reflected in uptake by a bottom-feeding fish species (largescale suckers). Average lead and cadmium concentrations in suckers from Northport are higher than any fish analyzed during a nationwide survey of metals in fish. This underscores the degree of contamination in this reach of the Columbia River.
- 6. Whole fish data from 1993 will provide a firm basis for detecting changes in metals contamination of the Columbia River and upper Lake Roosevelt.

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APPENDIX A

1993 Sampling Methods, Laboratory Analysis, and Data Quality

APPENDIX A

This section describes sampling methods, laboratory analysis, and data quality for 1993. They are generally consistent with methods used during the 1992 trend monitoring effort and earlier Lake Roosevelt surveys conducted by Ecology during 1990. Details of methods used during 1990 and 1992 are described in:

- Serdar, D., A. Johnson, and K. Seiders. 1993. Interim Report on Monitoring Contaminant Trends in Lake Roosevelt. Washington State Department of Ecology, Olympia, WA.
- Johnson, A., D. Serdar, and S. Magoon, 1991a. Polychlorinated Dioxins and -furans in Lake Roosevelt (Columbia River) Sportfish. Pub. No. 91-4, Washington State Department of Ecology, Olympia, WA.
- Johnson, A., D. Serdar, and K. Seiders, 1991c. PCDDs/PCDFs in Columbia River Suspended Particulate Matter. Memo to Carl Nuechterlein, Washington State Department of Ecology, Olympia, WA.

1993 Sampling Methods, Laboratory Analysis, and Data Quality

Suspended Particles

Two Sedisamp II continuous-flow centrifuges (model 101IL) were used to collect the particle sample at Northport during October 5-7, 1993. Sample collection was timed with normal operations at Celgar and Cominco.

The particle sample was collected in a manner described by Johnson *et al.* (1991c) and Serdar *et al.* (1993). Columbia River water was pumped from an intake situated in the main current approximately fifty feet offshore. Depth of the water at the sampling point was twelve feet, and the intake was periodically adjusted to 2, 5, or 10-ft depths to approximate a depth-integrated sample. Water was fed to the centrifuge over a period of 68 hours at an average flow of approximately 0.75 gallons (2.8 L) per minute. Total volume centrifuged was approximately 3,050 gallons (11,540 L).

All tubing and fittings were teflon-lined. Centrifuge bowl parts were constructed of high quality stainless steel. All surfaces coming in contact with the samples were precleaned by scrubbing with Liquinox detergent, followed by sequential rinses with hot tap water, 10% HNO₃, de-ionized water, and acetone.

The particle sample was placed in a specially cleaned container for trace chemicals analysis, stirred thoroughly, and split for PCDD/PCDF and metals analyses. Total weight of the samples was approximately 81 grams.

Analysis of 2,3,7,8-substituted PCDD/PCDF congeners was conducted at Triangle Laboratories (Research Triangle Park, NC) using high resolution GC/MS EPA method 8290. PCDD/PCDF data were reviewed by Stuart Magoon of the Ecology/EPA Manchester

Environmental Laboratory. All data met EPA method 8290 recommendations for continuing calibration, internal standard recoveries, and isotopic abundance ratios with some exceptions. Four PCDDs/PCDFs did not meet method 8290 criteria for isotopic abundance ratios and were qualified as estimated maximum possible concentrations (EMPCs).

Two other analytes were present below the practical quantitation limits and are qualified as estimates (J). 2,3,4,6,7,8-HxCDF was detected in the method blank at a concentration greater than 20% than that of the particle sample, and the result was rejected (B).

The particle sample was also analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF in duplicate to assess precision. Precision, expressed as relative percent difference (RPD), was very good for 2,3,7,8-TCDF analysis (7%). 2,3,7,8-TCDD was not detected.

Metals analysis was conducted at the Manchester Laboratory. Samples for zinc, lead, copper, arsenic, and cadmium were digested using EPA method 3050 modified by the addition of 200 uL hydrofluoric acid (HF) to the nitric acid (HNO₃) mix and analyzed using ICP method 200.7. For mercury, the sample was prepared and analyzed using EPA cold vapor method 245.1 modified for sediment using contract laboratory procedures (CLP).

Metals data were reviewed by Bill Kammin of the Manchester Laboratory. All data met EPA recommendations for instrument calibration and procedural blanks. Except for mercury, spiked sample analyses were within acceptable limits. Mercury spike recoveries were poor, probably due to the high native concentration relative to the spiking level. Analytical precision was assessed through duplicate analysis of arsenic (RPD = 43%). Analytical accuracy was assessed through analysis of a standard reference material, NIST 2704 (Buffalo River sediment). Recoveries of zinc, lead, copper, arsenic, cadmium, and mercury were 87-104% of certified values.

XAD Resins

Dissolved PCDDs/PCDFs were measured by extraction with XAD resins. Columbia River water clarified by centrifugation was pumped through two 330 mL resin columns connected in series. Tubing and fittings were of teflon; the pump (positive displacement) was of stainless steel, teflon, and ceramic construction. All surfaces coming in contact with the sample were cleaned as described above.

Approximately 575 liters of Columbia River water were extracted in the first column, and 542 liters in the second column prior to pump failure. Total time of pumping was approximately 34 hours. Flow rates were highly variable, ranging from 0.14 to 0.41 L/min. at a pressure of approximately 40 psi.

To estimate "breakthrough" or retention efficiency of the XAD, the first column in the sample series and the column used as a field blank were pre-spiked with the following radio-labelled compounds:

³⁷Cl₄-2,3,7,8-TCDD

¹³C₁₂-2,3,4,7,8-PeCDF ¹³C₁₂-1,2,3,4,7,8-HxCDF ¹³C₁₂-1,2,3,4,7,8-HxCDD ¹³C₁₂-1,2,3,4,7,8,9-HpCDF

Retention of these compounds on the first column averaged greater than 99%: Breakthrough to the second column in the series averaged less than 1%.

Although analysis of the pre-spiked compounds showed little breakthrough, sample analytes were present in extracts from both columns. In cases where analytes were detected in both extracts, concentrations were nearly equal. One possible explanation is that PCDDs/PCDFs in colloidal form are not completely retained by either centrifugation or extraction with XAD resin.

Twenty-five liters of de-ionized water were pumped through an additional column to serve as a field blank. 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8,9-HpCDF were detected at 0.002 and 0.008 ng (0.08 and 0.3 pg/L), respectively. Retention of the pre-spiked radio-labelled compounds was greater than 99% on average.

PCDD/PCDF data were reviewed by Stuart Magoon of the Ecology/EPA Manchester Environmental Laboratory. All data met EPA method 8290 recommendations for continuing calibration, internal standard recoveries, and isotopic abundance ratios with some exceptions. Five PCDDs/PCDFs did not meet method 8290 criteria for isotopic abundance ratios and were qualified as estimated maximum possible concentrations (EMPCs).

Of the six additional PCDDs/PCDFs detected, five were present below the practical quantitation limits and are qualified as estimates (J). 2,3,4,6,7,8-HxCDF was detected in the method blank at a concentration greater than 20% than that of the particle sample, and the result was rejected (B).

Lake Whitefish Tissues

Lake whitefish were collected by gill net near Kettle Falls on October 6, 1993. Measurements for total length and weight were recorded in the field. Fish were then wrapped in aluminum foil with identification tags, and sealed in zip-loc bags. Specimens were subsequently placed on ice until muscle and egg samples were resected upon returning from the field.

Scales were used to determine fish age. Ages of fish collected during 1992 and 1993 were determined by John Sneva of the Washington State Department of Fish & Wildlife. John Sneva also analyzed a subset of scale samples from the Lake Roosevelt whitefish collected during 1990 which had previously been analyzed by a biologist from the Upper Columbia United Tribes Fisheries Research Center (UCUT-FRC). There was only agreement on one of seven scale samples aged, and John Sneva's interpretation of the samples yielded ages that averaged 19% lower than those of UCUT-FRC. Therefore, there does not appear to be comparability among years.

Muscle resection was done in a manner identical to previous Ecology surveys (Johnson et al., 1991a; Serdar et al., 1993). Briefly, 40 g of skinless epaxial muscle was excised from each fish. The muscle was removed from an area above the lateral line and anterior of the dorsal fin. Egg samples consisted of the posterior third of each egg mass in females. Samples were placed in containers specially cleaned for low-level organics analysis. All sampling equipment was cleaned after each composite by scrubbing with Liquinox detergent, followed by sequential rinses with hot tap water, 10% HNO₃, de-ionized water, and acetone.

Fish were grouped randomly prior to resection. Muscle from five fish were composited for each sample. One sample was a composite of muscle from four fish. Since eggs were only found in five individual fish, two composites contained eggs from two fish, while the third egg sample was from a single fish. Six muscle and three egg composites were homogenized and analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF at Triangle Laboratories using EPA method 8290. Three muscle samples were re-analyzed for the full complement of 2,3,7,8-substituted PCDDs/PCDFs. Triangle also analyzed samples for percent lipids and percent non-polar lipids.

PCDD/PCDF and percent lipid data were reviewed by Stuart Magoon of the Manchester Laboratory. All data met EPA method 8290 recommendations for continuing calibration, internal standard recoveries, and isotopic abundance ratios. RPDs for duplicate analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF in one muscle sample were 36% and 1%, respectively. RPDs for duplicate analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF in one egg sample were 13% and 6%, respectively.

Largescale Sucker Tissues

Largescale suckers were collected by electroshocking in the vicinity of Northport on October 6-7, 1993 and near Kettle Falls on October 5, 1993. Upon collection, fish were measured for total length and weight, wrapped in aluminum foil with identification tags, sealed in ziploc bags, and placed on ice until returning from the field at which time they were frozen. Scales were collected for age determination. Subsequently, it was learned that otoliths are required for age determination of largescale suckers. Therefore, ages of the specimens are not known.

Samples were homogenized whole with three passes through a Hobart meat grinder and placed in specially cleaned containers for trace metals analysis. All processing equipment was cleaned after each fish with Liquinox detergent, followed by sequential rinses with hot tap water, 10% HNO₃, and de-ionized water. Homogenates were analyzed for metals at the Manchester Laboratory. Samples for zinc, lead, copper, and cadmium analysis were prepared for analysis using EPA method 3051. Zinc and copper analysis was by ICP method 200.7/6010. Lead was analyzed by EPA method 239.2 (GFAA) modified for solid materials. Cadmium was analyzed by EPA method 213.2 (GFAA) modified for solid materials. Samples for mercury analysis were prepared and analyzed by EPA cold vapor method 245.1 modified for solid materials.

Metals data were reviewed by Bill Kammin of the Manchester Laboratory. All data met

EPA recommendations for instrument calibration and procedural blanks. Four matrix spike analyses were done for each metal. Of these, three lead spikes, two mercury spikes, one copper spike, and one cadmium spike were outside of acceptable limits. Bill Kammin suggested that nonhomogeneity of the sample may have accounted for some of the poor spike recoveries.

Precision was assessed through duplicate analyses of four samples for each metal. Mean RPDs for metals were: 12% for zinc; 38% for lead; 21% for copper; 3% for cadmium; and 4% for mercury. Analytical accuracy was assessed through analysis of two standard reference materials: CRCC DOLT-1 (dogfish liver) and CRCC DORM-1 (dogfish muscle). A comparison of certified values for DOLT-1 and DORM-1 to Manchester's analyses of these samples are shown below, expressed as percent recoveries.

0%	D	ecovery	,
70	ĸ	ecoverv	•

	Zinc	Lead	Copper	Cadmium	Mercury
DOLT-1	70%	85 %	81 %	100%	134%
DORM-1	66%	94%	84%	108%	91%

APPENDIX B

Lake Whitefish Data

APPENDIX B-1 - Biological Data on Individual Whitefish

1. Samples Collected During 1990

	- M			TOTAL	4,200	EST.	
ECOLOGY			DATE	LENGTH	WEIGHT	AGE	
SAMPLE NO.	SPECIES	LOCATION	COLLECTED	(mm)	(g)	(yrs)	SEX
	Lk. Whitefish	Off Colville R.	5/1/90	400	650	3	UN
	Lk. Whitefish	Off Colville R.	5/1/90	467	1035	5	UN
188243	Lk. Whitefish	Off Sherman Cr.	5/2/90	494	1291	5	UN
100219	Lk. Whitefish	Off Sherman Cr.	5/2/90	387	707	4	UN
***************************************	Lk. Whitefish	Off Colville R.	5/2/90	502	1565	5	UN
L	Lac. Willongii	on corvine ic.	mean =	450	1050	4.4	O.V
ſ	I le Whitefiah	Off Caladilla D	£ /1 /0.0	400	60.5	4	7 13 1
	Lk. Whitefish	Off Colville R.	5/1/90	408	685	4	UN
100044	Lk. Whitefish	Off Sherman Cr.	5/2/90	495	1484	4	UN
188244	Lk. Whitefish	Off Colville R.	5/2/90	406	816	4	UN
	Lk. Whitefish	Off Colville R.	5/2/90	461	1059	5	UN
, [Lk. Whitefish	Off Colville R.	5/2/90	518	1285	5	UN
			mean =	458	1066	4.4	
To a second	Lk. Whitefish	Off Colville R.	5/1/90	466	1455	5	UN
	Lk. Whitefish	Off Sherman Cr.	5/2/90	393	693	3	UN
188245	Lk. Whitefish	Off Sherman Cr.	5/2/90	466	1179	5	UN
	Lk. Whitefish	Off Sherman Cr.	5/2/90	448	1121	5	UN
	Lk. Whitefish	Off Colville R.	5/2/90	404	853	4	UN
			mean =	435	1060	4.4	
	Lk. Whitefish	Off Sherman Cr.	8/4/90	429	901	3	UN
	Lk. Whitefish	Off Colville R.	10/11/90	535	2099	5	F
428109	Lk. Whitefish	Off Colville R.	10/11/90	498	1408	5	UN
	Lk. Whitefish	Off Colville R.	10/11/90	455	1126	4	UN
	Lk. Whitefish	Kettle Falls	N/A	467	N/A	N/A	UN
L		motion and	mean =	477	1384	4.2	OIV
Γ	Lk, Whitefish	Off Sherman Cr.	8/4/90	450	983	4	UN
	Lk. Whitefish	Off Sherman Cr.	8/4/90	525	1618	4	F
428110	Lk. Whitefish	Off Sherman Cr.	8/4/90	323 411	728	4 4	r UN
420110	Lk. Whitefish	Off Colville R.		495			
	Lk. Whitefish	Off Colville R.	8/5/90 10/11/90	493 496	1408	N/A	UN
L	LK. WIIICHSII	On Colvine K.	mean =	496	1368 1221	4	UN
-	All and the state of the state	•	mean –	7/3	1221		
	Lk. Whitefish	Off Sherman Cr.	8/4/90	521	1555	4	UN
400111	Lk. Whitefish	Off Colville R.	8/4/90	433	821	4	UN
428111	Lk. Whitefish	Off Colville R.	8/4/90	460	1102	4	UN
	Lk. Whitefish	Off Colville R.	8/5/90	510	1404	4	UN
	Lk. Whitefish	Off Colville R.	10/11/90	467	1257	3	UN
			mean =	478	1228	3.8	
458157	Lk. Whitefish	Off Colville R.	10/11/90	535	2099	5	F
	Lk. Whitefish	Off Sherman Cr.	8/4/90	525	1618	4	F
			mean =	530	1858	4.5	

2. Samples Collected During 1992

ECOLOGY	annama		DATE	TOTAL LENGTH	WEIGHT	EST. AGE	
SAMPLE NO.	SPECIES	LOCATION	COLLECTED	(mm)	(g)	(yrs)	SEX
	Lk. Whitefish	Off Colville R.	10/1/92	536	2427	6	F
	Lk. Whitefish	Off Colville R.	10/1/92	561	2207	4	M
408540	Lk. Whitefish	Off Colville R.	10/1/92	517	1792	3	F
	Lk. Whitefish	Off Colville R.	10/1/92	481	1428	3	M
	Lk. Whitefish	Off Colville R.	10/1/92	500	1540	4	M
			mean =	519	1879	4	
	Lk. Whitefish	Off Colville R.	10/1/92	484	1311	3	M
	Lk. Whitefish	Off Colville R.	10/1/92	516	1646	4	M
408541	Lk. Whitefish	Off Colville R.	10/1/92	512	1605	5	M
	Lk. Whitefish	Off Colville R.	10/1/92	482	1401	2	M
	Lk. Whitefish	Off Colville R.	10/1/92	446	1374	2	M
·	A CANADA SA MANANA		mean =	488	1467	3.2	
	Lk. Whitefish	Off Colville R.	10/1/92	463	1298	2	UNI
	Lk. Whitefish	Off Colville R.	10/1/92	390	614	1	M
408542	Lk. Whitefish	Off Colville R.	10/1/92	466	1408	2	M
	Lk. Whitefish	Off Colville R.	10/1/92	470	1277	2	M
	Lk. Whitefish	Off Colville R.	10/1/92	507	1846	3	F
L		011 001 mo 10	mean =	459	1289	2	1
Community	Lk. Whitefish	Off Colville R.	10/1/92	512	2074	4	F
	Lk. Whitefish	Off Colville R.	10/1/92	494	1903	3	F
408543	Lk. Whitefish	Off Colville R.	10/1/92	535	2378	4	F
	Lk. Whitefish	Off Colville R.	10/1/92	533	2377	5	F
	Lk. Whitefish	Off Sherman Cr.	9/30/92	581	2713	4	F
L	Lax. Willerigh	On oneman cr.	mean =	531	2289	4	1.
	Lk. Whitefish	Off Colville R.	10/1/92	486	1566	3	F
	Lk. Whitefish	Off Colville R.	10/1/92	480	1371	3	M
408544	Lk. Whitefish	Off Colville R.	10/1/92	536	1851	4	M
	Lk. Whitefish	Off Colville R.	10/1/92	472	1459	$\frac{7}{2}$	M
	Lk. Whitefish	Off Colville R.	10/1/92	509	1706	3	M
L.	LR. WIIICHSII	On Colvine K.	mean =	30 9	1591	3	IVI
	Lk. Whitefish	Off Colville R.	10/1/92	471	1210	2	M
	Lk. Whitefish	Off Colville R.	10/1/92	535	2144	8	UNI
408545	Lk. Whitefish	Off Colville R.	10/1/92	496	1651	3	M
1003 13	Lk. Whitefish	Off Colville R.	10/1/92	517	1712	5	M
	Lk. Whitefish	Off Colville R.	10/1/92	420	1171	6	M
Ę.,	LJK. WIIICHSII	On Colvine R.	mean =	488	1578	4.8	IVI
	Lk. Whitefish	Off Colville R.	10/1/92	507	1846	3	F
408546	Lk. Whitefish	Off Colville R.	10/1/92	581	2713	4	F
	Lk. Whitefish	Off Colville R.	10/1/92	494	1903	3	F
	Lk. Whitefish	Off Colville R.	10/1/92	487	1703	3	F
L.	Lac. Willough	on colvine R.	mean =	517	2064	3.2	Г
	Lk. Whitefish	Off Colville R.	10/1/92	512	2074	4	F
408547	Lk. Whitefish	Off Colville R.	10/1/92	533	2377	5	г F
100317	Lk. Whitefish	Off Colville R.	10/1/92	535 535	2378	3 4	r F
L	LR. WILLOUGH	On Colvine IV.	mean =	527	2276	4.3	r
	Lk. Whitefish	Off Colville R.	Off Colville R.	536			E
					2427	6	F
408548	I k Whitefich	Off Colvilla D	() tt ('Alimilia D	£ 1''			
408548	Lk. Whitefish Lk. Whitefish	Off Colville R. Off Colville R.	Off Colville R. Off Colville R.	517 486	1792 1566	3	F F

APPENDIX B-1 (Cont'd) - Biological Data on Individual Whitefish

3. Samples Collected During 1993

ECOLOGY		•	DATE	TOTAL LENGTH	WEIGHT	EST. AGE	
SAMPLE NO.	SPECIES	LOCATION	COLLECTED	(mm)	(g)	(yrs)	SEX
F	Lk. Whitefish	Off Colville R.	10/6/93	372	700	1	M
418350	Lk. Whitefish	Off Colville R.	10/6/93	500	1520		
410330	Lk. Whitefish	Off Colville R.	10/6/93			5	F
	Lk. Whitefish	Off Colville R.	, ,	504	1386	3	UN
Į.	LK. WIIIICHSH	On Colvine R.	10/6/93	472	1410	2	UN
			mean =	462	1254	2.8	
	Lk. Whitefish	Off Colville R.	10/6/93	531	2065	5	M
	Lk. Whitefish	Off Colville R.	10/6/93	369	590	1	M
418351	Lk. Whitefish	Off Colville R.	10/6/93	366	607	$\tilde{1}$	M
	Lk. Whitefish	Off Colville R.	10/6/93	546	2029	5	F
	Lk. Whitefish	Off Colville R.	10/6/93	515	1408	6	M
Ŀ		on corrinore.	mean =	465	1340	3.6	171
Г							
-	Lk. Whitefish	Off Colville R.	10/6/93	376	686	1	UN
	Lk. Whitefish	Off Colville R.	10/6/93	376	678	1	M
418352	Lk. Whitefish	Off Colville R.	10/6/93	364	562	1	M
	Lk. Whitefish	Off Colville R.	10/6/93	593	2597	7	F
	Lk. Whitefish	Off Colville R.	10/6/93	459	1192	2	M
			mean =	434	1143	2.4	
	Lk. Whitefish	Off Colville R.	10/6/93	489	1441	2	UN
	Lk. Whitefish	Off Colville R.	10/6/93	528			
418353	Lk. Whitefish	Off Colville R.			1935	6	UN
410333	Lk. Whitefish	Off Colville R.	10/6/93	475	1193	2	M
			10/6/93	376	854	1	M
L	Lk. Whitefish	Off Colville R.	10/6/93	481	1635	3	UN
			mean =	470	1412	2.8	
	Lk. Whitefish	Off Colville R.	10/6/93	509	1578	3	UN
	Lk. Whitefish	Off Colville R.	10/6/93	467	1242	2	UN
418354	Lk. Whitefish	Off Colville R.	10/6/93	530	2098	5	F
	Lk. Whitefish	Off Colville R.	10/6/93	466	1398	2	UN
	Lk. Whitefish	Off Colville R.	10/6/93	481	1410	3	UN
_	- Control of the Cont		mean =	491	1545	3	011
Γ	I le Whitefiel	Off Call Har D	101/100	260	510		***
	Lk. Whitefish	Off Colville R.	10/6/93	360	510	1	UN
119255	Lk. Whitefish	Off Colville R.	10/6/93	538	1736	3	F
418355	Lk. Whitefish	Off Colville R.	10/6/93	483	1196	2	M
	Lk. Whitefish	Off Colville R.	10/6/93	360	555	1	M
	Lk. Whitefish	Off Colville R.	10/6/93	450	1245	2	M
			mean =	438	1048	1.8	
418360	Lk. Whitefish	Off Colville R.	10/6/93	546	2029	5	F
	Lk. Whitefish	Off Colville R.	10/6/93	593	2597	7	F
L.			mean =	570	2313	6	•
418361	 Lk. Whitefish	Off Colville R.	10/6/02	£00	1500		1
410301			10/6/93	500	1520	5	F
L	Lk. Whitefish	Off Colville R.	10/6/93	530	2098	5	F
			mean =	515	1809	5	
418362	Lk. Whitefish	Off Colville R.	10/6/93	538	1736	3	F

UNK=unknown N/A=Not Analyzed

APPENDIX B-2 - 2,3,7,8-TCDD/TCDF Data on Whitefish Composite Samples

1. Muscle Samples

		MEAN				%		
		TOTAL	MEAN	MEAN		NON-	2,3,7,8-	2,3,7,8-
	ECOLOGY	LENGTH	WEIGHT	AGE	%	POLAR	TCDD	TCDF
YEAR	SAMPLE NO.	(mm)	(g)	(yrs)	LIPID	LIPID	(pg/g)	(pg/g)
1990	188243	450	1050	4.4	3.4	N/A	2.3	154
1990	188244	. 458	1066	4.4	1.4	N/A	1.9	131
1990	188245	435	1060	4.4	7.1	N/A	1.9	120
1990	428109	477	1384	4.2	8.5	N/A	2	157
1990	428110	475	1221	4	7.7	N/A	1.9	118
1990	428111	478	1228	3.8	7.6	N/A	1.2	78
1992	408540	519	1879	4	9.9	7.1	0.64	46
1992	408541	488	1467	3.2	11	7.7	0.25	15
1992	408542	459	1289	2	. 9	6.6	0.18	12
1992	408543	531	2289	4	14	12	1.6	150
1992	408544	497	1591	3	12	9.2	0.68	46
1992	408545	488	1578	4.8	14	11	1.2	98
1993	418350	462	1254	2.8	6.7	6.8	0.31	12.7
1993	418351	465	1340	3.6	7	5.8	0.89	68.4
1993	418352	434	1143	2.4	6.4	5.8	0.84	57.5
1993	418353	470	1412	2.8	11.2	11	0.46	27.8
1993	418354	491	1545	3	10.7	9.4	0.48	29.5
1993	418355	438	1048	1.8	5.6	5.6	U(0.3)	2.6

2. Egg Samples

		MEAN				%		
		TOTAL	MEAN	MEAN		NON-	2,3,7,8-	2,3,7,8-
	ECOLOGY	LENGTH	WEIGHT	AGE	%	POLAR	TCDD	TCDF
YEAR	SAMPLE NO.	(mm)	(g)	(yrs)	LIPID	LIPID	(pg/g)	(pg/g)
1000								
1990	458157	530	1858	4.5	45.4	N/A	8.5	787
1992	408546	517	2064	3.2	9	6.8	0.5	36
1992	408547	527	2276	4.3	11	8.1	1.1	72
1992	408548	513	1928	4	16	10	1.2	91
1993	418360	570	2313	6	14	25	2.3	162
1993	418361	515	1809	5	13.4	12.7	2.1	105
1993	418362	538	1736	3	14.4	8.7	U(4.5)	72

N/A=Not Analyzed

U=Undetected at quantitaion limits in parentheses

APPENDIX B-3 - Additional PCDD/PCDF Analysis of Whitefish Muscle (pg/g, parts per trillion; wet weight basis)

		Sample No.	Sample No.	Sample No.
Compound	TEF	418350	418351	418354
2,3,7,8-TCDD	1	U(0.4)	0.44	U(0.5)
2,3,7,8-TCDF	0.1	7.8	44.8	20.9
Other PCDDs/PCDFs:				
PCDDs				
1,2,3,7,8-PeCDD	0.5	U(0.6)	U(0.2)	U(0.7)
1,2,3,4,7,8-HxCDD	0.1	U(0.6)	U(0.2)	U(0.7)
1,2,3,6,7,8-HxCDD	0.1	U(0.5)	U(0.2)	U(0.6)
1,2,3,7,8,9-HxCDD	0.1	U(0.6)	U(0.2)	U(0.7)
1,2,3,4,6,7,8-HpCDD	0.01	0.95 J	U(0.3)	U(0.9)
OCDD	0.001	4.4	0.57 EMPC	U(1.5)
PCDFs				
1,2,3,7,8-PeCDF	0.05	U(0.4)	U(0.1)	U(0.5)
2,3,4,7,8-PeCDF	0.5	U(0.4)	0.32 Ј	U(0.5)
1,2,3,4,7,8-HxCDF	0.1	U(0.4)	U(0.1)	U(0.4)
1,2,3,6,7,8-HxCDF	0.1	U(0.3)	U(0.1)	U(0.3)
2,3,4,6,7,8-HxCDF	0.1	U(0.4)	U(0.1)	U(0.4)
1,2,3,7,8,9-HxCDF	0.1	U(0.4)	U(0.1)	U(0.5)
1,2,3,4,6,7,8-HpCDF	0.01	U(0.3)	U(0.1)	U(0.4)
1,2,3,4,7,8,9-HpCDF	0.01	U(0.5)	U(0.2)	U(0.7)
OCDF	0.001	U(0.9)	U(0.4)	U(1.3)

TEF=Toxic Equivalent Factor

U=Undetected at quantitation limits in parentheses

J=Estimate

EMPC=Estimated Maximum Possible Concentration

APPENDIX C

Largescale Sucker Data

1. Samples Collected in the Kettle Falls Area

				TOTAL		
ECOLOGY			DATE	LENGTH	WEIGHT	
SAMPLE NO.	SPECIES	LOCATION	COLLECTED	(mm)	(g)	SEX
418300	Largescale Sucker	Off Colville R.	10/5/93	495	1267	M
418301	Largescale Sucker	Off Colville R.	10/5/93	561	1706	F
418302	Largescale Sucker	Off Colville R.	10/5/93	576	2024	UNK
418303	Largescale Sucker	Off Colville R.	10/5/93	568	2156	F
418304	Largescale Sucker	Off Colville R.	10/5/93	485	1565	M
418305	Largescale Sucker	Off Colville R.	10/5/93	544	1954	UNK
418306	Largescale Sucker	Off Colville R.	10/5/93	592	2238	UNK
418307	Largescale Sucker	Off Colville R.	10/5/93	530	1660	M
418308	Largescale Sucker	Off Colville R.	10/5/93	552	1815	UNK
418309	Largescale Sucker	Off Colville R.	10/5/93	509	1468	M
418310	Largescale Sucker	Off Colville R.	10/5/93	485	1404	M
418311	Largescale Sucker	Off Colville R.	10/5/93	556	1870	F
418312	Largescale Sucker	Off Colville R.	10/5/93	556	1691	UNK
418313	Largescale Sucker	Off Colville R.	10/5/93	553	1854	F
418314	Largescale Sucker	Off Colville R.	10/5/93	551	1897	F

2. Samples Collected in the Northport Area

	TOTAL							
ECOLOGY			DATE	LENGTH	WEIGHT			
SAMPLE NO.	SPECIES	LOCATION	COLLECTED	(mm)	(g)	SEX		
418320	Largescale Sucker	Northport Bridge	10/6/93	452	1024	UNK		
418321	Largescale Sucker	Northport Bridge	10/6/93	505	1765	M		
418322	Largescale Sucker	Northport Bridge	10/6/93	522	1737	M		
418323	Largescale Sucker	Northport Bridge	10/6/93	495	1358	F		
418324	Largescale Sucker	Northport Bridge	10/6/93	560	1885	F		
418325	Largescale Sucker	Northport Bridge	10/6/93	490	1253	UNK		
418326	Largescale Sucker	Off Sheep Cr.	10/6/93	480	1291	UNK		
418327	Largescale Sucker	Off Sheep Cr.	10/6/93	518	1677	F		
418328	Largescale Sucker	Off Sheep Cr.	10/6/93	564	1775	UNK		
418329	Largescale Sucker	Off Sheep Cr.	10/6/93	537	1495	F		
418330	Largescale Sucker	Off Sheep Cr.	10/6/93	580	2087	F		
418331	Largescale Sucker	Off Sheep Cr.	10/6/93	497	1577	UNK		
418332	Largescale Sucker	Northport Bridge	10/7/93	529	1499	UNK		
418333	Largescale Sucker	Northport Bridge	10/7/93	487	1482	M		
418334	Largescale Sucker	Off Sheep Cr.	10/7/93	492	1182	UNK		

UNK=Unknown

1. Samples Collected in the Kettle Falls Area

ECOLOGY	%					
SAMPLE NO.	MOISTURE	ZINC	COPPER	LEAD	CADMIUM	MERCURY
418300	70	26.6	1.0	4.40	0.377	0.14
418301	65	17.0	1.1	3.45	0.364	0.20
418302	67	15.5	0.79	1.88	0.264	0.173
418303	65	19.4	1.68	2.14	0.405	0.191
418304	68	23.5	1.57	3.08	0.31	0.143
418305	69	18.1	1.2	2.71	0.321	0.143
418306	69	20.4	1.7	3.02	0.341	0.177
418307	73	21.9	0.77	2.77	0.234	0.175
418308	73	25.8	1.6	6.01	0.382	0.139
418309	67	29.6	1.78	3.06	0.362	0.191
418310	71	24.5	1.1	2.69	0.312	0.187
418311	69	19.4	1.3	2.47	0.392	0.198
418312	70	40.1	0.75	3.70	0.63	0.15
418313	70	24.4	1.3	2.58	0.335	0.219
418314	68	19.7	0.74	1.71	0.259	0.201

2. Samples Collected in the Northport Area

ECOLOGY	%	ZD (C	COPPER	1 E I D	GADAWA (
SAMPLE NO.	MOISTURE	ZINC	COPPER	LEAD	CADMIUM	MERCURY
418320	78	70	6.75	10	0.495	0.347
418321	70	59.4	6.12	14	0.53	0.085
418322	69	55	7.0	6.4	0.358	0.155
418323	73	74.6	7.78	13.3	0.293	0.122
418324	73	136	20.1	14	1.0	0.088
418325	71	68.9	6.72	10.2	0.47	0.201
418326	70	76.8	8.78	9.74	0.428	0.069
418327	71	43.9	4.61	6.54	0.468	0.0871
418328	71	62.5	9.96	7.4	0.573	0.096
418329	75	118	11.4	23.3	0.533	0.086
418330	69	101	16.6	15	0.63	0.075
418331	73	109	13.6	12.7	0.36	0.093
418332	69	82.9	11.9	9.09	0.341	0.108
418333	68	112	16.1	10.5	0.327	0.142
418334	76	97.8	8.21	17.2	0.404	0.088