INTRA- AND INTER-LABORATORY VARIABILITY IN PAPER INDUSTRY TCDD/TCDF ANALYSIS

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ABSTRACT

Studies were conducted to quantify variability for pulp industry wastewater effluent, pulp and sludge analyses. Intralaboratory variability studies indicated that there is a potential for greater between batch variability in results than for within a batch. Intralaboratory relative standard deviations for replicate analyses ranged from 6% to 60%. Interlaboratory studies, using standard reference materials showed relative standard deviations from 15% to 35%. There appeared to be little dependance of variability on concentration, suggesting matrix effects were very important. Analysis of reference standards indicated that 13% to 17% variability can be attributed to differences in calibration standards.

INTRODUCTION

There has been a great deal of research conducted in the US over the past few years attempting to better understand and reduce the formation of PCDDs/PCDFs formed in the bleaching process. These studies have been of a screening or research nature. The analytical work for those studies has involved a number of different laboratories and procedures. Within a given study, the adverse effect of differences in analytical procedures or laboratory performance can be mitigated by restricting the analyses to one laboratory. However, it would be desirable to use the emerging data collectively to provide a broader database to investigate, for instance, the significance of a given process parameter. The intra- and inter-laboratory variability must be understood and taken into consideration to better define the limitations in how the data from different studies might be used. Also, if regulatory agencies intend to use all available information for the purpose of developing guidelines for regulations, it is essential that the intra- and inter-laboratory variability be fully understood. This paper summarizes a compilation of available information concerning this variability.

RESULTS AND DISCUSSION

Wastewater Treatment Plant Effluent

Intralaboratory Variability Intralaboratory variability has been investigated at a single laboratory using the NCASI analytical procedure (NCASI, 1989). The information available allows comparison of within batch and between batch variability as well as a comparison of method variability on different effluent sources. The information is summarized in Table 1 (additional studies in progress when Abstract submitted).

Table 1. Intralaboratory Effluent Variability for the NCASI Procedure

		TCDD			TCDF	
	Mean	Relative Std. Dev.		Mean	Relative Std. Dev.	
	Concentration	Within		Concentration	Within	
Source	ppq	Batch	Overall	ppq	Batch	Overall
A	37	39%	56%	99	22%	22%
B	81	7%	7%	333	6%	11%
C	6.5	22%	60%	14	8%	60%

There clearly exists greater overall variability relative to that which occurs within batches. Also, the relative standard deviation varies significantly between different sample sources suggesting significant matrix effects. The average overall relative standard deviation was 41% for TCDD and 31% for TCDF.

Interlaboratory Variability Interlaboratory variability has been evaluated through the use of standard reference effluent samples in comparison studies. A number of different effluent/wastewater samples have been distributed to different US laboratories for analysis. In general, the laboratories were allowed to use the analytical procedures which they would normally use for pulp and paper industry clients. Thus, there are between 3 to 6 different procedures represented in the data set. The results are summarized in Table 2.

Table 2. Interlaboratory Wastewater Analysis Comparison Summary

			TCDD		TCDF	
		Number of	Mean		Mean	
		Participating	Concentration		Concentration	
Sample	Matrix	Laboratories	ppq	RSD	ppq	RSD
P-1C	C Filtrate	4	48	42	110	43
P-1E	E Filtrate	4	3540	12	13000	16
P-1UE	Untreated Eff	4	329	26	905	38
P-1EF	Effluent	4	97	46	460	16
ILC-1	Effluent	4	116	22	1780	20
ILC-2	Effluent	4	23	81	86	4
ILC-3	Effluent	4	ND	NA	16	99
ILC-4	Effluent	4	101	12	1060	10
ILC-6	Effluent	3	36	26	202	10
ILC-7	Effluent	4	7	50	29	26
ILC-9	Effluent	6	75	37	396	23

The average interlaboratory relative standard deviation was 35% and 28% for TCDD and TCDF, respectively. In general, there was a trend towards better comparability at higher concentrations but this was not universally true. Thus, it appears that individual matrix effects may be more significant than analyte concentration.

Sludge and Pulp

Intralaboratory Variability Intralaboratory variability for pulp and waste treatment plant sludge were also tested for the NCASI procedure (NCASI, 1989). Samples were submitted in separate batches to allow comparison of within batch and between batch precision. The results are summarized in Table 3.

Table 3. Intralaboratory Variability for Pulp and Sludge for the NCASI Procedure

		TCDD			TCDF	
	Mean	Relative Std. Dev.		Mean	Relative Std. Dev.	
	Concentration	Within		Concentration	Within	
Sample	ppt	Batch	Overall	ppt	Batch	Overall
Pulp	5.3	8%	18%	100	4%	6%
Sludge	43	16%	18%	223	12%	14%

SUMMARY

The data indicate there is greater intralaboratory wastewater analysis variability from batch to batch than within one set of samples. This was less significant for pulps and there were essentially no differences for sludges.

The average interlaboratory relative standard deviations for the three sample groups ranged from 15% to 38% with the sludge matrix showing the least variability. The ranges within each sample group were generally larger. The interlaboratory variability was similar to, or slightly larger than, the overall intralaboratory variability. In most cases, only one set of interlaboratory comparison samples were submitted to the laboratories. Therefore, since batch to batch precision may be greater than between batch precision, the interlaboratory comparability data may underestimate overall variability.

There appeared to be no significant dependance of the interlaboratory variability on concentration. This suggests that individual sample matrix effects may overshadow concentration dependant differences in precision.

The variability associated with the analysis of a common analytical standard indicated that a large portion of the interlaboratory variability can be attributed to differences in calibration standards.

A number of different sources of analytical variability have been identified and estimated. This variability makes it difficult to compare results obtained from one laboratory to another and, in some cases, from one laboratory at one time to another. In mill trials or in survey studies where relative comparisons are to be made, the effect of those sources of variability on the study can be minimized by using a single laboratory for the entire study. If multiple laboratories are necessary to complete the study, use of common analytical standards and analytical procedure should help to minimize variability. Interlaboratory splits of samples should also be included to provide quantitative information on intercomparibility of data.

The analytical variability observed in these studies clearly indicates that the procedures used by the different laboratories are not presently suitable for compliance monitoring in a regulatory control program. Additional method development will be required to develop analytical procedures suitable for compliance/non-compliance testing.

REFERENCES

NCASI (1989). NCASI Procedures for the Preparation and Isomer Specific Analysis of Pulp and Paper Industry Samples for 2378-TCDD and 2378-TCDF. NCASI Technical Bulletin No. 551, NCASI, New York, N.Y.

Interlaboratory Variability Information on interlaboratory variability for pulp and sludge analyses was obtained through the use of standard reference materials. The reference materials were collected, dried, blended and mixed by NCASI to insure homogeneity. Since this preprocessing is normally conducted by the laboratory performing the analysis, the resulting interlaboratory comparison represents only variability associated with sample analyses. The laboratories were allowed to use the analytical procedures which they would normally use for pulp and paper industry clients so there are between 4 to 6 different procedures represented in the data set. Both internal process pulps and final bleached pulps (collected off the last washer) were included in the interlaboratory comparisons. One secondary sludge and nine combined dewatered sludges were used in the evaluation. The results are summarized in Table 4.

Table 4. Interlaboratory Variability for Pulp and Sludge Analyses

Sample	Matrix	Number of Participating Laboratories	TCDD Mean Concentration ppt	RSD	TCDF Mean Concentration ppt	RSD
PI303	C Pulp	4	18	15%	67	24%
PI304	E Pulp	4	11	19%	37	75%
ILC1	Bleached Pulp	4	5.6	68%	39	67%
ILC2	Bleached Pulp	4	3.6	12%	4.7	69%
ILC3	Bleached Pulp	4	8.5	35%	9.1	17%
ILC4	Bleached Pulp	4	4.5	23%	53	26%
ILC6	Bleached Pulp	4	12	16%	77	10%
ILC7	Bleached Pulp	4	2.2	9%	6.3	7%
ILC9	Bleached Pulp	6	16	24%	95	15%
PI305	Sludge	4	79	26%	249	76%
PI306	Sec. Sludge	4	337	17%	2150	44%
ILC1	Sludge	4	127	13%	1810	18%
ILC2	Sludge	4	29	5%	163	11%
ILC3	Sludge	4	49	8%	68	4%
ILC4	Sludge	4	20	12%	175	18%
ILC5	Sludge	4	9.6	20%	54	16%
ILC6	Sludge	4	154	15%	650	35%
ILC7	Sludge	4	13	20%	46	10%
ILC9	Sludge	6	142	12%	822	14%

The average pulp interlaboratory relative standard deviation was 25% for TCDD and 34% for TCDF. There was no apparent correlation of the relative variability and concentration. The interlaboratory variability was similar to the intralaboratory variability for TCDD but was significantly higher for TCDF.

The average sludge interlaboratory relative standard deviation was 15% for TCDD and 25% for TCDF. These averages are virtually identical to the overall intralaboratory variability observed for the NCASI analytical procedure. There was no apparent correlation with relative variability and concentration.

Analytical Standards

A limited study was undertaken to determine the significance of analytical standards to the overall variability of analytical results. In this study, NCASI distributed TCDD and TCDF standards to 4 different laboratories. The laboratories were instructed to add their normal internal standards and to analyze and report the concentrations of the native analytes. The relative standard deviation for the reported TCDD results was 13%. The TCDF relative standard deviation was 17%. Thus, a significant portion of the variability observed for each of the three sample groupings could be simply due to differences in analytical standards.

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