

SOLVED AND REMAINING PCDD AND PCDF PROBLEMS IN THE PULP INDUSTRY

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ABSTRACT

Modern technology, including washing, pre-oxygen bleaching and partly substituting chlorine for chlorine dioxide has highly reduced the levels of tetraCDFs and tetraCDDs in bleached pulp from Sweden. The levels of higher chlorinated congeners in recycled pulp as well as in tall oil and tall resin is another problem that has been identified.

INTRODUCTION

During DIOXIN '86 in Fukuoka, Japan Rappe *et al.* reported that samples of crab hepatopancreas and sediments collected outside a pulp mill on the Swedish west coast had elevated levels of PCDDs and PCDFs as compared to background samples (1). For 2,3,7,8-tetraCDF and 2,3,7,8-tetraCDD the levels were at least ten times higher in the samples collected outside the mills than in the background samples. This was the first report in the open scientific literature of a connection between pulp mill effluents and PCDDs and PCDFs. This observation has been followed by numerous investigations on levels of PCDDs and PCDFs in various products and emissions from the pulp industry in Europe, USA and Canada.

After some initial controversy it is now generally accepted that bleaching of pulp using free chlorine can generate PCDDs and PCDFs. A typical "bleaching pattern" has been identified including 2,3,7,8-tetraCDD, 2,3,7,8- and 1,2,7,8-tetraCDF (1,2). It has also been shown that the contamination levels can be highly reduced by using less free chlorine and also partly substituting the free chlorine by chlorine dioxide as well as prebleaching with oxygen (3,4,5).

During DIOXIN '89 in Tornoto Rappe *et al.* (6) reported on very low levels of the typical "bleaching pattern" in two samples of bleached pulp from Sweden. In the same report the results from the analysis of two samples of recycled pulp were also presented indicating higher levels in this type of products, especially for the higher chlorinated congeners not included in the "bleaching pattern".

In this presentation we report on additional analyses showing the same trend for bleached pulp as well as recycled pulp. We also report on the analysis of tall oil and tall resin, two other by-products from the pulp industry.

EXPERIMENTAL

The analytical method for pulp samples has been reported earlier (3,6). An extensive validation study showed good accuracy and precision also for the higher chlorinated congeners (6). The method includes Soxhlet extraction using ethanol followed by clean-up and the final analyses using HRGC/HRMS (3). The analytical method for tall oil and tall resin is in principle the same and has been described elsewhere (7).

RESULTS AND DISCUSSION

Bleached pulp

During the last 5 years approximately 300 samples of bleached pulp have been analyzed in our laboratory. In all samples we have found 2,3,7,8-tetraCDF at varying levels, in most samples also 2,3,7,8-tetraCDD, normally at levels 7-10 times lower than that of 2,3,7,8-tetraCDF. Most of the samples came from Scandinavia, but samples were also received from producers in Southern Europe, South America and Australia. Both softwood and hardwood samples have been analyzed. Counted as International Toxic Equivalents (I-TEQ), using the I-TEF suggested by US EPA (8), the levels were normally in the range of 1-15 pg/g dry pulp.

During the last 3 years we have analyzed approximately 100 samples of Swedish bleached pulp, where oxygen prebleaching has been used as well as smaller amounts of chlorine and partial substitution of chlorine for chlorine dioxide. These samples were primarily softwood pulp. The typical levels for these pulp samples are 0.1 - 1.0 pg I-TEQ/g dry pulp. This indicates that technology now exists by which the dioxin problem can be highly reduced. No visible migration of PCDDs and PCDFs could be seen from milk cartons containing less than 1 pg I-TEQ/g dry pulp (9).

Recycled pulp

In most countries the use of recycled pulp is highly encouraged due to various reasons including conservation of resources. In Sweden a substantial fraction of the toilet paper now consists of recycled pulp. Within the Swedish Dioxin Survey two samples of recycled pulp were collected at the mills, analyzed and reported at DIOXIN '89 in Toronto (7). Counted as I-TEQ these samples contained around 4 pg/g dry pulp, but interestingly enough the normal "bleaching pattern" was quite low, while the levels of octaCDD and octaCDF were in the range 100-600 pg/g dry pulp.

We have now analyzed three samples of consumers' products from Sweden and USA based on recycled pulp. Two of the samples were toilet paper and one was a facial tissue. We have also analyzed one sample of the recollected paper from the same Swedish mill, which is the starting material for the recycled pulp. The results are given in Table 1.

The observed levels are lower than in the pulp samples reported on earlier (7) although the same general trend can be seen as earlier; the congener profile is dominated by the hepta- and octachlorinated congeners. The levels in the recycled paper were 3 times higher than in the finished recycled pulp indicating no new source during the process in this factory. The sample of deinking sludge had higher levels than the pulp (7). The major portion of the recycled pulp consists of newspapers, journals and other printed material. For that reason we have analyzed one sample of black ink used at a local Swedish newspaper. The results of this analysis are also given in Table 1.

Tall oil and tall resin

Crude tall oil is separated from the black liquor and distilled to produce tall oil, tall resin and pitch as a residue. One sample of tall oil and tall resin has been analyzed and reported to have levels of I-TEQ in the range of 9 - 200 pg/g (10). If these samples are representative of the production of tall oil and tall resin in Sweden, a substantial part of the total amount of PCDDs and PCDFs produced during the pulping and bleaching can be found in these products.

Tall oil and tall resin are widely used in many industrial branches including the production of liquid and soft soap, paint and additives for printing, glue and adhesives.

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Table 1. Levels of PCDDs and PCDFs found in products based on recycled pulp and printing ink.

	Toilet paper USA	Facial tissue USA	Recycled paper Sweden	Toilet paper Sweden	Printing ink Sweden
2378/46/47/48/1249/79-TCDF	2.9	3.4	5.0	1.5	2.7
Sum TCDF	3.7	4.3	6.7	2.1	5.2
2378-TCDD	0.23	0.29	0.19	0.08	0.10
Sum TCDD	<1 *	<2 *	<1 *	<2 *	1.1
12378-PeCDF	0.07	0.10	0.17	0.04	2.7
23478/12679/12369-PeCDF	0.09	0.08	0.13	0.05	1.0
Sum PeCDF	0.53	0.45	0.90	0.40	19
12378-PeCDD	<0.03	<0.03	0.12	0.03	0.39
Sum PeCDD	0.04	-	<2 *	1.5	13
123478/123467-HxCDF	0.06	0.10	0.12	0.10	1.8
123678-HxCDF	0.03	0.05	0.03	<0.02	0.33
234678-HxCDF	0.03	0.05	0.05	0.08	0.37
123789-HxCDF	<0.04	<0.04	<0.04	<0.03	<0.1
Sum HxCDF	0.42	0.73	2.7	0.90	6.6
123478-HxCDD	<0.04	<0.04	<0.05	<0.04	0.52
123678-HxCDD	0.27	0.35	4.6	1.2	17
123789/123467-HxCDD	0.11	0.14	2.5	0.58	8.9
Sum HxCDD	1.8	2.2	31	8.7	130
1234678-HpCDF	1.0	1.1	24	4.1	3.5
1234789-HpCDF	<0.04	<0.04	<0.05	<0.03	0.86
Sum HpCDF	3.0	3.6	44	7.8	7.7
1234678-HpCDD	3.9	8.8	25	25	35
Sum HpCDD	7.2	17	52	37	72
OCDF	4.4	5.4	94	21	92
OCDD	65	110	170	91	72
Nordic Equivalents	0.73	0.95	2.3	0.87	4.5

< X * = less than, due to possible contribution from the background.