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PCDDs and PCDFs in the Wastewater from Chinese Pulp and Paper Industry

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Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs) in emissions from the pulp-bleaching process was characterized by US EPA as the nation's third largest dioxin source (Johnson, 1994). Zheng et al. (1997) reported the levels of PCDDs and PCDFs in the bleached pulp from five Chinese paper mills in the north of China which use non-wood plant fibers as raw materials. Many paper mills in China discharge the bleaching wastewater directly into rivers or lakes without any treatment. The wastewater may contain PCDDs and PCDFs and seriously pollute the environment, In this paper we present the detail results of PCDDs and PCDFs levels in the wastewater of different process stages from one of the biggest pulp and paper mills in the south of China.

MATERIALS AND METHODS

Paper Mill H is an integrated bleached kraft pulp and paper mill which is producing about 70,000 tons paper per year. More than 420,000 tons wastewater was discharged directly into Yangtse River, Cereal and rice straws together with reeds are main raw materials. Bleaching sequences include the following stages: C (chlorine), E (alkaline extraction) and H (hypochlorite). After bleached, the pulp is dispersed by water and calcium carbonate to be converted into various kinds of paper. Waste water generated in this process is called white liquor. Ten liters of each sample were collected from four discharging sites. Table 1 shows the description of the samples together with pH and total organic carbon (TOC).

The samples were accumulated together with suspended particulate matter by 250g XAD resin (Sepulcopak 2, Sepulco Inc.). The resin had been wetted by methanol and washed by deionized water. Prior to the accumulation, each sample was spiked with a mixture of 16 ^{13}C-lablled 2,3,7,8-substituted PCDD/F

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(Cambridge Isotope Laboratories) as surrogate internal standards. The elution agent is 100mL acetone followed by 100mL acetone:toluene (1: 1, v/v). Anhydrous sodium sulfate was used to absorb the residual water. The extracts were evaporated to 2-3 mL. The following clean-up and analytical method has been reported in detail by Wu et al (1998). ^{13}C-1,2,3,4-TCDD (Cambridge Isotope Laboratories) was spiked as recovery internal standard. About 5mL of each sample was taken for TOC analysis on TOC-5000A (Shimadzu Corp.).

Table 1. Description of various wastewater samples

Sampling Sites	C	EH	White liquor	Total effluent
pH	2.5	6.7	6.4	11.0
TOC (mg/L)	279	169	51.8	461

RESULTS AND DISCUSSION

Table 2 shows the concentrations and toxic equivalent quality (TEQ) in pg/L. The mean recoveries are in the range from 70% to 90%.

Counted as TEQ, it is clear that the sample from C stage showed highest levels of PCDDs and PCDFs, followed by that from EH stage and total effluent. White liquor had very low contamination level.

The results from C stage and total effluent correspond to the “bleach pattern” according to Stephen et al (1988). The pattern is dominated by the 2,3,7,8-TCDF and 2,3,7,8-TCDD isomers. High level of OCDF was also found from white liquor, C and EH stages. It corresponds to their latter study from TMP, unbleached sulfite and recycled pulp (Rappe et al, 1990). The reason for this may be different materials and production process, The results are quite different from that reported by Zheng et al (1997). They reported that none of TCDF isomer was detected in the pulps in their study. Sampling sites and analytical methods may be the main reasons because of the similar production process.

Total emission of wastewater from pulp and paper industry in China was about 2 billion tons in 1996 (Jiao, 1997). Similar process accounts for more than 90% for the input in China. So it is estimated that this source contributes about 20 g of TEQ emission per year in China.

Table 2. Results of PCDD/F from various wastewater samples (pg/L)

Congeners	C	EH	White liquor	Total effluent
Total Cl_4CDD	218.7	82.62	ND	9.96
Total Cl_5CDD	ND*	ND	ND	ND
Total Cl_6CDD	ND	ND	ND	ND
Total Cl_7CDD	ND	ND	ND	ND
OCDD	28.89	ND	8.75	ND
Total PCDDs	247.6	82.62	8.75	9.96
2378- Cl_4CDD	162.3	81.46	ND	9.96
12378- Cl_5CDD	ND	ND	ND	ND
123478- Cl_6CDD	ND	ND	ND	ND
123678- Cl_6CDD	ND	ND	ND	ND
123789- Cl_6CDD	ND	ND	ND	ND
1234678- Cl_7CDD	ND	ND	ND	ND
Total Cl_4CDF	991.9	40.47	ND	1.46
Total Cl_5CDF	3.43	ND	ND	ND
Total Cl_6CDF	ND	4.59	1.85	7.31
Total Cl_7CDF	72.50	ND	17.57	ND
OCDF	1231	14.25	523.1	ND
Total PCDFs	2299	59.31	ND	8.78
2378- Cl_4CDF	890.1	37.20	ND	1.46
12378- Cl_5CDF	1.92	ND	ND	ND
23478-Cl_5CDF	ND	ND	ND	ND
123478-Cl_6CDF	ND	ND	ND	ND
123678-Cl_6CDF	ND	ND	ND	ND
123789-Cl_6CDF	ND	ND	ND	ND
234678-Cl_6CDF	ND	ND	ND	ND
1234678-Cl_7CDF	72.50	ND	12.90	ND
1234789-Cl_7CDF	ND	ND	ND	ND
Total PCDD/F	2546	141.9	551.3	18.74
TEQ	253.4	85.20	0.66	10.11

*ND: not detected (<1.0pg/L), TEQ contribution assumed to be 0 pg/L.

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