

Levels of PCDDs and PCDFs in the Bleached Pulp from Chinese Pulp and Paper industry

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Trace of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are generated as by-products during the bleaching of pulp with chlorine (Rappe et al. 1989; Swanson et al. 1988; Voss et al. 1988). In the last years, some very detail studies in the field of pulp bleaching are carried out (Dimmel et al. 1993; Hrutfiord et al. 1992; Luthe et al. 1994; Luthe 1996; Santl et al. 1994), but the investigations were made only in these mills which use wood or recycled wastepaper for fiber. There is still no report on the levels of PCDDs and PCDFs in pulps that use non-wood plant fibers as raw materials. However, non-wood plant fibers in paper making today in China are dominant. Cereal and rice straws together with reeds account for 60% of raw materials in Chinese pulp and paper industry (Yu 1993). Bleaching of non-wood plant fibers in China usually requires only a single step of hypochlorite bleaching process. In this paper we present the results of PCDDs and PCDFs levels in some bleached pulps which were taken from five paper mills in the north of China.

MATERIALS AND METHODS

Each of the five mills is an integrated bleached kraft pulp and paper mill. Raw materials are pulped using the kraft process, bleached and converted on site into different kind of paper. Bleaching sequences including the following stages: C(chlorine), E(alkaline extraction), H(hypochlorite). Raw materials and bleaching sequences at the five mills are indicated in Table 1.

The analytical method has been published in detail (Swanson et al. 1988). Fifty grams of air-dry samples are spiked with a mixture of eight ^{13}C -labelled PCDD/Fs (Cambridge Isotope Laboratories) prior to their 24 hr

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Table 1. Description of bleached pulp samples

Mill	A	B	C	D	E
Raw material	rice straw	rice straw	cereal straw	reed	wood manufactur- ing residuals
Bleaching process	H	H	H	CEH	H

The sample from Mill D is collected after C-stage bleaching process.

Soxhlet extraction with toluene, following concentration by rotary evaporation. The bulk of the co-extracted organic material is removed by successively passing the extract through the following series of chromatographic columns: acid silica, acid-base silica multilayer, and basic alumina. Just prior to GC-MS analysis, two ^{13}C -labelled recovery standards (Cambridge Isotope Laboratories) are added for the quantification of surrogate recovery. One sample blank is analyzed for every five samples. All analyses are carried out by VG-7070E- HF GC/MS using a 60 m SP-2331 (Supelco) fused-silica column. Quantification of PCDDs and PCDFs is performed in selected-ion monitoring mode. For each congener, two most abundant ions of molecular ion clusters are measured.

RESULTS AND DISCUSSION

The results of the sample analyses which are expressed in pg/g of sample for the toxic 2378-substituted congeners and also in pg/g of TCDD-equivalents using I-TEQ are given in Table 2. The mean recoveries of the samples are in the range from 110 up to 125%.

The content of 2378-TCDD in the pulps from pulp and paper mills in China is higher than that of bleached hardwood and softwood pulps ever reported (Amendols et al. 1989; Kitunen et al. 1989; Rappe et al. 1990; Swanson et al. 1988;). The amounts of PCDFs are significantly low compared to those of PCDDs. A typical 'bleaching pattern' of bleached kraft wood pulps is dominated by 2378-TCDD, 2378-TCDF and 1378-TCDF isomers, but none of TCDF isomer is detected in the pulps in this study. The reason for this may be different genesis of these compounds.

The mechanisms of PCDDs and PCDFs formation during the bleaching of non-wood plant fiber pulps with hypochlorite are also studied. We have explored the possibility that PCDDs and PCDFs may be originated from dibenzo-p-dioxin (DBD), dibenzofuran (DBF) and chlorinated phenols (CPs). Five grams of unbleached non-wood fiber pulp are washed by diluting to 5% consistency with deionized water and injecting 0.1-1.0 ml of DBD,

Table 2. PCDDs and PCDFs in various pulp samples (pg/g dry pulp)

	A	B	C	D	E
2378-T ₄ CDD	20.9	17.2	22.5	15.2	26.1
12378-P ₅ CDD	28.8	35.2	17.9	25.7	21.2
123478-H ₆ CDD	28.9	41.7	18.3	46.3	23.1
123678-H ₆ CDD	35.3	ND	ND	ND	ND
123789-H ₆ CDD	5.1	39.8	10.3	6.2	14.6
1234678-H ₇ CDD	24.5	39.8	10.3	6.2	14.6
OCDD	53.7	111.9	68.9	290.9	40.4
234678-H ₆ CDF	13.2	1.2	ND	6.4	ND
1234678-H ₇ CDF	5.9	4.1	6.0	4.2	25.5
OCDF	9.8	2.0	3.8	69.8	18.9
I-TEQ	43.9	39.6	33.5	33.8	39.5

ND : not detectable (< 1.0 pg/g)

DBF, CPs(100 µg/ml methanol) while stirring. Pulp is then bleached with hypochlorite. Tetra- through octa- congeners of PCDDs and PCDFs analyses are performed as mentioned above. A comparison of the spike data with that of control for PCDDs and PCDFs analysis, no significant differences exist between the two. Hence it may be concluded that DBD, DBF and CPs are not PCDDs and PCDFs precursors during bleaching of non-wood fiber pulps with hypochlorite.

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