

FINDINGS OF US EPA/PAPER INDUSTRY
COOPERATIVE DIOXIN STUDY - THE 104 MILL STUDY

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ABSTRACT

Sampling and analysis in 1988 of effluents, sludge, and pulps from United States bleached chemical pulp producers for chlorinated dibenzo-dioxins and-furans (CDD/F) showed total releases and vector partitioning to effluent, sludge, and pulps varied significantly among mills. Some operating parameters were observed to influence CDD/F generation. Analysis of duplicate sample results showed good analytical reproducibility. Low detection levels (10 ppq in effluent) were reported in the large majority of non-detected measurements. Since the data were collected, many producers have altered operating conditions in order to attempt to reduce CDD/F levels.

INTRODUCTION AND BACKGROUND

In 1988, representatives of the American pulp and paper industry and the United States Environmental Protection Agency (US EPA) agreed to conduct a joint monitoring study of pulp mills for the purpose of determining levels, and factors that control levels, of chlorinated dibenzo-dioxins and-furans (CDD/F) that are released to the environment in the manufacture of wood pulp. All 104 mills in the country that produced chlorine-bleached chemical pulp on 173 bleach lines carefully followed a structured sampling program and a prescribed analytical protocol for measuring concentrations of 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8 tetra-chlorodibenzo furan (TCDF) in three chief export vectors of each mill. Sampled export vectors included two outflows from each mill's wastewater treatment system (effluent and sludge) and mill pulp from each bleach line (the highest brightness grade of pulp produced). Preliminary analytical results were reported at Dioxin 89. Data now reported are more complete and have been analyzed statistically which provides additional insight into detection limits, variability, partitioning among export vectors, and mass outputs. The effect of bleaching variables on the generation and release of TCDD/TCDF also were evaluated. Summary

statistics of concentrations of TCDD/TCDF in pulp, effluent and sludge are provided in Tables 1, 2 and 3, respectively for mills that produce hardwood kraft, softwood kraft and sulfite pulps. Note: For all data presented Mean, Median, 90th Percentile, Maximum are based on detected samples only.

Table 1: Summary Statistics of 2378-TCDD/F Concentrations in Pulp

	No. Detect Samples	No. ND Samples	Mean (ng/kg)	Median (ng/kg)	90th Pcntle (ng/kg)	Maximum (ng/kg)
Hardwood Kraft Pulps						
2378-TCDD	62	12	7.5	4.0	17	56
2378-TCDF	72	2	56	17	107	661
Softwood Kraft Pulps						
2378-TCDD	98	6	12	7.6	27	116
2378-TCDF	99	3	118	26	185	2620
Sulfite Pulps						
2378-TCDD	4	14	6.2	3.95	15	15
2378-TCDF	14	5	89.4	6.35	429	449

Table 2: Summary Statistics of 2378-TCDD/F Concentrations in Effluent

	No. Detect Samples	No. ND Samples	Mean (ng/kg)	Median (ng/kg)	90th Pcntle (ng/kg)	Maximum (ng/kg)
Kraft Mills						
2378-TCDD	90	17	0.076	0.035	0.19	0.64
2378-TCDF	104	7	0.48	0.10	1.1	8.4
Sulfite Mills						
2378-TCDD	12	13	0.013	0.012	0.023	0.023
2378-TCDF	21	4	0.11	0.035	0.38	0.84

Table 3: Summary Statistics of 2378-TCDD/F Concentrations in Sludge

	No. Detect Samples	No. ND Samples	Mean (ng/kg)	Median (ng/kg)	90th Pcntle (ng/kg)	Maximum (ng/kg)
Kraft Mills						
2378-TCDD	94	3	101	39	203	1,390
2378-TCDF	97	0	796	161	1728	17,100
Sulfite Mills						
2378-TCDD	18	1	13	4.7	48	58
2378-TCDF	16	0	99	63	350	584

DETECTION AND VARIABILITY

TCDD was detected in 85 percent of all samples analyzed and TCDF was detected in 96 percent of all samples. In at least one export vector of every mill, TCDD/TCDF was detected. Detection limits achieved in the analyses ranged from 0.1 to 4.9 ng/kg for pulps, and from 0.003 to 0.017 ng/kg for wastewater effluents. For TCDD, 83 percent of detection limits in effluent were less than or equal to 10 ppq; for TCDF, 100 percent of detection limits were at or below 10 ppq. This demonstrates that analytical techniques of laboratories utilized are generally capable of achieving detection levels of 10 ppq for effluent measurement.

Approximately 30 percent of all samples were either field or laboratory duplicates. Sample correlations by export vector between pairs of duplicate measurements were quite high exceeding 0.95 in most cases. Thus the proportion of total variability in measured concentrations of TCDD/TCDF that could be attributed to field sampling protocol or analytical technique was relatively small.

Mass output values were calculated by combining concentration data with the corresponding output volume for each export vector by mill. Total daily U.S. mass output from all mills were 1.8×10^{-3} kg TCDD/day and 1.5×10^{-2} kg TCDF/day. Average exports per mill were 2.3×10^{-5} kg TCDD/day and 2.2×10^{-4} kg TCDF/day. Significantly more TCDD/TCDF was released at kraft mills than at sulfite mills. Mills using activated sludge (ACT) wastewater treatment systems released less effluent-based TCDD/TCDF on the average but significantly more sludge-based TCDD/TCDF than mills using aerated stabilization basin (ASB) systems.

PARTITIONING

Relative amounts of TCDD/TCDF partitioned to pulp, sludge or effluent vectors were highly variable from mill to mill. For example, some mills partitioned less than 10 percent total TCDD/TCDF mass to effluent but in other mills effluent accounted for greater than 80 percent of total export.

CORRELATION WITH TREATMENT AND BLEACHING PARAMETERS

Correlations between total suspended solids (TSS) and TCDD/TCDF mass outputs from kraft mills were fairly weak, suggesting that TSS levels were only partially predictive of TCDD/TCDF found in sludge and effluents. For kraft mills using only ACT treatments, higher TSS levels were associated with lower sludge-based TCDD/TCDF exports but higher effluent-based TCDD/TCDF exports.

Greater chlorine usage was found to be associated with higher release levels of TCDD/TCDF. The same relationship held for the chlorine multiple in C-

stage bleaching although the association was somewhat less positive. Increased levels of chlorine dioxide substitution were correlated with slight reductions in TCDD/TCDF releases. There was, however, a large amount of variability in these data and as a consequence the correlations were weak. Oxygen delignification resulted in lower levels of TCDD/TCDF releases. However, mills that used the oxygen delignification process generally also used high levels of chlorine dioxide substitution so the relative effects of either technology separately were not discernible.

POSTSCRIPT

Subsequent to completion of the 104 Mill Study, many pulp producers have changed processing operations in an effort to reduce TCDD/TCDF formation. About 45 mills have forwarded to EPA additional TCDD/TCDF analytical results for one or more of the export vectors under the changed operating conditions. The Agency is currently evaluating these analytical results.

REFERENCES

1. Kirk-Othmer. 1982. Encyclopedia of Chemical Technology - Volume 19. John Wiley and Sons.
2. Shreve and Brink. 1977. Chemical Process Industries - Fourth Edition. McGraw-Hill.
3. United States Environmental Protection Agency-Office of Water. 1989 (August). Preliminary Data Summary for the Pulp, Paper and Paperboard Point Source Category. EPA 440/1-89-025.
4. United States Environmental Protection Agency-Office of Water Regulations and Standards. 1987 (February). The National Dioxin Study - Tiers 3,5,6, and 7. EPA 440/4-87-003.