A Summary of Data Reflective of U.S. Pulp and Paper Industry Progress In Reducing the TCDD/TCDF Content of Effluents, Pulps and Wastewater Treatment Sludges

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I Introduction

The first industry-wide effort to quantify TCDD/F formation from pulp bleaching in the U.S., the joint Industry/EPA '104 Mill Study' was carried out using samples collected over the early part of 1988. Since that time, pulp and paper companies in the U.S. have expended a great deal of effort to reduce the generation and release of TCDD/F. Over the ensuing period, NCASI has conducted several data solicitations in an effort to document the reductions that have taken place as a result of these efforts. Recently, the industry undertook a sampling program with the objective of generating a data set which could be directly compared to the results of the original '104 Mill Study'. This report summarizes the results of the earlier solicitations and those of the "1992 Industry-Wide Dioxin Profile". Data from a 1993 update to the 1992 Profile are also discussed.

All of the earlier solicitations and the 1992/3 Profile requested only data on concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. Information available to NCASI indicates that these two isomers constitute the vast majority of total 'toxic equivalents' (TEQ's) present in the three export vectors even when results are near the detection limit.

All data gathering activities have requested data on the TCDD/F content of pulps, sludges and effluents. This report summarizes the findings relative to TCDD/F in all three vectors as of the end of 1993. The '104 Mill Study' data discussed in this report were taken from the data base used to compile both the NCASI and EPA reports on the '104 Mill Study'.

The "1992 Industry-Wide Dioxin Profile" and the 1993 update specifically requested that companies generate data using the protocols used in the '104 Mill Study'. Instructions and protocol information was supplied to the participating companies along with the data request. Companies were encouraged to use laboratories and analytical methods used in their 'routine' monitoring programs since (a) commercial and company laboratories are *now well experienced* with dioxin analytical procedures and (b) data thus generated would be comparable to compliance monitoring data.

Cumulative frequency distributions (truncated to emphasize the lower concentrations) for TCDD in effluent, sludge and pulps are shown in Figures 1 through 3 respectively. Figures 1 and 3 exhibit a 'plateau' (at 5 ppq and 0.5 ppt respectively). These plateaus reflect the 'Minimum Levels' of U.S. EPA's Method 1613A, which many mills direct their contract laboratories to use. Under this method, the laboratory reports only that the sample contained 'less than' the 'Minimum Level' for non-detects. Where such results were reported to NCASI during these surveys, they are plotted as one half the detection limit. Where results are plotted at concentrations below the 'Minimum Levels' the results were reported in terms of sample-specific detection limits and plotted at one half of that limit.

Similar plots have been developed for the TCDF data and they show similar trends. In general, the plots show that as time has progressed, most measurements in all vectors have approached the limits of measurement, with only a few mills remaining above this level. Private communications to NCASI have indicated that these few mills are still in the process of implementing process changes.

B. Mass TCDD/F content of export vectors

The various data sets, adjusted as described in Section II, were used to calculate the mass TCDD/F content of all three export vectors (effluent, sludge and pulp) for each mill. For the '104 Mill Study', mass discharge rates from that study data were used in the calculation; for the 1990 and 1991 results new mass flow data were used if supplied; otherwise, the '104 Mill Study' flow data was used. New mass discharge data were solicited in the 1992/3 Profile. 'Mass discharge' means flow rate in mgd for effluent, production in air dried tons per day for pulp and generation rate in dry tons per day for sludge.

The mass content of each export vector was then summed across all mills. Results for each vector are summarized in Table 2 and discussed below.

1. Effluent

For the '104 Mill Study' effluent data set, a total content of 551 milligrams per day (mg/d) of 2,3,7,8-TCDD and 4620 mg/d of 2,3,7,8-TCDF were calculated as the total of all 104 mills. This amounts to a TEQ effluent content (for these two isomers) of approximately 977 mg/d. Similarly, for 1993, the effluent release rates were estimated at 55 mg/d for TCDD, 218 mg/d for TCDF and 76 mg/d for TEQ. The various content levels and the reductions they represent from '104 Mill Study' levels are summarized in Table 2. By 1993, the industry had accomplished a 92% reduction (on a TEQ basis) from '104 Mill Study' effluent levels.

II Methods used in handling data

A. '104 Mill Study' data

As noted above, data from the '104 Mill Study' referenced in this report were taken directly from the data base used in compiling the EPA and NCASI reports on the study. Additional data from five mills which volunteered for the earlier 'Five Mill Screening Study' (and were therefore not repeated in the '104 Mill Study') were also included in the data base used in this report. Data from a sixth mill, which voluntarily carried out measurements similar to those reported in the 'Five Mill Screening Study' were also added to the data base. In summary, data from all 104 bleached chemical pulp mills which existed at the time of the '104 Mill Study' have been used in preparing this report.

Where analytical results from the '104 Mill Study' were reported as 'non-detect' for either TCDD or TCDF, one half the reported limit of detection was used in calculations and plots. This practice was also used in the analysis of data from the other solicitations and the 1992/3 Profile.

B. The 1992/3 Industry-Wide Dioxin Profile

Data handling for the 1992/3 Profile were essentially the same as those described in the fore-going section. Where a mill did not provide data in response to either the 1992 Profile or the 1993 update, it was assumed to be still performing at the levels found in the '104 Mill Study'.

III Results

A. 1992 Industry Wide Dioxin Profile Results

Table 1 presents summary statistics from the 1992/3 data sets along with comparable statistics from the '104 Mill Study' for comparison. Maximum, 90th percentile, Mean and Median statistics are all self explanatory and show the dramatic changes that have been accomplished in five years. Rows labeled "% < ML" indicate the number of TCDD measurements in each data set that are less than the nominal 'Minimum Level' of EPA's proposed Method 1613A (10 ppq for effluents and 1 ppt for sludges and pulps).

Similarly, rows labeled "% < 10*ML" indicate the number of TCDF measurements that are less than 10 times the 'Minimum Level'. Ten times the 'Minimum Level' was chosen because the toxicity equivalence factor for 2,3,7,8-TCDF is one tenth that of 2,3,7,8-TCDD. The statistic shown reflects the number of TCDF measurements that are below the 'toxic equivalent' of a barely measurable level of TCDD.

2. Sludge

For the '104 Mill Study' sludge data set, a total content of 577 milligrams per day (mg/d) of 2,3,7,8-TCDD and 3615 mg/d of 2,3,7,8-TCDF were calculated as the total of all 104 mills. This amounts to a TEQ effluent content (for these two isomers) of 939 mg/d. Similarly, for 1993, the sludge release rates were estimated at 68 mg/d for TCDD, 330 mg/d for TCDF and 101 mg/d for TEQ. By 1993, the industry had accomplished an 89% reduction (on a TEQ basis) from '104 Mill Study' sludge levels.

3. Pulp

For the '104 Mill Study' pulp data set, a total content of 718 milligrams per day (mg/d) of 2,3,7,8-TCDD and 6660 mg/d of 2,3,7,8-TCDF were calculated as the total of all 104 mills. This amounts to a TEQ effluent content (for these two isomers) of 1384 mg/d. Similarly, for 1993 the pulp release rates were estimated at 64 mg/d for TCDD, 302 mg/d for TCDF and 94 mg/d for TEQ. By 1993, the industry had accomplished an 93% reduction (on a TEQ basis) from '104 Mill Study' pulp levels.

IV Conclusions

The data bases compiled as the basis for this report demonstrate that the U.S. industry's efforts to reduce TCDD/F formation in pulp bleaching have been extremely successful. As of the end of 1993, industry export vector TCDD/F contents have been reduced by over ninety percent on a TEQ basis.

Only a small percentage of mills are characterized by effluent concentrations above the nominal detection limit ('minimum level') for TCDD. In sludges, most mills are characterized by TCDD concentrations less than 10 ppt. The new data show that 90% of currently produced pulps have less than 2 ppt TCDD. Most of the data above these ranges are from mills that either have not supplied new data to NCASI or are still in the process of completing bleach plant modifications.

As of the 1993 data base, the total TCDD/F content of the export vectors from pulp bleaching is estimated at no more than 3 ounces per year on a TEQ basis. For various reasons, this estimate is considered somewhat conservative and actual releases from pulp bleaching are probably lower than the estimate.

Table 1

DATA SET STATISTICAL PARAMETERS

	EFFLUENT		SLUDGE		PULP	
	TCDD	TCDF	TCDD	TCDF	TCDD	TCDF
	ppq	ppq	ppt	ppt	ppt	ppt
104 MILL STUDY	[Data from 104 Mills Included]					
MAX	640	8400	1390	17100	116	2620
90th %	110	900	161	1300	22	157
MEAN	51	443	72	607	8.7	91.5
MEDIAN	21	68	16	78	4.4	18
% < ML	38	-	na	-	19	-
% < 10*ML	-	63	-	22	-	39
1992/3 DATA	[97 Mills Responding]					
MAX	80	510	133	735	10	323
90th %	6	33	31	98	10	159
MEAN	5	23	11	51	0.9	6.1
MEDIAN	ND(5)	3	2	9	0.5	0.6
% < ML	93	-	19	-	80	-
% < 10*ML	-	97	-	51	-	57

Table 2

SUMMARY OF SOLICITATION RESPONSES
104 Mill through 1993

	104 Mill			1992			1993		
	TCDD	TCDF	TEQ	TCDD	TCDF	TEQ	TCDD	TCDF	TEQ
		mg/d			mg/d			mg/d	
EFFL.	551	4260	977	62	282	90	55	218	76
PULP	718	6660	1384	69	353	104	64	302	94
SLUDGE	577	3615	939	95	336	129	68	330	101
SUM	1846	14535	3300	226	972	323	187	849	272

PERCENT REDUCTION FROM 104 MILL LEVELS

	104 Mill			1992			1993		
	TCDD	TCDF	TEQ	TCDD	TCDF	TEQ	TCDD	TCDF	TEQ
EFFL.				89	93	91	90	95	92
PULP				90	95	92	91	95	93
SLUDGE				83	91	86	88	91	89
TOTAL				88	93	90	90	94	92

Fig. 1 EFFLUENT DATA – 2,3,7,8-TCDD

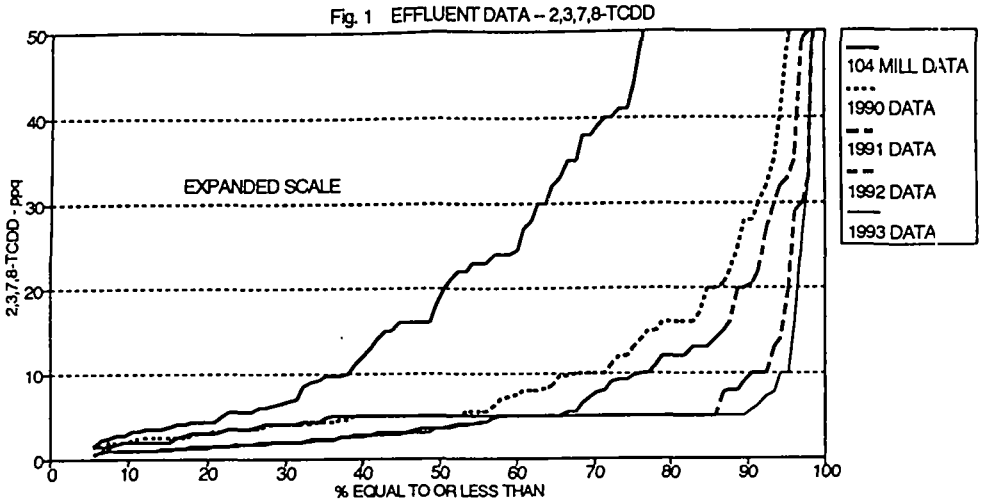

Fig. 2 SLUDGE DATA – 2,3,7,8-TCDD

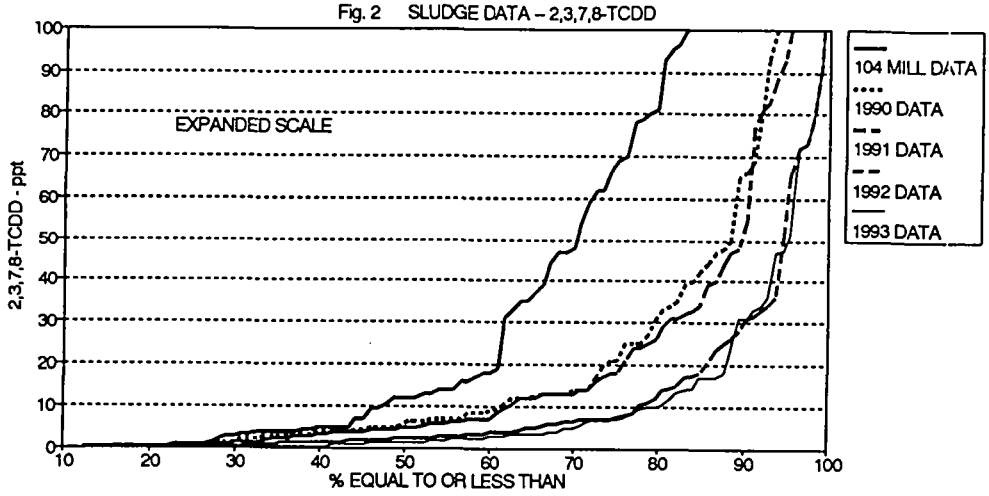

Fig. 3 PULP DATA – 2,3,7,8-TCDD