

Trace analysis of PCDDs and PCDFs in unbleached and bleached pulp samples

Christoffer Rappe and Nadja Wågman

Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden

ABSTRACT

Samples from two Swedish pulp mills were collected and analyzed for PCDDs and PCDFs using an analytical method with a detection limit of 0.03 pg/g pulp. The samples included brownstock, elemental chlorine free (ECF) and total chlorine free (TCF) pulp. We were not able to identify any 2,3,7,8-tetra CDD in any of the samples at this detection limit. On the other side, 2,3,7,8-tetra CDF could be identified in all samples, the incremental amount was approximately 0.2 pg/g corresponding to 0.02 pg TEQ/g.

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 mill 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, Canada and Japan.

The industry has responded to the problem, and now the formation of PCDDs and PCDFs during the pulp bleaching is minimized or totally eliminated. The introduced changes in the process are

- a) use of chlorine dioxide instead of free chlorine in the bleaching
- b) use of defoamers not contaminated by unchlorinated DBF or DBD
- c) extended cooking procedures
- d) more careful washings
- e) oxygen prebleaching
- f) avoid pentachlorophenol-contaminated wood shavings

BLEACHING WITH CHLORINE DIOXIDE

At DIOXIN '88 in Umeå, Sweden Axegård and Renberg (2) reported on a study concerning the formation of 2,3,7,8-tetraCDD and 2,3,7,8-tetraCDF during laboratory bleaching using varying chlorine dioxide substitution and chlorine multiple. The bleaching sequence was (C+D)ED, and the effect of decreased chlorine multiple was compensated by varying the amount of chlorine dioxide in the third state. At a detection limit of 1 pg/g pulp neither 2,3,7,8 tetra CDD or 2,3,7,8 tetra CDF was produced when bleaching with 100% chlorine dioxide (2).

In 1989 Berry *et al.* published a study on the same subject (3). They studied the formation of 2,3,7,8-tetraCDD and CDF at a fixed Kappa factor of 0.21 where the chlorine dioxide substitution varied between 0 - 100%. The authors reported no detectable concentration of 2,3,7,8 tetraCDD at any substitution level with a detection level of 2 pg/g and the concentrations of 2,3,7,8-tetraCDF decreased with increasing substitution of chlorine dioxide. The amount of 2,3,7,8-tetraCDF was reported to be below the detection level (2 pg/g) at 70% and 100% substitution (3).

Chlorine dioxide is primarily an oxidative reagent but it can also undergo various hydrolysis reactions under normal temperature, including the formation of hypochlorous acid and to some small extent also including free chlorine. Consequently bleaching of pulp with chlorine dioxide is not a *totally* elementary chlorine free process, and it cannot be totally excluded that minor amounts of chlorinated by-products are formed in the process. However, very few analytical data on the amount of PCDDs and PCDFs identified in pulp bleached with chlorine dioxide can be found in the open literature.

At our laboratory we now can analyze pulp samples at a detection level which is 20 - 100 times lower than the detection levels in the studies discussed above (2,3). The goal of the present study is to investigate if detectable concentrations of 2,3,7,8-tetraCDD and CDF can be found in pulp samples where the bleaching has been performed using 100% chlorine dioxide using this improved and much more sensitive analytical technique. For comparison we have also analyzed the unbleached brown-stock from the same mills as well as pulp bleached according to the total chlorine free (TCF) technology.

SAMPLES

Duplicate pulp samples were collected at two Swedish pulp mills, A and B. In mill A we collected the unbleached brownstock, pulp bleached using chlorine dioxide (ECF) pulp (C10/D90), as well as pulp bleached with total chlorine free technology (TCF). In mill B we collected the unbleached brownstock as well as the ECF pulp.

EXPERIMENTAL

The samples were cleaned up using a modification of the method described by Swanson (4). The samples were dried on aluminium foil in a fume cupboard for 24-48 hours. To homogenize the samples a mill was used. Prior to extraction, eleven ^{13}C -labelled isomers were added to the samples. These isomers are used for the correction of losses during the clean-up steps. The samples were extracted with toluene for 24 hours. Before evaporation, 50 μl of tetradecane was added and was used as a keeper in the clean-up steps, to avoid losses of PCDFs or PCDDs. After evaporation the samples were cleaned using a column system containing H_2SO_4 - and KOH -silica, with neutral silica between, under and over these silica layers. The samples were placed on the column in traces of n-hexane and extracted with the same solvent. The clean-up continued after evaporation with a basic aluminium column. A first fraction was eluted with n-hexane. A second fraction was eluted with n-hexane/methylenechloride (1 : 1) to a Carbo-pack-C column, which was used for separation of the PCDDs and PCDFs from similar pollutants. This carbon column was further eluted with toluene. After the last step, the volume was adjusted to 35 μl tetradecane and ^{13}C -12378-PeCDF and ^{13}C -1234678-HpCDF were added. These isomers were used for calculation of recovery of the internal standard.

A high resolution gas chromatograph (HRGC) combined with a high resolution mass spectrometer (HRMS) was used for the analysis:

HRGC: HP-5890 equipped with a 60 m J&W DB5 column

HRMS: VG 70-250 S

The quantification was made by relating the peak areas of the sample with the peak areas of a standard solution containing specific amounts of all toxic isomers and of the ^{13}C -isomers. The results were corrected for the recovery of the ^{13}C -labelled isomers. The TCDD-equivalents were calculated from the detected values of the 2378-substituted congeners.

RESULTS

A careful examination of the channels for the tetraCDDs shows that there is no visible sign of any peak for 2,3,7,8-tetraCDD in the ECF-bleached pulp at a detection level of 0.03 $\mu\text{g/g}$ pulp, (Mill A). The situation is the same for the TCF pulp from Mill B as well as for the two brownstocks from Mill A and B and the TCF-pulp from Mill A. A corresponding examination of the channels for the tetraCDFs reveals a somewhat different situation. In the ECF-pulp two isomers can be seen, the 2,3,7,8- and 1,2,7,8-tetraCDFs. These two isomers are considered to be typical for pulp bleaching (1,2,3,4). Lower concentrations of the same isomers can be found in the brownstock as well as the TCF-pulp and the laboratory blanks. The quantitative data is given in Table 1.

CONCLUSIONS

In spite of a very low detection level (0.03 pg/g pulp) we have not been able to find any formation of 2,3,7,8-tetraCDD during pulp bleaching using chlorine dioxide. The amount of 2,3,7,8-tetraCDF is around 0.2 pg/g pulp, corresponding to 0.02 pg TEQ/g pulp. These concentrations are 100 - 1000 times lower than the concentrations reported on by Sullivan using free chlorine (5).

The total world production of bleached pulp is 60×10^6 tonnes. Making the assumption that our results are representative for the industry and that equal amounts of the PCDDs and PCDFs can be found in the pulp and in the effluent, and using the figures given above, the total amount of TEQ formed during pulp bleaching using chlorine dioxide could be calculated to be 2.4 g TEQ/year.

This value should be compared to the emission from other sources. One example could be the emissions from one sintering plant at a steel mill in the Netherlands. According to Bremmer *et al.*, this figure is 24 g TEQ/year (6).

Recently Öberg *et al.* reported on a *de novo* synthesis of PCDDs and PCDFs during composting of garden wastes (7). This observation has been confirmed by Sievers and Schacht (8) who studied composting in Hamburg, Germany. In their study they quantified the amount formed in this natural *de novo* process to be in the range 1-3 pg TEQ/g compost (dry weight). A comparison between composting and pulp bleaching using chlorine dioxide shows that the amount formed during the natural process of composting is approximately 100 times higher than the amount formed during pulp bleaching using chlorine dioxide.

REFERENCES

1. Rappe, C., *et al.*, *Chemosphere*, **16**, 1603 (1987)
2. Axegård, P., and Renberg, L., *Chemosphere*, **19**, 661 (1989)
3. Berry, R.M., Fleming, B.I., Voss, R.H., Luthe, C.E., and Wrist, P.E. *Pulp and Paper Canada*, **90**, T279 (1989)
4. Swanson, S.E., Dioxins in the Bleach Plant. Thesis. University of Umeå, Sweden. 1988.
5. Sullivan, M.J. TAPPI Proceedings 1988 International Pulp Bleaching Conference, p. 91.
6. Bremmer, H.J., Troost, L.M., Kuipers, G., de Koning, J., and Sein, A.A. Emissies van Dioxinen in Nederland. Rapport 770501003, RIVM, Bilthoven, the Netherlands.
7. Öberg, L.G., Wågman, N., Andersson, R., and Rappe, C. *Organohalogen Compounds*, **11**, 297 (1993)
8. Sievers, S., and Schacht, U., *Organohalogen Compounds*, **22**, 48 (1995).

Table 1. Results from the analysis of the pulp samples (pg/g).

TCDF	Mill A									Mill B					
	Brownstock		ECF		Blank	Brownstock		TCF		Blank	Brownstock		ECF		Blank
1278	0.05	0.03	0.26	0.22	0.03	0.04	0.05	0.06	0.06	0.03	0.05	0.04	0.15	0.17	nd
1349, 1267	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	nd	nd
2378, 2346, 1249, 2348, 2347, 1279	0.06	0.07	0.29	0.25	0.05	0.07	0.06	0.08	0.09	0.04	0.06	0.06	0.15	0.14	0.04
2367	nd	nd	nd	nd	nd	0.02	0.02	nd	nd	nd	0.02	0.02	0.03	nd	0.02
TCDD															
1368	nd	nd	nd	nd	nd	0.11	0.11	<0.24	0.15	nd	0.05	nd	nd	nd	nd
1379	nd	nd	nd	nd	nd	0.09	0.14	<0.24	<0.41	nd	0.04	0.02	nd	nd	nd
PeCDF															
12348, 12378	nd	nd	0.14	0.10	nd	nd	nd	nd	nd	nd	nd	nd	0.05	0.05	0.01
23478, 12369, 12679	nd	nd	0.06	0.05	0.02	nd	nd	nd	nd	nd	nd	nd	0.03	0.03	0.02
OCDF	0.14	nd	nd	nd	nd	0.52	nd	nd	nd	nd	nd	nd	0.95	nd	0.09
OCDD	0.16	0.15	0.14	0.23	nd	0.42	0.30	0.31	0.25	nd	0.12	0.18	nd	nd	nd
I-TEQ	0.006	0.007	0.066	0.055	0.015	0.008	0.006	0.008	0.009	0.004	0.006	0.006	0.033	0.032	0.015
	nd-	TCDF	<0.02	HpCDF	<0.10										
		TCDD	<0.03	HpCDD	<0.15										
		PeCDF	<0.03	OCDF	<0.14										
		PeCDD	<0.04	OCDD	<0.14										
		HxCDF	<0.07												
		HxCDD	<0.10												

