Dioxin and Furan Concentrations in Fraser River Suspended Sediment

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1. Introduction

The Fraser River is an internationally renowned river, with an abundance and diversity of natural resources that rivals almost any other river in the world. The Fraser River is Canada's third largest river (1375 km) draining approximately one quarter (234,000 km^3) of the province of British Columbia.

Pulp and paper mills represent one of the major contaminant sources affecting the state of the aquatic environment in the Fraser River, as they contribute the largest proportion of industrial effluents discharged to the upper basin[1]. There are five pulp mills located on the upper Fraser River. These include three bleached kraft pulp mills located at Prince George and one bleached kraft pulp mill and one chemi-thermo-mechanical pulp at Quesnel.

Water-quality issues regarding pulp and paper mills have become increasingly important. In 1989, Mah *et al.*[2] showed that dioxins and furans were accumulating in bed sediment and fish collected downstream of the Fraser River mills. Sampling conducted by Merriman[3], showed elevated levels of these contaminants in suspended sediment collected downstream of a pulp mill on the Rainy River in northern Ontario. A more recent study[4] conducted in the Wapiti-Smoky River system in Alberta concluded that the environmental transport of dioxins and furans in that riverine system occurred predominately in the suspended sediments. In 1990, Derksen and Mitchell[5] found dioxins and furans in suspended sediment collected downstream of the Fraser River mills.

In 1991, federal and provincial legislation was passed requiring Fraser River Basin bleached kraft pulp mills to make process changes in order to reduce emissions of dioxins, furans and other organochlorine compounds. These regulations resulted in the introduction of pulp mill technology that modified the previous bleaching method which used 100% molecular chlorine to one that uses 40 - 100% chlorine dioxide substitution.

The objectives of this study were i) to determine if abatement measures introduced in 1991 to reduce dioxin and furan levels in mill effluent have been effective in reducing or eliminating these contaminants in the Fraser River receiving environment and ii) to determine levels of dioxins and furans in the receiving environment of the Fraser River under different flow conditions.

2. Methods

Sampling was conducted at four locations on the Fraser River during the fall low flow and winter (under ice) periods (Figure 1). Fall sampling dates included October 1992, November 1993 and November 1994, while the winter sampling was conducted in February 1993. Samples were collected at the following sites: i) 18 km upstream of all five of the Fraser River pulp mills at Shelley, ii) 59 km downstream of the Prince George pulp mills at Woodpecker, iii) 65 km downstream of the Quesnel mills (and the Prince George mills) at Marguerite, and iv) 450 km downstream of Marguerite at Yale.

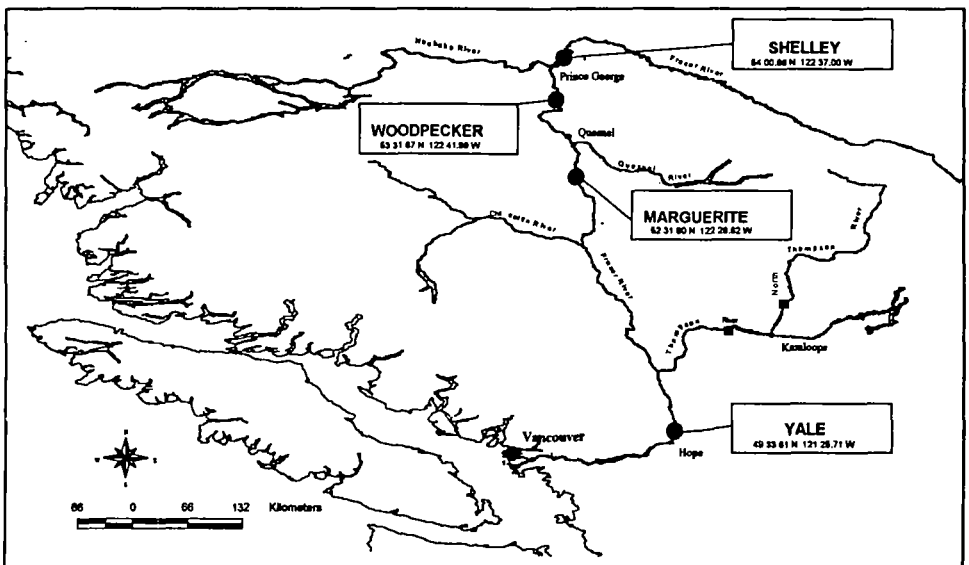

Figure 1 Suspended Sediment Sampling Sites in the Fraser River

All sampling equipment was made of stainless steel or Teflon and was heat treated (350°C) or solvent washed prior to use. Suspended sediment samples were collected using a Westfalia Separator model KA-2-06-175 continuous flow centrifuge. Sample water was pumped from the river and delivered to the centrifuge using stainless steel encased Teflon tubing. For a detailed description of the operation of the Westfalia centrifuge refer to Horowitz *et al.*[6] Except for February 1993, the centrifuge was operated at 4 L/min, as this flow velocity was found to be ideal for efficient recovery of suspended sediment (90-99%) and because loss of particles is restricted to those < 1 μm in diameter[7]. Due to the low suspended sediment concentrations in February 1993, the centrifuge was operated at 5.5 L/min in order to collect sufficient sample for analyses. Sampling periods ranged from a maximum of 81.50 hours in February 1993 to a minimum of 6.75 hours in October 1992. Once sufficient sample water was clarified, the centrifuge was stopped and the sediments were removed on site in a mobile field laboratory. The samples were placed into Teflon jars, weighed and than frozen (-20°C).

All dioxin and furan analyses were conducted by AXYS Analytical Laboratories, Sidney, British

Columbia, using gas chromatograghy with high resolution mass spectrometry.

3. Results and Discussion

Figure 2 presents the concentrations of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF) in suspended sediment measured at the Fraser River sites from 1992 to 1994. Also shown are the levels measured in 1990 by Derksen and Mitchell[5], prior to the 1991 abatement measures implemented by the pulp mills. From 1990 to 1994, the concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF downstream of the Fraser River mills were reduced by 92 and 97 percent, respectively.

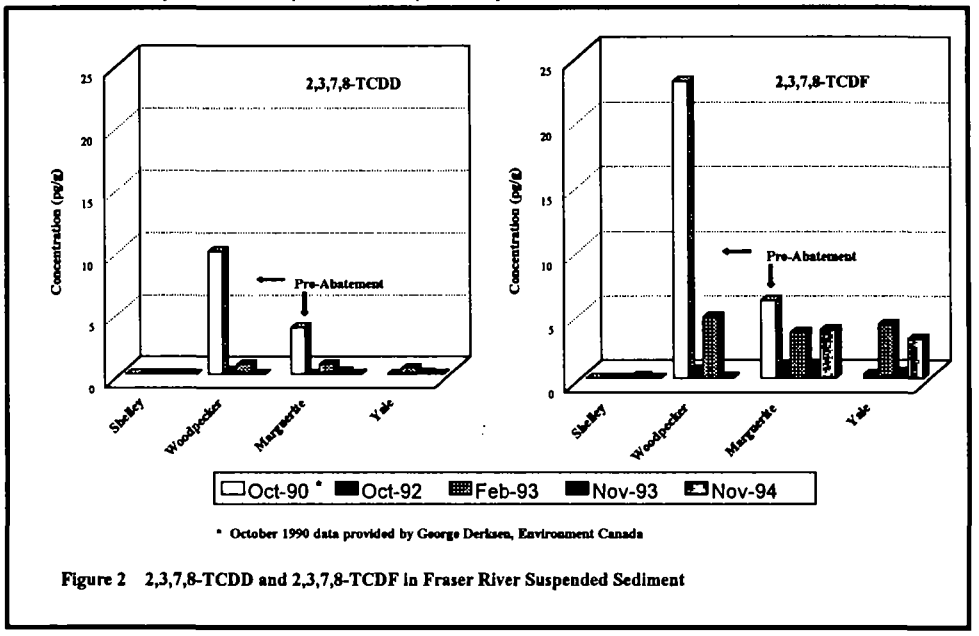

Figure 2 2,3,7,8-TCDD and 2,3,7,8-TCDF in Fraser River Suspended Sediment

For all sampling periods, dioxin and furan concentrations in suspended sediment measured downstream of the pulp mills were higher than those measured at the upstream reference site Shelley (Table 1). However, detectable levels of dioxins and furans (mainly hexachlorodibenzo-para-dioxin, heptachlorodibenzo-para-dioxin and octachlorodibenzo-para-dioxin) were found at all sites, including Shelley. According to Czuczwa and Hites[8], the most likely source of the higher chlorinated dioxin and furan congeners is combustion.

In this study the highest concentrations of dioxins and furans were measured during the low flow periods in February 1993 and November 1994. This is likely the result of both an increase in the concentration of pulp mill effluent (as a result of lower river flow) and a decrease in background suspended sediment concentration in the river. During this period (typically November through March), effluent concentrations in the Fraser River can reach an average of 1% v/v of river water[9] and suspended sediment concentrations can decrease to below 5 mg/L[10]. This increase in

contaminant concentration in the suspended sediment under low flow conditions was observed at all downstream locations.

Table 1 Dioxin and Furan Concentrations Measured in Suspended Sediment Samples Collected from the Fraser River (October 1992 - November 1994)

Sampling Site:	Shelley				Woodpecker			Marguerite				Yale			
Sample Date:	Oct. 1992	Feb. 1993	Nov. 1993	Nov. 1994	Oct. 1992	Feb. 1993	Nov. 1993	Oct. 1992	Feb. 1993	Nov. 1993	Nov. 1994	Oct. 1992	Feb. 1993	Nov. 1993	Nov. 1994
Dioxins (ppt/g)															
Total T4CDD	ND(0.3)	0.6	0.6	0.5	ND(0.2)	1.6	0.6	ND(0.2)	3.7	1.9	5	ND(0.2)	1.3	1.2	3
2,3,7,8 T4CDD	ND(0.3)	ND(0.1)	ND(0.1)	ND(0.3)	0.3	0.8	ND(0.1)	ND(0.2)	0.8	0.2	ND(3.0)	ND(0.2)	0.5	0.1	ND(0.6)
Total P5CDD	ND(0.4)	ND(0.2)	0.9	ND(0.3)	ND(0.2)	ND(0.1)	ND(0.2)	ND(0.4)	0.8	1.7	1.4	ND(0.2)	0.3	0.4	ND(0.7)
Total H6CDD	ND(0.6)	3.3	12.8	2.7	2.6	13	2.9	7	23	10	21.5	1.4	9.5	5.6	14
Total H7CDD	7.6	16	49.3	17	ND(0.9)	29.5	10	23	36	36	89.5	16	31	16	44
O8CDD	27.5	72	160	81	47	125	44	85	170	110	465	79.2	130	65	225
Furans (ppt/g)															
Total T4CDF	ND(0.2)	ND(0.1)		ND(0.3)	1	9.3	0.4	1.9	7.3	3.1	5.8	0.2	6.3	1.3	6.3
2,3,7,8-T4CDF	ND(0.2)	ND(0.1)	0.2	ND(0.3)	0.7	4.8	0.1	0.9	3.6	1.1	3.8	0.3	4.2	0.5	3.1
Total P5CDF	ND(0.4)	ND(0.2)	5.8	ND(0.3)	ND(0.2)	0.3	ND(0.2)	ND(0.2)	0.3	1.1	2.5	0.1	0.2	0.6	0.9
Total H6CDF	ND(0.4)	1.2	28.5	1.9	ND(0.3)	1.2	1.8	2.3	0.8	3.5	2.7	0.7	2.2	1.6	1.9
Total H7CDF	2.2	7.1	46	2.3	ND(0.4)	4.8	6.3	6.2	2.3	7.6	6.1	2.2	6.9	4.9	5.1
O8CDF	2.2	3.4	12	ND(3.0)	2.4	5.8	2.6	8	2.3	3.8	3.8	3	8	2.6	6.1

ND denotes below the indicated detection limit.

For all sampling periods, the highest concentration of all dioxin congeners were measured at Marguerite. The highest 2,3,7,8-TCDF concentrations were measured in February 1993 at Woodpecker and Yale. The higher 2,3,7,8-TCDF levels measured at Woodpecker are likely the result of this site's relatively close proximity to the Prince George mills. However, the higher 2,3,7,8-TCDF levels measured at Yale (265 km downstream of the nearest pulp mill) are likely the result of an additional loading[11] of this contaminant from a pulp and paper mill located at Kamloops on the Thompson River, which enters the Fraser River upstream of Yale (Figure 1).

4. Conclusions

1) The higher chlorinated dioxin and furan congeners (mainly hexachlorodibenzo-para-dioxin, heptachlorodibenzo-para-dioxin and octachlorodibenzo-para-dioxin) were measured at all sites, including the upstream reference site suggesting the ubiquitous presence of these contaminants in the Fraser river aquatic environment.

2) Dioxins and furans, including 2,3,7,8-TCDD and 2,3,7,8-TCDF, remain detectable in Fraser River suspended sediment collected up to 265 river kilometres downstream of the nearest pulp mill.

3) The levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in Fraser River suspended sediment are lower than levels measured in 1990. This reduction in concentration is likely the result of abatement measures implemented by the pulp mills in 1991.

4) Dioxin and furan levels are highest during the winter low flow period which is likely the result of reduced flow and suspended sediment concentration in the Fraser River at that time.

5. References

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