

## Dioxins and Furans in British Columbia Pulp Mill Effluent, (1987- 1995)

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### 1.0 Introduction

The **Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations (CDFR)** and the **Pulp and Paper Mill Defoamer and Woodchip Regulations (DWR)** promulgated under the authority of the federal **Canadian Environmental Protection Act (CEPA)** regulate chlorinated dioxin and furan discharges from Canadian Pulp and Paper Mills. These regulations became effective in May 1992. The estimated discharges of 2,3,7,8-TCDD (TCDD) and 2,3,7,8-TCDF (TCDF) prior to and after the regulations came into effect are examined in this paper.

### 2.0 Federal Regulatory Framework

**CEPA** is an Act designed to "protect Human Health and the Environment" and gives both the federal Minister of the Environment and Minister of Health responsibilities for the assessment of toxic chemicals in Canada. Assessment work undertaken by both departments determined that dioxins and furans are toxic substances as defined under **CEPA**.

The **CDFR** apply to mills that use a chlorine bleaching process and require mill operators to monitor the concentrations of dioxins and furans in the final effluent. The concentration in final effluents must be less than the defined limit of 15 parts per quadrillion (ppq) for TCDD and 50 ppq for TCDF. All B.C. mills applied for and received an exemption until Jan. 1, 1994 as provide for in Section 4.2 of the regulation .

The **DWR** prohibits the manufacture, import, offer for sale, sale or use of defoamers which contain more than 10 parts per billion (ppb) of dibenzo-para-dioxin (DBD) and/or 40 ppb of dibenzofuran (DBF). This is to prevent the formation of chlorinated dioxins and furans in a pulp or paper mill which uses a chlorine bleaching process. The **DWR** further prohibits the import, offer for sale or sale of woodchips that have been made from wood that has been treated with polychlorinated phenols (PCP) for use in any pulp or paper mill in Canada. This is to prevent contamination by dioxins or furans.

## 4.0 Calculation of Loading Estimates

Pre-regulatory effluent concentrations of TCDD and TCDF were obtained with the co-operation of the data managers of the 17 mills regulated under the CDFR. Effluent data generated prior to 1990 is a mixture of high resolution and low resolution gas chromatography/mass spectroscopy (GC/MS) information and may not meet the federal regulatory quality assurance program. The arithmetic mean was calculated where there was more than one sample collected in a month. The SFDRS is not yet operational therefore an EXCEL spreadsheet was created to estimate the effluent loading data for TCDD/TCDF. All the monthly concentration means were entered into the EXCEL spreadsheet which was then copied to retain the original data. The monthly mean was used to estimate TCDD/TCDF concentrations prior to chlorine substitution programs (in general this was from 1987 to 1989). If there were no measured values prior to chlorine substitution the value was calculated using the slope of the existing data extrapolated back to the date when substitution was initiated.

Concentrations of TCDD/TCDF showed significant declines after chlorine substitution programs were initiated and linear regression analysis was applied to the concentration data beginning with the earliest data after chlorine replacement was initiated. The earliest data point became the Y-intercept. Missing monthly concentrations were calculated by interpolating from the y-intercept forwards (or backwards) in time using the calculated y-intercept value and the slope. The calculated values were inserted into the second EXCEL file for months where there was no data. Monthly loadings were calculated using the arithmetic mean of the monthly effluent flow rate times the (real or calculated) TCDD/TCDF concentrations. These loadings are summarized in Table 2, Figure 3 and Figure 4 and supersede the values reported by Environment Canada in 1994<sup>(1,2)</sup>.

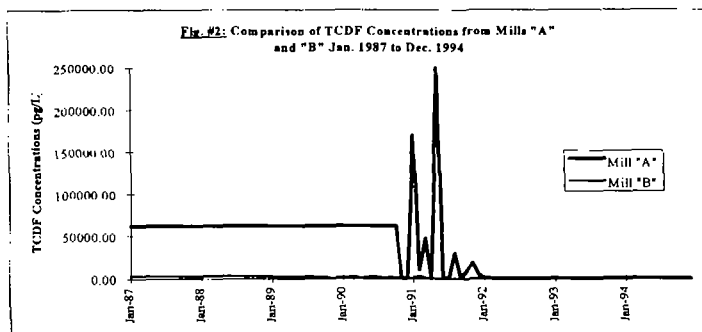
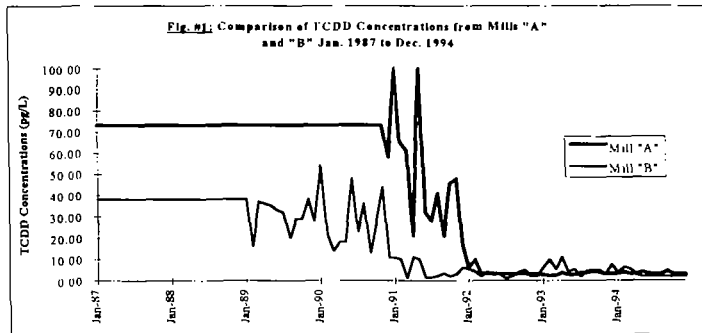
**Table 2: Estimated Daily Discharge of TCDD and TCDF in Final Effluent from British Columbia Pulp and Paper Mills. (1987 - 1995)**

Year *	No. of Data Pts	TCDD All Mills mg/d	TCDD Fraser Basin Mills mg/d	TCDF All Mills mg/d	TCDF Fraser Basin mg/d
1987	4	163	57	8,867	703
1988	6	163	57	9,427	692
1989	33	161	63	8,390	602
1990	85	86	37	6,399	392
1991	161	54	28	13,692	196
1992	131	17	3.4	151	15.5
1993	147	9.9	1.6	105	22
1994	152	5.3**	1.1**	51	15.5
1995	12	4.2**	1.1**	29	4.1
% Reduction 1987-1995		97%	97%	99.6%	98%

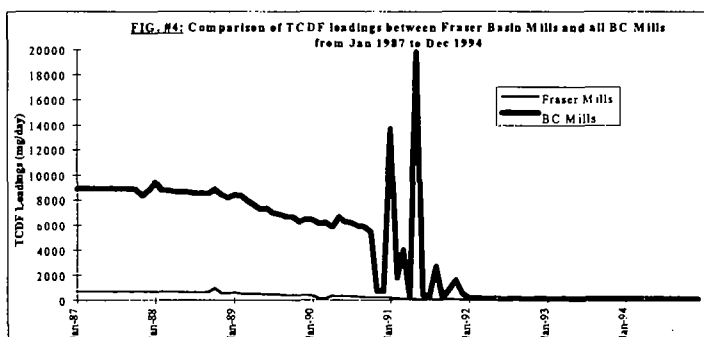
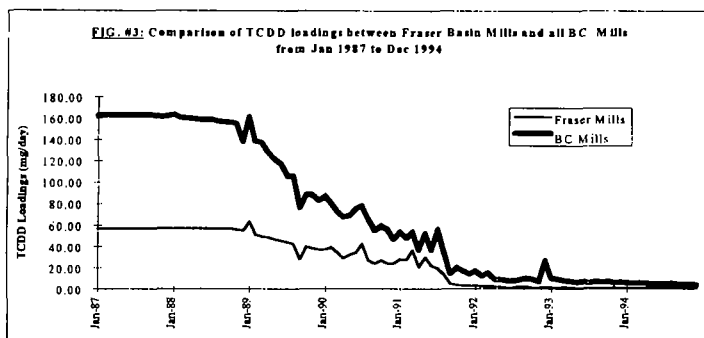
\*Loading value at January each year, \*\*In 1994/95, most TCDD concentrations were reported nondetectable at a limit of 2.0 picograms/litre (pg/L). The detection limit was used as the reported value.

5.0 Trends in the Effluent Concentrations and Loading for TCDD and TCDF.

Figures #1 and #2 show the range in responses of TCDD/TCDF concentrations in final effluent after the mills initiate chlorine substitution programs. Mill "A" is virtually a step function after the mill implemented 80% chlorine substitution in a single process change. Mill "B" is a more typical concentration profile where incremental changes to an average of 90% chlorine substitution occurred over a 4 year period.



Figures #3 and #4 compare the trends in monthly loadings for TCDD/TCDF which indicate that the primary reductions occurred between January 1990 and January 1991. Post January 1991 data suggest that fine tuning of the mills chlorine substitution, brown stock washing and process stages, allowed 14 of the 17 mills to achieve full compliance with the federal concentration limits before January 1, 1994.



## 6.0) Conclusion

Pre-regulatory discharges of TCDD and TCDF are estimated to be 163 mg/day and 9,427 mg/day respectively in 1987. This is approximately 5.6 and 18 times higher respectively than previously reported.<sup>(1,2)</sup> Since 1987, the B.C. pulp and paper mills have reduced the discharge of TCDD and TCDF by more than 97% and 99.6% respectively.

### References and Acknowledgements

- 1) Krahn, P. K., Gee, J., Jardine, S., "Compliance Ratings of British Columbia Pulp and Paper Mills with Respect to Federal Regulations", Proceedings, Canadian Pulp and Paper Association, 1994 Western Technical Conference, Jasper Alberta.
- 2) Krahn, P. K., "Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations - CEPA", "Section 6.0, Compliance Status Summary Report, British Columbia, Fiscal 1993-1994", Environment Canada Regional Program Report 94-04.

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**Compliance Status.** The **CDFR** applies to seventeen mills which use chlorine bleaching and the **DWR** applies to all 26 mills in B.C. The Fraser River is a major focus of a federal initiative and 4 mills that discharge into the river are regulated by the **CDFR**. As early as 1987, the B.C. mills initiated aggressive technical changes to comply with the regulations. (Table 1)

**Table 1: Technical Changes undertaken at B.C. Pulp and Paper Mills to comply with Federal Regulations.**

1987	Self regulated banning of chlorophenate contaminated wood chips
1988	Chlorine dioxide substitution program begins at some mills
1988	Identification of Dioxin and Furan precursors in defoamers begin.
1989	30% to 50% Chlorine Dioxide substitution begins at some mills
1989	Some mills begin the change to water-based defoamers.
1990	Atmospheric diffusion washer installed at one mill
1990	Some mills begin O <sub>2</sub> delignification and change bleaching sequences
1991	Many mills begin complete substitution of chlorine
1991	Improve brown stock washing
1992	Most mills chlorine substitution programs are complete
1993	Some mills begin dredging of treatment lagoons to remove sludge
1993	Incinerator fly ash identified as a source of TCDF at some mills.
1994	Most mills complete contaminated sludge isolation/removal
1995	All 17 mills achieve compliance with the federal dioxin regulations

All mills are in compliance with the **DWR** and there were no recorded instances involving the use of PCP contaminated wood chips or DBD/DBF contaminated defoamers since May of 1992.

In 1994, there were 18 exceedances of the 50 ppq limit for TCDF at 5 B.C. mills and no reported exceedances of the 15 ppq limit for TCDD. Most mills reporting exceedances did not have elevated concentrations of dioxins or furans in the bleach plant effluent. It was determined that cross contamination of residual sludges which were being removed from treatment lagoons and salt water laden hog fuel were the cause of some of the furan exceedances. All mills reporting exceedances were issued "Warning Letters" and as of March 1995 are in full compliance with the regulations.

### 3.0 Data Management

Environment Canada is currently leading the design and development of a computerized Single Format Data Reporting System (SFDRS) which will connect all 26 B.C. Pulp and Paper mills to the federal Envirodat system and the B.C. provincial SEAM system. Final effluent data (including dioxins and furans) will be available through the federal electronic Bulletin Board System (BBS) which is scheduled to be complete in 1996.