INTERIM REPORT ON MONITORING CONTAMINANT TRENDS IN LAKE ROOSEVELT

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ABSTRACT

The Washington State Department of Ecology monitored contaminants in Lake Roosevelt during 1992 as part of a two-year study to document the impact of pollution controls being implemented upstream in Canada. Contaminants monitored were 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; commonly referred to as dioxin), 2,3,7,8-tetrachlorodibenzofuran (TCDF), and metals (zinc, lead, copper, arsenic, cadmium, and mercury). The major source of TCDD/TCDF is believed to be the Celgar pulp mill in Castlegar, B.C. The Cominco lead-zinc smelter in Trail, B.C., is the major source of metals contamination.

Columbia River suspended particulate matter (particulates) were collected near the international border over a three-day period and analyzed for polychlorinated dioxins and furans (PCDDs/PCDFs) and metals. Lake whitefish (*Coregonus clupeaformis*) were collected from Lake Roosevelt near Kettle Falls and analyzed for TCDD/TCDF in muscle tissue and eggs. Liver tissues from largescale suckers (*Catostomus macrocheilus*) collected near the border were analyzed for metals and metallothionein, a metal-binding protein. Activities of *delta*-aminolevulinic acid dehydratase (ALA-D), a blood enzyme inhibited by lead exposure, were measured in largescale sucker blood to determine if this species exhibited a biochemical change due to ambient lead concentrations.

TCDD and TCDF data were compared to results from similar surveys of Lake Roosevelt conducted by Ecology during 1990. The metals data will be used as a baseline for future trend monitoring efforts.

Columbia River particulates showed a substantial decrease in TCDF from 1990 (6.2 vs. 99 pg/g or parts per trillion). TCDD was not detected in particulates during either year. Estimated loads of TCDF entering Lake Roosevelt were calculated from single particulate

samples (analyzed in duplicate) collected each year. TCDF loads dropped from 30 mg/day in 1990 to 2.1 mg/day in 1992. The reduction in TCDF loads appears to be consistent with recent mill modifications at Celgar designed to reduce dioxin and furan discharge to the Columbia River.

TCDD and TCDF residues in lake whitefish muscle were significantly lower in 1992 compared to 1990. Mean TCDD and TCDF concentrations in 1992 were 0.8 and 62 pg/g, respectively, down from 1.9 and 126 pg/g in 1990. TCDD and TCDF residues in whitefish eggs were about one tenth the concentrations found in a single sample analyzed in 1990.

Metals concentrations in particulates were comparable to those in bottom sediments from depositional areas in Lake Roosevelt, suggesting that discharges from Cominco continue to represent a metals problem to the lake. Loading estimates for particulate-bound metals to Lake Roosevelt were generally within ranges discharged through Cominco's sewers.

Concentrations of cadmium, lead, and mercury in sucker livers were significantly higher in fish from the Columbia River at Northport than in fish from Lake Wenatchee, a reference lake. Mean zinc and copper concentrations were similar. Liver metallothionein levels were slightly higher in the Northport fish compared to those from Lake Wenatchee.

ALA-D activity was significantly higher in Lake Wenatchee suckers compared to Northport suckers. Inhibition of ALA-D, however, did not result in depressed hemoglobin levels.

Recommendations for 1993 are to repeat the particulate and whitefish collection and analysis, but modify the fish tissue sampling for metals to better monitor zinc and copper.

INTRODUCTION

In 1992, EPA provided the Washington State Department of Ecology (Ecology) Clean Lakes funding to initiate contaminant monitoring in Lake Roosevelt during 1992-1993. The goal of the study is 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 (TCDD; commonly referred to as dioxin), 2,3,7,8-tetrachlorodibenzofuran (TCDF), and metals (zinc, lead, copper, arsenic, cadmium, and mercury). 1992 sample collection was completed during September-October and results are reported here. The 1993 monitoring effort is slated for October.

Background on Chemical Contamination of Lake Roosevelt

The Celgar bleached kraft pulp mill in Castlegar, B.C., located approximately 50 river km above the international border (Figure 1), is considered to be the major source of chlorinated dioxins and furans to Lake Roosevelt. During the past five years, Canadian investigators have found substantial concentrations of TCDD and 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 in 1990 to assess the degree of contamination in Lake Roosevelt. Results showed elevated levels of TCDF and, to a lesser extent, TCDD in several species of fish and in bottom sediments (Johnson *et al.*, 1991a and b). The amounts of dioxins and furans entering Lake Roosevelt were also estimated by analyzing a three-day composite sample of suspended particulate matter (particulates) from the Columbia River near the border (Johnson *et al.*, 1991c).

Contamination of Lake Roosevelt by mercury, lead, cadmium, zinc, copper, and arsenic 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 15 river km 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).

Objectives of Ecology's Monitoring Program

Specific objectives of the 1992/1993 trend monitoring effort and rationale for sampling design are outlined below:

(1) <u>Determine if and how TCDD/TCDF concentrations are changing in Lake Roosevelt as a result of process modifications and effluent treatment at Celgar</u>.

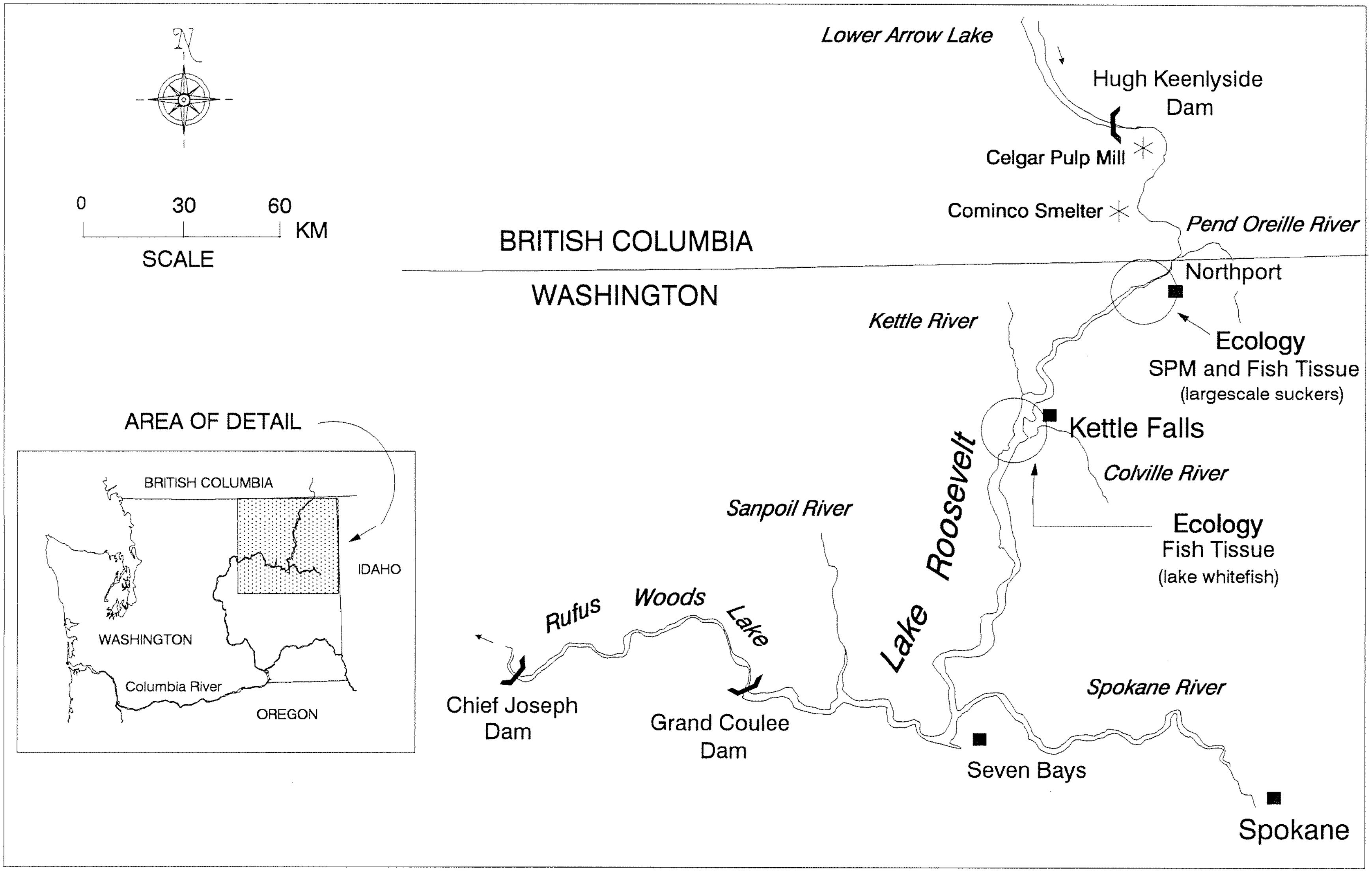

Figure 1. Sampling Sites for Ecology's 1992/1993 Contaminant Monitoring Program in Lake Roosevelt

Data on lake whitefish (*Coregonus clupeaformis*) and suspended particulates from Ecology's 1990 surveys form the basis for detecting trends in TCDD/TCDF contamination. Process changes affecting TCDD and TCDF discharges by Celgar immediately prior to and following the 1990 surveys are shown in Table 1.

Sampling sites and methods were consistent between 1990 and 1992. Figures 1 and 2 shows where the particulate samples were collected in 1990 and 1992. In both cases, samples were three-day composites collected at Northport during September-October. As in 1990, six composites samples of muscle from five whitefish each were analyzed for TCDD/TCDF. Whitefish were collected near Kettle Falls in both cases (Figure 1).

Particulate samples were analyzed instead of whole water samples because TCDD and TCDF have low solubility in water and high affinity for particulate matter, and anticipated concentrations in whole water are far below currently achievable detection limits. An estimate of daily TCDF loading calculated from the 1990 particulate sample analysis showed good agreement with a load estimate calculated from TCDF concentrations in Celgar effluent, measured in early 1989 (30 mg/day for both estimates) (CPPA, 1989; Johnson *et al.*, 1991e).

Lake whitefish were chosen for monitoring because, along with white sturgeon, they were the most contaminated of the seven fish species analyzed in 1990 (Johnson *et al.*, 1991a and b). Analysis was limited to TCDD and TCDF because previous Ecology data showed other polychlorinated dioxins and furans (PCDDs/PCDFs) were not substantial contributors to overall toxicity (in terms of TCDD equivalents, or TEQs) in fish. Whitefish eggs were also analyzed because the single egg sample from 1990 had extremely high TCDD/TCDF levels. Eggs may be particularly useful for long-term monitoring if they continue to show high TCDD/TCDF after concentrations in muscle have declined.

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

Unlike dioxins and furans, significant reductions in metals discharges by Cominco are not expected to occur until after the 1992-1993 monitoring period (see Tables 1 and 2). Sample sizes for the historical data on metals contamination are not sufficient to establish a meaningful basis for trend monitoring. The 1990 particulate sample was not analyzed for metals. Therefore, collection of metals data is geared toward establishing a baseline for future trend monitoring.

The 1992 particulate sample was analyzed for zinc, lead, copper, arsenic, cadmium, mercury, and other less important metals. These data provide an estimate of metals concentrations in the particulate phase of Columbia River water.

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

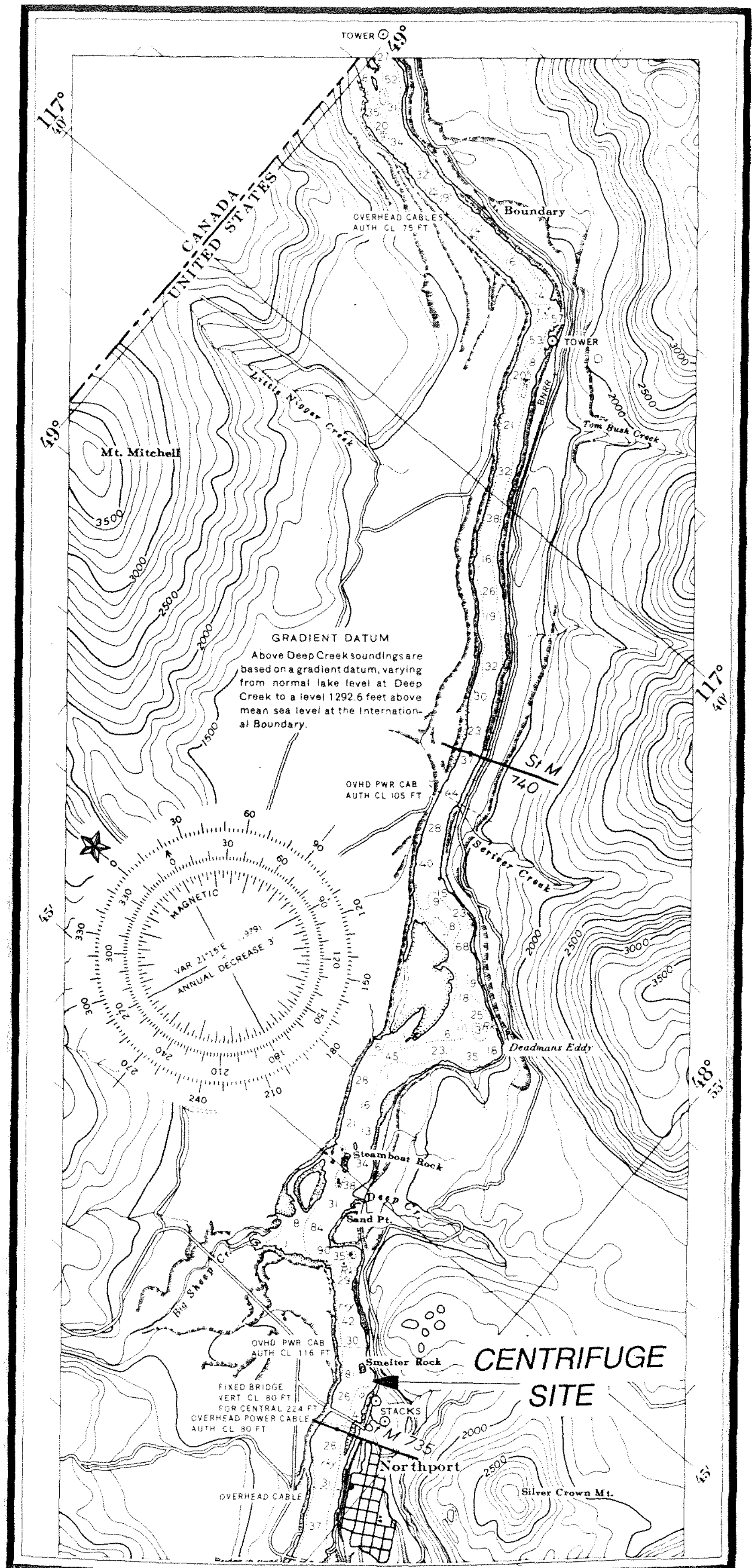

Figure 2. Sampling Site for Particulates

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 selected for analysis because: (1) variability due to sample heterogeneity was expected to be reduced compared to whole-body analyses (Schmitt, personal communication) and (2) it had better potential as an indicator of mercury exposure than whole fish. Lake Wenatchee, located in the Columbia River drainage, was chosen as a reference site for largescale sucker collection because recent data show it has low concentrations of metals in fish and bottom sediments (Johnson and Norton, 1990).

Physiological and biochemical changes in suckers due to metals exposure was assessed through measurement of liver metallothionein concentrations and the *delta*-aminolevulinic acid dehydratase (ALA-D) activities in blood. Metallothionein, a protein which plays a role in storage and transport of heavy metals, is induced by exposure to mercury, copper, cadmium, and zinc. Exposure to lead has been shown to inhibit ALA-D in a variety of fish species (Schmitt *et al.*, 1984; Dwyer *et al.*, 1988). ALA-D is an enzyme which catalyzes the formation of porphobilinogen (PBG), a hemoglobin precursor. Inhibition of ALA-D, therefore, could potentially result in depressed hemoglobin levels.

Reductions in Contaminant Discharges by Canadian Industries

Celgar Pulp Mill

Celgar Pulp Company operates a bleached kraft pulp mill on the Columbia River 3 Km west of Castelegar, B.C. The mill has discharged untreated effluent since it began operation in 1960. Recent production has been about 560 air dried tons (ADt) per day of high quality bleached pulp.

In 1991, the Celgar Expansion Review Panel approved an expansion and modernization plan for Celgar to be completed in 1994. In addition to more than doubling its output to 1200 ADt/day, the plan called for implementation of process changes and secondary treatment which are expected to reduce TCDD and TCDF levels in the final effluent to below present detection limits (Celgar Expansion Review Panel, 1991).

Celgar has already begun to implement pulping and bleaching modifications which have been reported to result in reduced production and discharge of TCDD and TCDF. Among these changes are an increase in chlorine dioxide substitution for elemental chlorine and use of defoamers which do not contain PCDD/PCDF precursors. Table 1 shows major process changes at Celgar which have, or are expected to, improve quality of the final effluent.

Cominco Smelter

Cominco Ltd. operations in Trail have been in existence since the turn of the century and remain the world's largest integrated lead-zinc smelter and refiner. Cominco also operates a fertilizer plant at the same location, utilizing residual sulfur from the metallurgical plant as feedstock.

Table 1. Summary of Process Changes 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 expected 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); McLaren (personal communication)

Discharge of slag and liquid effluent from Cominco are considered to be the primary source of metals loadings to the Columbia River in British Columbia (B.C. Ministry of Environment, 1979; Smith, 1987). 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, and is discharged as a slurry after metals recovery. Recent chemical analysis of discharged Cominco slag shows it is composed of about 2.5% zinc, 0.5% copper, and less than 0.1% lead (Cominco, 1991a; Nener, 1992).

Although slag was originally believed to be biologically inert, results of recent bioassays have shown that it is not (Godin and Hagen, 1992; Nener, 1992). Nener found the slag was deleterious to five aquatic organisms, including rainbow trout, because of either (1) toxicity associated from metals, especially copper and zinc, which leached from the slag; or (2) physical abrasion to soft tissues.

Cominco plans to complete a facility for land disposal of slag in 1995. This facility was originally slated for operation in 1996, but Cominco moved the timeline forward eighteen months based on unfavorable results of the slag bioassays (Watson, 1992).

Over the past 15 years, Cominco has expanded and modernized operations at Trail. Several process and effluent treatment changes have reduced metals loading to the Columbia prior to the present monitoring effort. Table 2 lists the major process changes at Cominco and the reported impact of each on metals in mill discharges.

Table 2. Major Changes at Cominco and Effect on Metals Loading to the Columbia River.

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
Late 1993	Elimination of sewer 07 discharge	Reductions in zinc, lead, copper, arsenic, cadmium, and mercury
September 1994	Collection and treatment of surface water runoff	
1995	Elimination of slag discharge to the river	Reductions in zinc, copper, and lead

Source: Cominco (1991b)

METHODS

Sampling Methods and Laboratory Analysis

Suspended Particulate Matter

Two Sedisamp II continuous-flow centrifuges (model 101IL) were used to collect the particulate sample from September 29 - October 2, 1992, at Northport. Sample collection was timed with normal operations at Celgar and Cominco (C. Johnson, personal communication; McLaren, personal communication).

The 1992 sampling was coordinated with similar work conducted at Northport by the U.S. Geological Survey as part of their larger study of chemicals in Lake Roosevelt. 1990 particulate sample collection was coordinated with upstream sample collection by

Environment Canada. Results of these studies, which include data on dioxins, furans, and metals in particulates, are not yet available.

The particulate sample was collected in a manner described by Johnson *et al.* (1991c). Briefly, 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 adjusted to 2, 5, and 10-ft depths to obtain a depth-integrated sample. Water was fed to the centrifuge over a period of 59 hours at an average flow of approximately 0.75 gallons (2.8 L) per minute. Total volume centrifuged was approximately 2,700 gallons (10,200 L).

Samples of intake water were periodically collected for analysis of conventional parameters (Table 3). Specific conductance, temperature, and total suspended solids were similar between years and within ranges normally observed at Northport during September-October (USGS, 1980-1991). River flow was approximately 50% higher in 1992 than in 1990, but both were within normal ranges seen during early autumn. Total organic carbon (TOC) and pH were substantially higher in 1990. Equipment/operator error were possibly responsible for the low 1992 pH reading, since values were below those normally observed in the Columbia River at Northport (USGS, 1980-1991).

Table 3. Summary of Columbia River Water Quality at Northport, October 9-12, 1990, and September 29 - October 2, 1992 (mean ± SD; samples at centrifuge intake).

Variable	1990 (n=8)	1992 (n=7)
Specific Conductance (μmhos/cm)	148 ± 2	135 ± 2
Temperature (°C)	13.0 ± 0.6	14.7 ± 1.0
pH (s.u.)	8.2 ± 0.2	7.1 ± 0.2*
Total Suspended Solids (mg/L)	2.0 ± 0.5	1.4 ± 0.5
Total Organic Carbon (mg/L)	3.3 ± 0.1	1.3 ± 0
Dissolved Organic Carbon (mg/L)	NA	1.1 ± 0.1
Average Flow at International Border (cfs)	61,600	94,000

NA=Not Analyzed
*Low values possibly due to equipment/operator error.

Total amount of material collected in 1992 was 68 grams (wet). Based on the average total suspended solids (TSS) concentration in water of 1.4 mg/L and a 78.8% moisture content of the particulate sample, efficiency of suspended solids removal from Columbia River water was near 100%.

The particulate sample was analyzed in duplicate for TCDD, TCDF and other 2,3,7,8-substituted PCDD/PCDF congeners. Analysis was conducted by the Enseco California Analytical Laboratory using high resolution GC/MS EPA method 8290.

Metals were analyzed in duplicate by the Battelle laboratory in Sequim, Washington. Material for aluminum, arsenic, copper, iron, manganese, lead, and zinc analysis was freeze dried, ground, and analyzed using energy dispersive X-ray fluorescence (XRF). Remaining material was acid-digested and analyzed for cadmium using GFAA and mercury using CVAA.

Lake Whitefish Tissues

Lake whitefish were collected by gillnet September 30 - October 1, 1992. Fish selected for analysis were chosen randomly. Measurements for total length and weight were made in the field, and scales were collected for subsequent age determination. Age results will be published in the project summary report to be issued in 1994. Specimens were then placed on ice until muscle and egg samples were resected upon returning from the field.

Muscle resection was done in a manner identical to previous Ecology surveys (Johnson *et al.*, 1991a; Serdar *et al.*, 1991). 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.

Fish were grouped randomly prior to resection. Muscle from five fish, and eggs from three or four fish (there were not enough females for equal composites) were composited for each sample, diced, mixed, then sent to Alta Analytical Laboratory (California) for TCDD/TCDF analysis using EPA method 8290. Six muscle and three egg composites were analyzed for TCDD/TCDF. Alta also analyzed samples for percent lipids and percent non-polar lipids.

Largescale Sucker Tissues

Largescale suckers were collected by electroshocking in Lake Wenatchee on September 27 and the Columbia River near Northport on September 28, 1992. Upon collection, fish were measured for length and weight, and scales were collected for age determination. Fish were then anesthetized with MS-222 and blood was drawn with via heart puncture using a sterile syringe and stainless steel 21 gauge needle. Blood samples were immediately emptied into acid-washed, heparinized cryovials, and placed in liquid nitrogen. Livers were then removed in the field and placed in an acid-washed polyvinyl specimen cup and stored on dry ice.

Blood samples were sent to the U.S. Fish & Wildlife Service lab in La Crosse, Wisconsin, for analysis of ALA-D. ALA-D was measured in duplicate according to the method described by Schmitt *et al.* (1984, 1993). Hemoglobin levels were determined according to the method recommended by Larsen and Snieszko (1961).

Sucker livers were split for (1) metals analysis at Ecology's Manchester Environmental Laboratory and (2) metallothionein assessment at the Institute of Ocean Sciences laboratory in Sidney, B.C. Arsenic, copper, and high-level cadmium analyses in liver tissues were done by ICP; lead and low-level cadmium by GFAA; and mercury by GFAA. Metallothionein levels were measured according to the method described by Thompson and

Cosson (1984). Total protein content was determined by the Bradford method (Bradford, 1976).

Data Quality

Data quality was assessed by analyses of standard reference materials (SRMs) and matrix spikes, and duplicate laboratory analyses. Manchester Laboratory staff also reviewed analytical data for isotopic abundance ratios (PCDD/PCDF analysis only), initial and continuing calibration standards, and serial dilution analyses (metals analysis only). Overall, quality of the data was good and all data were considered acceptable for use.

No special problems were encountered with the analysis of the particulate sample for PCDDs/PCDFs or the lake whitefish muscle and eggs for TCDD, TCDF, and % lipids. Results of duplicate analyses were in close agreement for these samples (Appendix, Tables A-1 and A-2). Relative percent differences, a measure of range about the mean, were 15% for TCDF in particulates (TCDD not detected), no differences for TCDD in fish tissues, and 44% and 3% for TCDF in muscle and eggs, respectively.

Results of duplicate metals analyses were also very close for the particulate and liver samples (Appendix, Tables A-3 and A-4). Percent differences were generally less than 10%.

Standard reference materials were analyzed to evaluate accuracy of metals analysis (similar materials were not available for PCDDs/PCDFs) (Appendix, Table A-5). For sediment reference materials, accuracy and precision were very good. Values fell within or near the certified range for NIST-1646 and NIST-2704. Battelle's results on NIST-1646 have been consistently high for mercury (Crecelius, written communication). However, mercury results showed excellent agreement with a third reference material, BEST-1.

Metals analysis of dogfish liver reference material (DOLT-1) was also generally good (Appendix, Table A-5). Cadmium and mercury results were within the certified range, and zinc and copper results were near certified values. Results of lead analysis were approximately 55% of the certified value. Therefore, the lead data reported here for liver samples may underestimate actual concentrations.

RESULTS AND DISCUSSION

TCDD/TCDF in Suspended Particulate Matter and Fish Tissue

Table 4 shows concentrations of TCDD, TCDF, and other PCDDs/PCDFs detected in particulates in 1990 and 1992. TCDD and TCDF data are plotted in Figure 3. The TCDF concentration in 1992 was an order of magnitude lower than in 1990 (6.2 vs. 99 pg/g). TCDD was not detected in either the 1990 or 1992 samples (detection limits of 0.8 and 1.6 pg/g, respectively).

Table 4. PCDD/PCDF Concentrations in Suspended Particulate Matter at Northport in 1990 and 1992 (mean ± range in pg/g, parts per trillion; dry weight basis).

Compound	1990	1992
2,3,7,8-TCDD	U(0.8)	U(1.6)
2,3,7,8-TCDF	99 ± 22	6.2 ± 0.4
Other PCDDs/PCDFs Detected:		
PCDDs		
1,2,3,4,6,7,8-HpCDD	11 ± 1	31 ± 6
OCDD	79 ± 9	214 ± 30
PCDFs		
1,2,3,7,8-PeCDF	1.0 ± 0.1	U(1.8)
2,3,4,7,8-PeCDF	1.4 ± 0.2	U(2.6)
OCDF	4.6 ± 0.7	U(14)
TEQ =	**10.8**	**1.1**
% TOC	7.6	2.2
% Solids	26.2	21.2

U=Undetected at detection limits in parentheses

Table 5. Estimated Concentration and Loads of TCDD and TCDF in the Columbia River at Northport in 1990 and 1992.

	Water Concentration (pg/L, parts per quadrillion)		Loads to Lake Roosevelt (mg/day)	
Compound	1990	1992	1990	1992
2,3,7,8-TCDD	<0.002	<0.002	<0.3	<0.5
2,3,7,8-TCDF	0.2	0.009	30	2.1

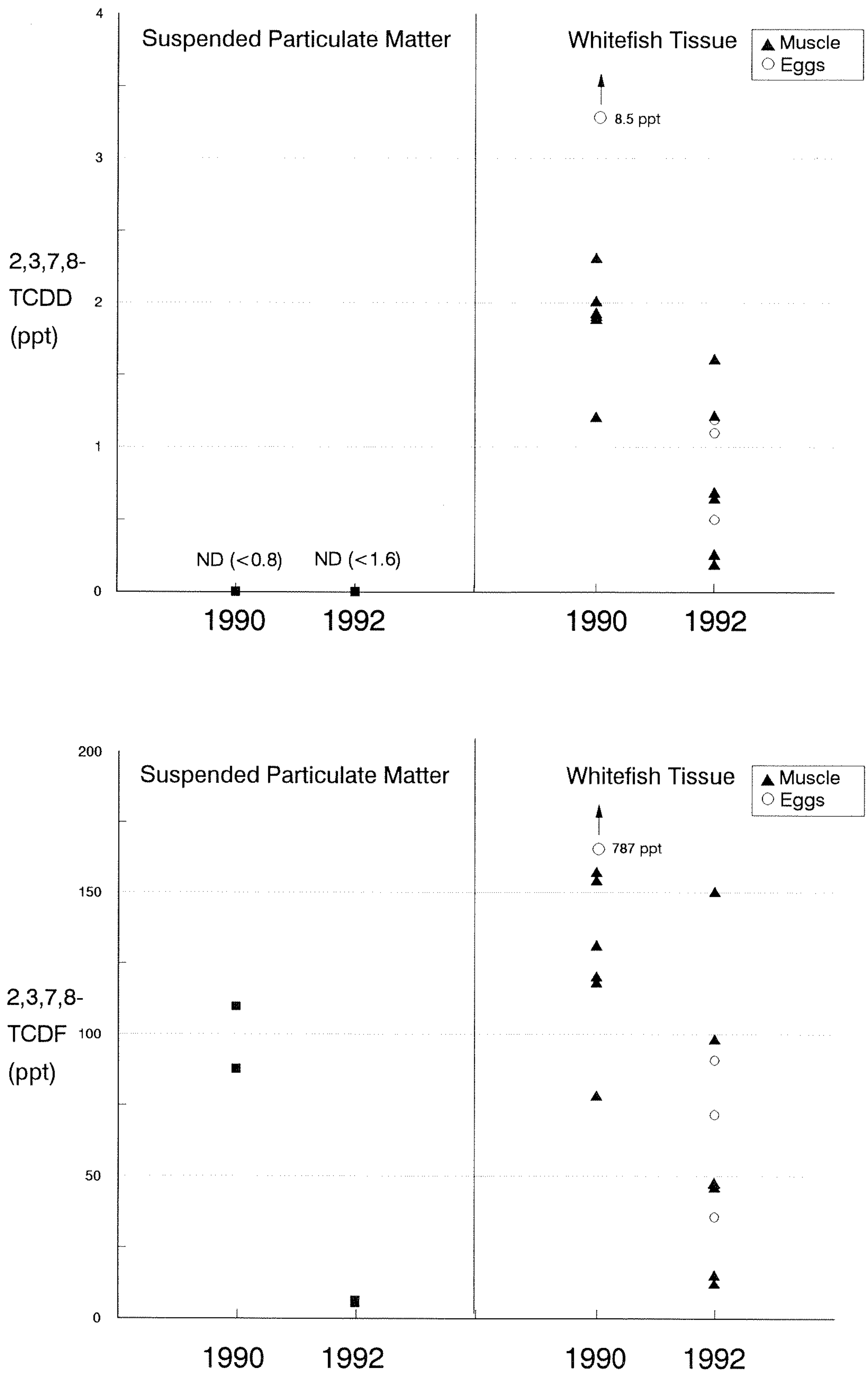

Figure 3. TCDD and TCDF Concentrations in Suspended Particulate Matter and Fish Tissue Collected from Lake Roosevelt During 1990 and 1992 (ND=Not Detected)

Other compounds detected in both the 1990 and 1992 particulate samples included hepta- and octachlorinated dioxins. While these congeners were found at higher concentrations in 1992 than 1990, their low toxicity compared to TCDF makes their presence less important.

The particulate data were used to estimate TCDD/TCDF concentrations in Columbia River water at Northport and loads to Lake Roosevelt (Table 5). The 1992 estimates were calculated based on an average TSS concentration of 1.4 mg/L (Table 3) and average river flow of 94,000 cfs (2,662,00 L/s) at the international border (USGS NASQAN Station 12399500).

As shown in Table 5, concentrations of TCDF in the particulate phase of Columbia River water and loading to Lake Roosevelt in 1992 were reduced by an order of magnitude from the 1990 estimates. TCDD loads were estimated at less than 0.5 mg/day. These values probably underestimate actual concentrations because the dissolved TCDD/TCDF fraction was not measured. U.S. Geological Survey analyzed the dissolved fraction during their 1992 Northport sampling, and results should be available later this year.

Toxic equivalents, expressed in terms of TEQs, also decreased by an order of magnitude from 1990. Although concentrations of 1,2,3,4,6,7,8-HpCDD and OCDD increased in 1992, TCDF remained as the greatest contributor to overall toxicity.

Loads were also calculated based on concentrations in Celgar pulp mill effluent collected during the particulate sampling period (September 29, 1993; data provided by Celgar). Total discharges of TCDF and TCDD by Celgar were estimated at 2.0 and 0.8 mg/day, respectively. This agrees well with the 2.1 mg/day of TCDF and maximum possible 0.5 mg/day TCDD (based on detection limits) calculated from particulate sample analysis.

Concentrations of TCDD and TCDF in whitefish muscle and eggs are summarized in Table 6a; data for individual samples are plotted in Figure 3. Mean muscle concentrations in 1992 were approximately half of those in 1990. Differences for both TCDD and TCDF were significantly different between years (Mann-Whitney U test for ranked sums, $p<0.05$). In eggs, TCDD and TCDF levels dropped by an order of magnitude from 1990.

Lipid content of the 1990 egg sample was extremely high (45%). However, muscle samples for the present study contain twice the mean lipid of 1990 samples (12% vs. 6.0%). Consequently, lipid normalization of TCDD/TCDF narrows the differences between years for eggs, but increases 1990-to-1992 differences for muscle tissue (Table 6b).

Table 6a. TCDD and TCDF Concentrations, Lipid Content, and Size of Lake Whitefish Collected Near Kettle Falls in 1990 and 1992 (mean ± SD; TCDD and TCDF in pg/g, parts per trillion; wet weight basis).

	Muscle		Eggs	
Compound	1990 (n=6)	1992 (n=6)	1990 (n=1)	1992 (n=3)
2,3,7,8-TCDD	1.9 ± 0.4	0.8 ± 0.6	8.5	0.9 ± 0.4
2,3,7,8-TCDF	126 ± 29	62 ± 53	787	66 ± 28
TEQ	14 ± 3.2	6.9 ± 5.9	87	7.6 ± 3.2
% Total Lipid	6.0 ± 2.9	12 ± 2	45	12 ± 4
% Non-Polar Lipid	NA	9 ± 2	NA	8 ± 2
Total Length (mm)	462 ± 18	497 ± 25	530	519 ± 7
Weight (g)	1,168 ± 133	1,682 ± 354	1,858	2,089 ± 175

NA=Not Analyzed

Table 6b. Total Lipid-Normalized TCDD and TCDF Concentrations in Lake Whitefish Collected Near Kettle Falls in 1990 and 1992 (mean ± SD in pg/g lipid, parts per trillion; wet weight basis).

	Muscle		Eggs	
Compound	1990 (n=6)	1992 (n=6)	1990 (n=1)	1992 (n=3)
2,3,7,8-TCDD	49 ± 46	6.1 ± 3.3	19	7.7 ± 2.2
2,3,7,8-TCDF	3,330 ± 3,200	480 ± 360	1,750	540 ± 130

NA=Not Analyzed

Metals in Suspended Particulate Matter

Results of metals analyses of particulates are shown in Table 7 and compared to previous data on bottom sediments. Aluminum, iron, and manganese were found at the highest concentrations, followed by zinc, lead, and copper. Arsenic, cadmium, and mercury concentrations were one-to-two orders of magnitude lower than other metals analyzed (excluding aluminum and iron).

Zinc, lead, and copper concentrations were similar to those found in bottom sediments from Frenchman Point Rocks and Gifford during Ecology's 1986 Lake Roosevelt survey (Table 7).

Frenchman Point Rocks is located just downstream from Kettle Falls; Gifford is located approximately 45 km downstream of Kettle Falls. Kettle Falls appears to mark the beginning of the depositional zone for fine-grained sediments in Lake Roosevelt (Johnson *et al.*, 1988).

Cadmium and mercury concentrations in the 1992 particulate sample were three and five times higher, respectively, than sediments from Gifford, the site with the highest concentrations of these metals during the 1986 survey. These data indicate that input of this material continues to represent a metals problem for Lake Roosevelt.

Table 7. Concentrations of Metals in Columbia River Suspended Particulate Matter at Northport Compared to Lake Roosevelt Bottom Sediments (mean ± range of duplicate analyses; ug/g, parts per million; dry weight basis).

Metal	1992 Particulates	1986 Bottom Sediments from Frenchman Pt. Rocks/Gifford
Manganese	1,794 ± 12	550/850
Zinc	1,478 ± 8	1,090/1,060
Lead	554 ± 4	434/467
Copper	352 ± 6	165/111
Arsenic	44.2 ± 0.5	8.7/11.6
Cadmium	16.1 ± 0.2	5.7/5.7
Mercury	13.7 ± 0.2	2.0/2.7
Aluminum(%)	4.50 ± 37	1.67/2.16
Iron(%)	3.47 ± 0.1	3.26/3.48

Particulate-bound metals loads at Northport were calculated from concentrations in particulates and compared to discharges by Cominco during Ecology's sampling period (Table 8). Loading from Cominco was calculated from data on total metals in metallurgical and storm sewers (provided by C. Johnson, B.C. Ministry of Environment). These calculations do not include contributions from slag discharges.

Particulate-bound zinc and lead agreed well with sewer discharges from Cominco, while arsenic and cadmium were within a factor of two. Estimates of copper loads were not in close agreement with Cominco discharge, suggesting other sources of copper existed. Preliminary results from the 1992 U.S. Geological Survey's study indicate that slag particles are present in Columbia River particulate matter. This probably represents a source of zinc and copper enrichment. The mercury load calculated from the particulate sample was about one-fourth the load calculated from Cominco's average daily discharge during the sampling period. Loads of mercury from Cominco may have been exaggerated due to a mercury spill on October 1 (C. Johnson, personal communication).

Table 8. Estimated Loads of Particulate-Bound Metals at Northport Compared to Average Daily Discharge of Metals from Cominco Sewers, September 29-October 2, 1992 (mean ± SD in kg/day; dry weight basis).

Metal	Loads to Lake Roosevelt	Daily Discharge from Cominco's Sewers (n=3)
Zinc	490	330 ± 24
Lead	180	160 ± 17
Copper	120	7.0 ± 0.7
Arsenic	15	8.2 ± 2.7
Cadmium	5.3	10.0 ± 3.0
Mercury	4.6	21 ± 33*

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

Metals, Metallothionein, and ALA-D Activity in Sucker Tissue

Table 9 shows concentrations of metals in largescale sucker liver tissue from Northport and the Lake Wenatchee reference area. Concentrations of cadmium, lead, and mercury were three-to-six times higher in the Northport samples. Zinc and copper concentrations were similar between fish from the two lakes.

Statistical comparisons of metals concentrations between sites were made by log-transforming data, checking for normality using the Kolmogorov-Smirnov test, and testing for difference between means using a Students *t* (one tailed, $p<0.05$). Cadmium, lead, and mercury concentrations were significantly higher in livers of suckers from Northport. Differences in zinc and copper concentrations were not significant between sites.

The absence of clear differences in zinc and copper concentrations between the Lake Wenatchee and Lake Roosevelt fish is unexpected. Previous whole-body analysis of suckers from upper, middle, and lower reaches of Lake Roosevelt had significant between-site differences in zinc, copper, and lead concentrations (Johnson *et al.*, 1988).

Table 9. Concentrations of Metals in Livers of Largescale Suckers Collected near Northport and Lake Wenatchee (Background Area) September 27 & 28, 1992 (mean ± SD in ug/g, parts per million; wet weight basis).

Metal	Northport (n=17)	Lake Wenatchee (n=16)
Zinc	54.0 ± 20.5	49.8 ± 15.0
Copper	22.2 ± 15.5	19.3 ± 10.1
Cadmium	*7.36 ± 4.74	*1.80 ± 1.73
Lead	*1.33 ± 1.23	*U(0.20)
Mercury	*0.084 ± 0.066	*0.032 ± 0.027

* Significant difference between sites at $p<0.05$
U=Undetected at detection limit in parentheses

Liver metallothionein was elevated in Northport suckers but was not significantly higher than levels in fish from Lake Wenatchee (Students *t*, $p<0.05$). Mean metallothionein levels in Northport and Lake Wenatchee samples were 333 and 274 nmoles per g of liver.

Induction of liver thionein in fish is considered to be a physiological response to increased metals exposure. Metals are sequestered or bound by thionein (metal + thionein = metallothionein) in liver, thereby reducing the availability of the metals to elicit toxic effects.

Previous studies have shown that fish exposed to sublethal concentrations of copper, zinc, cadmium, mercury, or other metals may exhibit increased tolerance to cadmium and copper, probably as a result of metallothionein induction (Klaverkamp *et al.*, 1984). It appears that fish from Northport were exposed to metals concentrations insufficient to induce metallothionein to levels substantially higher than those from Lake Wenatchee. Therefore, sucker metallothionein does not appear to be a useful component of metals monitoring in Lake Roosevelt at this time.

Activity of the enzyme ALA-D was significantly reduced in Northport fish compared to those from Lake Wenatchee (Student's *t*, $p<0.001$). Mean ALA-D activity was 165.81 nmole PBG/g/h in Northport fish (n=18) and 369.11 nmole PBG/g/h in Lake Wenatchee fish (n=15) [units are nmoles PBG (porphobilinogen) formed per gram of blood per hour].

Depressed ALA-D activity, however, apparently did not result in lower hemoglobin levels in Northport fish relative to the reference area. Northport samples had mean hemoglobin levels of 10.47 g/dL compared to 9.82 g/dL for Lake Wenatchee samples.

Reduced ALA-D activity and resulting hematological effects in fish are poorly defined and inconsistent. A review of previous studies has shown reductions in hemoglobin levels do not necessarily accompany low ALA-D activity in fish (Caldwell, 1993). However, reduced

ALA-D activity may indicate other detrimental biochemical changes caused by chronic lead exposure, including decreases in the mechanical strength and elasticity of vertebrae (Dwyer *et al.*, 1988).

CONCLUSIONS

Results from particulate samples analyzed during Ecology's 1992 monitoring effort show substantial reduction of TCDF loads to Lake Roosevelt compared to conditions in 1990. This improvement almost certainly results from recent process changes at the Celgar pulp mill. As in 1990, TCDD continued to be undetected in Columbia River particulate matter in 1992.

The 1992 data also suggest a significant reduction in contamination of lake whitefish muscle and eggs by TCDF and TCDD has taken place since 1990. Data from a second year of monitoring in 1993 will help fully establish the accuracy of these conclusions.

A baseline was established for metals concentrations in Columbia River particulate matter and in fish tissue. Results on particulates indicated current input of zinc, copper, cadmium, lead, mercury, and arsenic continue to contaminate the lake. The livers from largescale suckers appear to be a potentially useful indicator of cadmium, lead, and mercury levels in Lake Roosevelt. Analysis of the enzyme ALA-D in blood samples from these fish showed a biochemical change due to lead exposure.

RECOMMENDATIONS FOR 1993

1) The sampling conducted for dioxins and furans in Lake Roosevelt fish and suspended particulate matter should be repeated. The metals analysis of suspended particulates should also be repeated.

2) Although useful baseline data were obtained on cadmium, lead, and mercury in fish liver samples, the zinc and copper analyses did not yield similar results. Other types of fish tissue samples, probably including whole fish, are needed to supplement the existing data and provide a basis for monitoring zinc and copper. A proposal for revising the 1993 sampling plan for metals in fish tissue will be prepared for approval by EPA.

3) Analysis of metallothionein should be dropped in 1993.

4) Analysis of ALA-D should continue in 1993.

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APPENDIX

Table A-1. Results of Duplicate PCDD/PCDF Analysis of Suspended Particulate Matter (pg/g, parts per trillion; dry weight basis).

	Particulates (Sample No. 408560)		
Compound	Analysis #1	Analysis #2	Relative Percent Difference
PCDDs			
1,2,3,4,6,7,8-HpCDD	37 J	25	39%
Total HpCDDs	80	57	34%
OCDD	245	184	29%
PCDFs			
2,3,7,8-TCDF	6.6 J	5.7 J	15%
Total TCDFs	33	24	32%

J=Estimate

Table A-2. Results of Duplicate Analysis of Lake Whitefish Muscle and Eggs (pg/g, parts per trillion; wet weight basis).

	Muscle (Sample No. 408542)			Eggs (Sample No. 408546)		
Compound	Analysis #1	Analysis #2	Relative Percent Difference	Analysis #1	Analysis #2	Relative Percent Differnce
2,3,7,8-TCDD	0.18	0.18	0%	0.50	0.50	0%
2,3,7,8-TCDF	15	9.6	44%	36	35	3%
% Lipid	10	8.0	22%	8.0	10	22%
% Non-Polar Lipid	7.1	6.0	17%	6.0	7.6	24%

Table A-3. Results of Duplicate Metals Analysis of Suspended Particulate Matter (ug/g, parts per million; dry weight basis).

Metal	Method	Analysis #1	Analysis #2	Relative Percent Difference
Mn	XRF	1772	1796	1.3%
Zn	XRF	1486	1471	1.0%
Pb	XRF	557	550	1.3%
Cu	XRF	347	358	3.1%
As	XRF	44.7	43.8	2.0%
Cd	GFAA	16.3	15.9	2.5%
Hg	CVAA	13.5 J	13.9 J	2.9%
Al(%)	XRF	4.14	4.87	16%
Fe(%)	XRF	3.46	3.48	0.6%

J=Estimate

Table A-4. Results of Duplicate Metals Analyses of Largescale Sucker Livers from Northport and Lake Wenatchee (ug/g, parts per million; wet weight basis).

Sample No.	Location		Zn ICP	Pb GFAA	Cu ICP	Cd ICP or GFAA	Hg CVAA
408516	Northport		48.2 J	0.50 J	20.1	3.25	0.064
"	"		44.9 J	0.53 J	19.4	3.19	0.070
		RPD =	7%	6%	4%	2%	9%
408530	Northport		25.4 J	0.46 J	9.0	2.42	NA
"	"		24.1 J	0.67 J	9.3	2.32	NA
		RPD =	5%	37%	3%	4%	-
408517	Northport		NA	NA	NA	NA	0.165
"	"		NA	NA	NA	NA	0.138
		RPD =	_	-	-	-	18%
408500	Lake Wenatchee		40.5	U(0.20)	13.3	0.78	NA
"	"		41.7	U(0.20)	13.7	0.85	NA
		RPD =	3%	-	3%	9%	-
408503	Lake Wenatchee		NA	NA	NA	NA	0.011
"	"		NA	NA	NA	NA	0.091
		RPD =	_	-	-	-	19%
408513	Lake Wenatchee		65.7 J	U (0.20)	20.2	0.27	NA
"	"		59.9 J	U (0.20)	20.6	0.26	NA
		RPD =	9%	_	2%	4%	-
408506	Lake Wenatchee		NA	NA	NA	NA	0.036 J
"	"		NA	NA	NA	NA	0.036 J
		RPD =	_	-	-	-	0%

J=Estimate
U=Undetected at detection limits in parentheses
NA=Not Analyzed

Table A-5. Results of Sediment and Fish Liver Standard Reference Material Analyses (mean ± range of duplicates; ug/g,parts per million; dry except for liver [wet]).

Standard Reference Material	Mn	Zn	Pb	Cu	As	Cd	Hg	Al(%)	Fe(%)
Estarine Sediment (NIST-1646)									
Present Analysis	342 ± 10	132 ± 0	27.4 ± 1.0	20.4 ± 0.1	12.4 ± 0.3	0.36 ± 0.01	0.081 ± 0.003	6.34 ± 0.94	3.39 ± 0.02
Certified Value	375 ± 20	138 ± 6	28.2 ± 1.8	18 ± 3	11.6 ± 1.3	0.36 ± 0.07	0.063 ± 0.012	6.25 ± 0.20	3.35 ± 0.10
Buffalo River Sed. (NIST-2704)									
Present Analysis	585 ± 10	454 ± 4	157 ± 1	99.8 ± 1.2	27.8 ± 0.9	3.53	NA	6.58 ± 0.19	4.12 ± 0.03
Certified Value	555 ± 15	438 ± 12	161 ± 17	98.6 ± 5.0	23.4 ± 0.8	3.45 ± 0.22	NA	6.11 ± 0.16	4.11 ± 0.10
Marine Sediment (BEST-1)									
Present Analysis	NA	NA	NA	NA	NA	NA	0.096 ± 0.001	NA	NA
Certified Value	NA	NA	NA	NA	NA	NA	0.092 ± 0.009	NA	NA
Dogfish Liver (NRCC DOLT-1)									
Present Analysis	NA	99.8 ± 14.6	0.74 ± 0.02	18.8 ± 0.1	NA	4.26 ± 0.23 (S.D.)	0.194 ± 0.014 (S.D.)	NA	NA
Certified Value	NA	92.5 ± 2.3	1.36 ± 0.29	20.8 ± 1.2	NA	4.18 ± 0.28	0.225 ± 0.037	NA	NA

(shaded) Outside of Certified Range
NA=Not Analyzed
S.D. = Standard Deviation of 4 (for Cd) or 5 (for Hg) analyses.