

## INTERLABORATORY VARIABILITY ON THE DETERMINATION OF PCDD/PCDF IN PULP AND PAPER MILL EFFLUENTS

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### INTRODUCTION

In support of the Canadian Environmental Protection Act (CEPA) regulations, Environment Canada has developed a reference method<sup>1</sup> to identify and quantify the release of PCDD/PCDF in pulp and paper mill effluents<sup>2</sup>. Under the regulation, effluents must not contain a measurable concentration of either 2,3,7,8-TCDD or 2,3,7,8-TCDF. Other PCDD/PCDF species including all 2,3,7,8-substituted congeners must be monitored. Results of an interlaboratory study on 2,3,7,8-TCDD and 2,3,7,8-TCDF were reported at the Dioxin '92 conference<sup>3</sup>. This paper focuses on the determination of and the magnitude of interlaboratory variability for all 2,3,7,8-substituted PCDD/PCDF congeners.

### STUDY DESIGN

Procedures for selecting mill samples, preparation and distribution of samples have been described<sup>3</sup>. A total of ten laboratories were invited to participate in this study. Each laboratory received 8 one-liter sub-samples of each effluent, and a set of calibration standards, spiking solutions and recovery standards. Effluent I was fortified with native congeners. Laboratories were requested to adhere to the critical elements specified in the reference method while allowing users an ample degree of flexibility in sample preparation methods.

### RESULTS AND DISCUSSION

Upon receipt and examination of the analytical results from ten participating Canadian/American laboratories, it was decided that data from three laboratories did not meet performance specifications<sup>1</sup> and were excluded from this study. Analytical performance for 2,3,7,8-TCDD and 2,3,7,8-TCDF were summarized in the previous paper<sup>3</sup>. Similar criteria were used to screen data for the remaining 2,3,7,8-substituted PCDD/PCDF.

By applying both Grubbs and Dixon statistical tests at the 5% significant level to detect within-laboratory outliers in reported concentration values, decisions were made to reject a number of PCDD/PCDF results submitted by different laboratories. In total, about 20 data points in Effluent I and 15 data points in Effluent II were considered as outliers and were not

taken into consideration for further calculations. Standard deviations of the analyses for PCDD/PCDF in each sample were then calculated for each laboratory.

Table 1 and 2 present the interlaboratory comparisons of PCDD/PCDF concentrations for effluent I and effluent II. Correlation between the mean and median values for most congeners in effluent I is quite good however the values reported for H<sub>7</sub>CDD and 1234789 H<sub>7</sub>CDF suggest that some extreme values are included in the data. Effluent II comparisons reveal the same phenomenon for H<sub>7</sub>CDD and OCDF at detection limit values as well as for OCDD at a higher concentration. The variation encountered for other congeners cannot be adequately assessed due to small concentration and degrees of freedom. Comparison of the laboratory mean with the interlab median for effluent I indicated that most laboratories are within  $1 \pm 0.3$  for all PCDD/PCDF species. Notable exceptions include the results for TCDF reported by Labs C and G and results for OCDF reported by Labs B and D. The high ratio for some target compounds in effluent II is not surprising in view of the small degrees of freedom. A notable exception is the variation reported for OCDD at a median value of 36 pg.

In Table 3, the calculated interlaboratory standard deviations are presented. The high values for 1234678-H<sub>7</sub>CDD, OCDD, and OCDF in effluent I are indicative of the poor precision involved in determining the reported concentrations. The precision is also poor for the same dioxin congeners at a lower concentration as noted in effluent II. The high % relative pooled standard deviation values of most of the other congeners in effluent II are the result of the inability of most laboratories to quantitate at such low concentrations. These are included for illustration purposes only. Such results should not be viewed with statistical significance.

Interlab average detection-limit measurements are given in Table 4. The reported detection limit values show a wide range among the laboratories (eg. 0.4 to 5.7 pg/L for TCDF and 0.4 to 24 pg/L for OCDD). The high variation of reported detection limit values is likely due to a combination of factors which might include the differences in instrument sensitivity, injection system, column bleed and the cleanup and quantitation methods used by each laboratory.

In conclusion, despite the common standards and stringent performance criteria adhered to by all laboratories, significant variations in concentrations were reported for several 2,3,7,8-substituted congeners. The interlaboratory variation however, appeared to be better than previous interlaboratory studies<sup>5,6</sup> due to the aforementioned factors.

## REFERENCE

1. Environment Canada, Report EPS 1/RM/19, February, 1992.
2. Department of Environment, Canada Gazette, Part I, December 14, 1991 *Pulp and Paper Mill Effluent, Chlorinated Dioxins and Furans Regulations*.
3. Chiu, C., et al, *Dioxin' 92*, vol 8, sec.13, p 27, 1992.
4. Keith, L.H., et al, *Analytical Chemistry*, vol 55, No 14, P.2217, December, 1982.
5. Chiu, C., et al, *Chemosphere*, vol 19, p 7-12, 1989
6. Tashiro, C., et al, *Chemosphere*, vol 20, p 1319-1324, 1990.

**Table 1. Interlab Medians and Interlab Means for Effluent I and II.**

	Interlab Median(pg/L)		Interlab Mean(pg/L)	
	I	II	I	II
2378-TCDD	20.86	4.07	21.54	4.58
12378-P5CDD	36.57	3.43	37.31	3.43
123478-H6CDD	39.69	*	39.42	*
123678-H6CDD	40.89	1.00	41.26	1.00
123789-H6CDD	116.06	*	112.01	*
1234678-H7CDD	58.27	6.63	66.78	11.83
OCDD	571.25	36.00	579.69	54.10
2378-TCDF	32.43	29.00	35.50	28.58
12378-P5CDF	39.35	2.15	40.10	2.76
23478-P5CDF	42.39	1.57	42.04	2.73
123478-H6CDF	39.18	1.90	39.72	2.18
123678-H6CDF	227.75	0.95	221.71	0.95
234678-H6CDF	38.38	1.46	36.82	1.46
123789-H6CDF	39.75	1.00	38.45	1.00
1234678-H7CDF	227.50	2.60	231.00	16.23
1234789-H7CDF	40.81	*	31.79	*
OCDF	80.88	6.36	84.36	10.66

I: Effluent I; II: Effluent II; \*: All measurements were reported as "Not Detected".

**Table 2. Comparison of Lab Mean/Interlab Median Ratios.**

	Lab Mean / Interlab Median													
	B		C		D		E		F		G		H	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
2378-TCDD	0.85	0.96	0.81	0.86	0.95	0.62	1.00	1.63	1.26	1.00	1.31	1.77	1.05	1.03
12378-P5CDD	0.93	*	0.94	*	0.96	*	1.00	*	1.11	*	1.13	1.56	1.07	0.44
23478-H6CDD	0.86	*	0.94	*	1.13	*	0.90	*	1.10	*	1.02	*	1.00	*
23678-H6CDD	0.96	*	0.84	*	1.23	*	1.02	*	1.02	*	0.99	1.00	1.00	*
23789-H6CDD	1.07	*	0.81	*	1.00	*	1.01	*	1.02	*	0.88	*	0.97	*
34678-H7CDD	2.15	6.21	0.99	1.10	0.96	0.80	0.97	1.79	1.14	1.00	1.11	0.80	1.01	0.80
OCDD	1.29	3.86	0.89	1.00	1.03	0.48	1.00	1.50	0.97	0.89	1.07	2.12	0.85	0.67
2378-TCDF	1.07	1.00	1.39	1.17	0.99	0.77	0.91	0.93	1.01	0.96	1.32	1.02	0.99	1.05
12378-P5CDF	1.01	*	0.97	1.33	0.99	0.52	0.93	*	1.18	*	1.08	2.63	1.00	0.67
23478-P5CDF	0.89	*	1.14	3.27	1.01	0.94	0.87	*	0.99	*	1.05	*	1.00	1.00
123478-H6CDF	1.03	*	1.02	1.84	1.00	*	0.95	*	1.11	*	0.98	1.00	0.99	0.61
123678-H6CDF	1.01	*	0.95	1.05	0.88	*	1.04	*	1.03	*	0.92	*	1.00	0.95
234678-H6CDF	1.01	*	1.00	0.68	1.10	*	0.93	*	0.88	*	0.77	1.32	1.02	*
123789-H6CDF	1.03	*	0.93	*	0.64	*	1.03	*	1.00	*	0.99	1.00	1.16	*
234678-H7CDF	1.04	17.12	0.95	1.00	1.04	*	1.00	*	1.08	*	1.00	0.62	0.99	*
234789-H7CDF	0.97	*	0.92	*	0.52	*	1.04	*	1.03	*	1.00	*	1.00	*
OCDF	1.69	4.35	0.95	*	0.62	*	0.99	1.52	1.00	*	1.02	0.48	1.02	0.35

**Table 3. Pooled Interlaboratory Standard Deviations.**

	No. of Labs		Pooled Standard Deviation(pg/L)		Degree of Freedom		% Relative Standard Deviations	
	I	II	I	II	I	II	I	II
2378-TCDD	7	7	1.67	1.04	46	46	7.8	22.8
12378-P5CDD	7	2	2.86	1.45	44	6	7.7	42.2
123478-H6CDD	7	*	4.14	*	47	*	10.5	*
123678-H6CDD	7	1	2.69	0.00	44	1	6.5	0.0
123789-H6CDD	7	*	8.75	*	48	*	7.8	*
1234678-H7CDD	7	7	24.10	10.14	45	40	35.0	85.7
OCDD	7	7	149.35	43.27	48	46	25.8	80.0
2378-TCDF	7	7	4.93	2.46	48	48	13.9	8.6
12378-P5CDF	7	4	2.66	1.64	44	18	6.6	59.3
23478-P5CDF	7	3	3.76	1.19	45	10	8.9	69.8
123478-H6CDF	7	3	4.18	1.28	47	6	10.5	58.7
123678-H6CDF	7	2	22.62	0.20	47	2	10.2	21.1
234678-H6CDF	7	2	6.74	0.47	47	4	18.3	32.2
123789-H6CDF	7	1	4.59	0.00	48	1	11.9	0.0
1234678-H7CDF	7	3	15.99	13.58	47	6	6.9	83.6
1234789-H7CDF	7	*	3.49	*	47	*	10.4	*
OCDF	7	4	28.90	8.87	49	10	34.3	83.2

\*: not detected.

**Table 4. Interlaboratory Detection Limits.**

	Interlab Ave. D.L.		Maximum		Minimum		Pooled S.D.	
	I	II	I	II	I	II	I	II
TCDD	2.78	2.82	11.64	10.30	0.40	0.49	1.48	1.55
P5CDD	3.09	3.50	7.09	8.13	0.50	0.48	1.59	2.22
H6CDD	3.78	3.66	6.00	6.88	0.80	0.83	1.23	1.39
H7CDD	4.90	4.79	9.23	11.78	1.40	0.70	1.33	2.31
OCDD	5.73	7.63	12.88	24.38	1.00	0.40	2.07	3.11
TCDF	1.37	2.42	3.30	5.68	0.50	0.40	0.51	0.88
P5CDF	2.23	4.72	4.76	17.86	0.30	0.66	0.81	3.47
H6CDF	2.94	3.53	5.15	7.28	0.70	0.71	1.09	1.86
H7CDF	3.69	7.78	8.21	22.00	1.19	0.88	1.17	2.90
OCDF	5.32	5.72	12.33	17.25	1.80	1.54	1.72	2.51

All values are in pg/L.