# Dioxin (2,3,7,8-TCDD) and Furan (2,3,7,8-TCDF) in Mountain Whitefish (*Prosopium williamsoni*) from the Fraser River, 1994

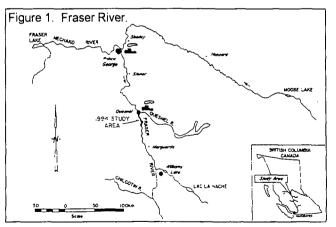
### Mellor, C.<sup>(1)</sup>, Van Oostdam, J.<sup>(2)</sup>, Zirnheit, N.<sup>(1)</sup>

(1) Ministry of Environment, Lands and Parks, Environmental Protection, 400-640 Borland St., Williams Lake, British Columbia, V2G 4T1

(2) Ministry of Environment, Lands and Parks, 765 Broughton St., Victoria, British Columbia, V8V 1X4

Four bleached kraft mills and one non-chlorine bleaching thermo-mechanical mill operate on the Fraser River between Prince George and Quesnel (Figure 1). Previous studies by Environment Canada<sup>(1)</sup>, BC Environment and the pulp mills<sup>(2)</sup> have shown elevated levels of dioxins and furans in Fraser River fish resulting in a number of human health consumption advisories. These and other studies<sup>(3)</sup> also showed elevated dioxin and furan levels in bottom and suspended sediments upstream of Quesnel. It was suspected that suspended sediment transport was the main mechanism, carrying contaminants from the Prince George area pulp mills to the Quesnel sampling site, where deposition in the bed sediments would occur. Subsequent studies on the Fraser and other major rivers have concluded that dioxins and furans are transported predominately in suspended sediments<sup>(4,5)</sup>.

The Fraser River is home to many species of fish. including many sport and commercial fish consumed by humans. Historical data from the Fraser River show that mountain whitefish exhibited the highest levels of dioxins and furans of all species of fish studied. A study on the Columbia River has shown that there may be a seasonal difference in dioxin and furan levels in mountain whitefish<sup>(6)</sup>.



Effective January 17, 1992, provincial amendments to the Pulp Mill and Pulp and Paper Mill Liquid Effluent Control Regulation required a reduction of AOX (Adsorbable Organic Halogen) discharges to 1.5 kg AOX per air dried tonne (ADt) by December 31, 1995.



These amendments also required complete elimination of AOX produced by the bleaching process by December 31, 2002<sup>(7)</sup>. By the end of 1993, all of the mills along the Fraser River had made the modifications necessary to meet the reduction to 1.5 kg AOX per ADt. Federal regulations also required elimination of dioxins and furans from defoamers, and prohibited mills from using contaminated wood chips<sup>(7)</sup>.

In March of 1994, mountain whitefish and largescale sucker were collected downstream of the confluence of the Quesnel and Fraser rivers, an area which had previously exhibited high levels of dioxins and furans. This study addressed the following two questions:

1) Do mountain whitefish (MWF) tissues contain higher levels of dioxins and furans during spring low flow (before freshet) conditions than during fall?

2) Are tissue levels of dioxins and furans continuing to decline in the species sampled?

### Materials and Methods

MWF and Largescale sucker (LSS) were collected on March 24 and 25, 1994, downstream of the confluence of Quesnel and Fraser Rivers (Figure 1). Zenon Environmental Laboratories (Burnaby, B.C. and Burlington, Ont.) analyzed the samples using high resolution GC/MS. The sampling protocol, including specimen handling and dissection procedures, are outlined in Mellor, et al. (1995)<sup>(8)</sup>. The following sample sizes and size classes were selected for fish collection: 10-22 cm (n=20), >22-29 cm (n=6) and > 29 cm (n=6). Field sampling was carried out using a BC Environment boat equipped with a Coffett VV-15 electroshocker ("boom" style). In total, ten MWF and nineteen LSS were collected and dissected for muscle and liver composite and individual analyses. The small sample size may be attributed to the use of electroshocking vs. netting; a better result may have been obtained using nets in the cold waters, or a combination of both techniques. Analyses for dioxins, furans, 58 different Polychlorinated biphenyls (PCB) congeners, PCB total and % lipid were conducted. LSS and PCB data are presented in a separate report<sup>(6)</sup>.

### Results and Discussion

Table 1 presents fresh weight and lipid-normalized 2,3,7,8-TCDD and 2,3,7,8-TCDF for the ten MWF. Individual muscle 2,3,7,8-TCDD and 2,3,7,8-TCDF values were generated for all specimens except the smallest class size. Lipid-normalized 2,3,7,8-TCDD values ranged from ND to 193.5 pg/g, with the oldest fish (6 years) having the highest lipid-normalized 2,3,7,8-TCDD level. Lipid-normalized 2,3,7,8-TCDF values ranged from 17.3 to 81.3 pg/g, but the highest concentrations were not in the oldest fish.

Composite samples were analyzed for all three size classes and compared to the average value for each size class (Table 1). Average 2,3,7,8-TCDD and 2,3,7,8-TCDF values were 0.7 to 1.6 times the composite values. The average of the individual lipid concentrations were slightly lower than the composite values; higher composite % lipid will decrease the lipid-normalized value.

Table 1. 1994 Mountain whitefish muscle 2,3,7,8-TCDD and 2,3,7,8-TCDF fresh weight and lipid-normalized data (pg/g).

Sex	Age	Length	Weight	%	2,3,7,8	Lipid	2,3,7,8	Lipid
	(years)	(cm)	(g)	lipid	TCDD	Normalized *	TCDF	Normalized
						2,3,7,8-		2,3,7,8-TCDF
						TCDD		
Indiv	vidual sa	mples						
F	3+	23.4	160	8.09	ND(0.74)1	-	1.4	17.3
F	2+	24	140	4.43	ND(0.77)	-	1.1	24.8
М	3+	25.4	200	6.97	0.79	11.33	2.6	37.3
М	4+	26.4	160	1.65	ND(0.84)	-	1	60.6
F	4+	27.2	220	8.86	2.7	30.5	7.2	81.3
F	4+	31.3	340	5.44	ND(0.58)	•	1.5	27.6
F	4+	33.2	510	7.02	2.4	34.2	2.2	31.3
F	6+	38.2	720	8.27	16	193.5	4.5	54.4
Indi	vidual a	verages						
>22-	29 cm			6	0.7	8.4	2.7	44.3
>29 cm				6.91	6.1	75.9	2.7	37.8
Соп	iposite s	samples						
10-22 cm (Ages 2+,2+)				5.39	ND(0.71)	-	1.2	22.3
>22	29 cm			6.32	0.74	11.7	1.8	28.5
>29 cm				7.63	5.8	76	2.2	28.8

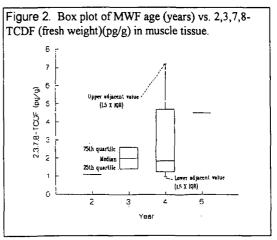
\* lipid-normalized calculation: (2,3,7,8-TCDD/% lipid) x 100

1. ND=Not Detected; (0.74) indicates detection limit for sample

Comparison of individual and composite data from 1990<sup>(2)</sup> provided similar results; average values were 0.94 and 1.06 times the composite. This suggests that composite sample analysis is a suitable alternative to individual analysis, thereby keeping costs down for these studies.

Figure 2 is a box plot comparing age of MWF and 2,3,7,8-TCDF in muscle for all but the smallest class size. The majority of fish sampled were ages 3 and 4. The 4 year class had a high variability in 2,3,7,8-TCDF values, but the concentrations in 2 and 6 year old fish were within this variability. This indicates that the apparent linear relationship between age and 2,3,7,8-TCDF (fresh weight) is a function of the number of samples and probability<sup>(9)</sup>.

Figure 3 compares historical values of 2,3,7,8-TCDD (fresh weight) and 2,3,7,8-TCDF (fresh weight) in muscle.

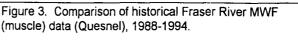


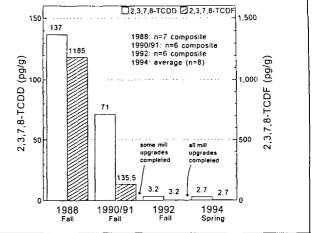
ORGANOHALOGEN COMPOUNDS Vol.24 (1995)

## ENV

All values are composites with the exception of 1994 concentrations. Only 8 of 10 1994 samples had individual values which could be averaged; the smallest class size was composite data only and was omitted. Levels of both contaminants decreased noticeably after mill upgrades in 1991 and 1992. No increase in MWF contaminant levels in spring vs. fall was noted.

Figure 4 gives an age comparison for previous Fraser River studies of MWF. The 1994 study has

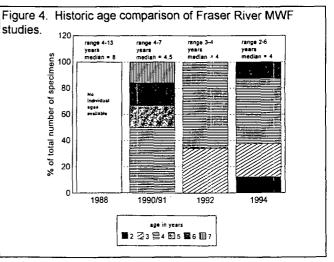




the same median age as the 1992 study (median=4 years), but has a larger age range (2-6 years (1994) vs. 3-4 years for 1992). It may be suggested that since fish bioaccumulate toxins with age, the younger fish in the 1992 and 1994 studies may partially account for the decrease in contaminant concentrations. However, establishing a linear relationship without a large sample size can be misleading, as demonstrated in Figure 2.

### Conclusions

1) The results do not indicate that MWF have higher contaminant levels in body tissues in the spring (before freshet). Since levels in Fraser River fish tissue are now very low, it would be difficult to find evidence of any large seasonal differences in tissue concentrations without large (and impractical) sample sizes.



2) Dioxin and furan levels in MWF muscle tissue decreased markedly between 1990 and 1992. Since 1992, it is believed that the changes in contaminant levels are due mainly to upgrades in pulp mills located along the Fraser River, continued flushing of sediments, and declining levels in fish food organisms.

### **Acknowledgments**

The authors would like to acknowledge the assistance of Rob Dolighan, Fisheries Branch, Williams Lake, B.C., who ran the electroshocker boat; and also BC Environment staff who assisted with the field work.

### <u>References</u>

(1) Mah, F.T.S., D.D. MacDonald, S.W. Sheehan, T.M. Tuominen and D. Valiela. 1989. Dioxins and furans in sediment and fish from the vicinity of ten inland pulp mills in British Columbia. Water Quality Branch, Inland Waters Conservation and Protection, Pacific and Yukon Region, Environment Canada, Vancouver, B.C.

(2) Dwerynchuk, L.W., T.G. Boivin, and G.S. Bruce. 1993. Fraser and Thompson Rivers dioxin/furan trend monitoring program 1992. Final report. Prepared for: Northwood Pulp and Timber Ltd., Cariboo Pulp and Paper Company, and Weyerhaeuser Canada Ltd. Hatfield Consultants Ltd. West Vancouver, B.C. November 1993.

(3) Derksen, G. and G. Mitchell. (in prep). Characterization of physical and chemical attributes of Fraser River suspended solids - 1990 and 1991. Environment Canada, Environmental Protection, Pacific and Yukon Region.

(4) Sekela, M., R. Brewer, C. Baldazzi, and G. Moyle. 1995. Change in contaminant concentration in Fraser River suspended sediments and water during the onset of freshet (Marguerite - 1993). Environment Canada, Environmental Conservation Branch, Pacific and Yukon Region.

(5) Owens, J.W., S.M. Swanson, and D.A. Birkholz. 1994. Bioaccumulation of 2,3,7,8-Tetrachlorodibenzo-p-dioxin, 2,3,7,8-Tetrachlorodibenzofuran and extractable organic chlorine at a bleached kraft mill site in a northern Canadian river system. Env. Tox. Chem. 13(2): 343-354.

(6) Liebe, R., P. Cobban, B. Holms, J. Parchomchuk, T. Tripp, and J. Van Oostdam. 1994. Dioxins and furans in Columbia River Mountain Whitefish, 1993. BC Environment, Water Quality Branch, Victoria.

(7) Ministry of Environment, Lands and Parks. 1994. B.C.'s Pulp Mills: Effluent Status Report. Industrial Waste and Hazardous Contaminants Branch, Victoria, B.C.

(8) Mellor, C., J. Van Oostdam, and N. Zirnhelt. (in prep.). 2,3,7,8-TCDD, 2,3,7,8-TCDF and Polychlorinated Biphenyls (PCBs) Concentrations in Mountain whitefish (*Prosopium williamsoni*) and Largescale sucker (*Catostomus macrocheilus*) in the Fraser River, 1994. BC Environment, Environmental Protection, Williams Lake, BC.

(9) Holms, B. Personal communication, 1995. Freshwater Programs Unit, Monitoring and Reporting Section, BC Environment, Victoria.