

PROFILES OF PCDD/FS IN EFFLUENTS FROM NON-WOOD PULP AND PAPER MILLS

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Abstract

The levels and patterns of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in effluents using Cl₂ and ClO₂ bleaching from two non-wood pulp and paper mills in China were investigated. The PCDD/F values ranged from 0.47 to 2.57 pg I-TEQ/l in Cl₂ bleaching effluents, higher than the values in improved ClO₂ bleaching effluents which were varied from 0.32 to 0.50 pg I-TEQ/l. The pattern of PCDD/Fs in effluents of wheat pulp was similar to the pattern of PCDD/Fs in wood kraft pulp, but was different to that in effluents using reeds as materials.

Introduction

During the 1980s the fact that chlorine (Cl₂) used for pulp bleaching is connected to the release of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) into the environment was proven in Sweden, the U.S., Canada and other countries^{1,2}. Previous detailed studies on the formation of PCDD/Fs in the bleaching of softwood kraft pulp have indicated: (1) That a major part of the PCDD/Fs are formed in the C-stage of the bleaching with chlorine (Cl₂) sequence; (2) That a typical pattern of tetrachlorinated congeners was formed, as was also identified in mill effluents, sediment and crab samples collected in the vicinity of pulp mills^{3,4,5}.

However, the investigations mentioned above were made only in the mills which use wood or recycled wastepaper for fiber. However non-wood plant fibers such as wheat, cereal, rice and reeds are extensively used as raw material for paper production in China⁶. We have previously reported levels of PCDD/Fs in pulps that use non-wood plant fibers as raw materials in China. In this study, an investigation on the levels and profiles of PCDD/Fs in effluents of two large pulp mills which use wheat and reeds for fiber was carried out.

Material and methods

Effluents samples including the C (chlorine), E (alkaline extraction) and W (discharged wastewater) stages were taken from two large pulp mills which used non-wood plant fibers as raw materials in September 2006. Each of 20 L of the effluent samples was enriched with XAD-2 resin in glass adsorption chromatography column, XAD-2 together with cotton filters were analyzed.

The PCDD/Fs analysis was performed using the isotope dilution technique based on U.S. EPA Method 1613B. After air-dried, samples were spiked with a mixture containing 15

$^{13}\text{C}_{12}$ labeled 2,3,7,8-substituted PCDD/F internal standards prior to their 24 h Soxhlet extraction with 250 mL *n*-hexane/dichloromethane (1:1), following concentration by rotary evaporation. The bulk of the co-extracted organic material was removed by successively passing the extract through the following series of chromatographic columns: acid-base silica column, multilayer silica column (from top to bottom: anhydrous sodium sulfate, 1 g silica-gel, 10 g 44% silica gel-sulfuric acid, 1 g silica-gel, 5 g 33% silica gel-sodium hydroxide, 1 g silica-gel, 2 g 10% AgNO_3 silica-gel, 1 g silica-gel) and basic alumina. The final eluates were condensed to about 20 μL by a stream of nitrogen. Prior to analysis, $^{13}\text{C}_{12}$ -labeled 1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD were added as injection standards for calculating recovery. The PCDD/Fs were analyzed by high-resolution gas chromatograph (Agilent 6890 GC with a 60 m DB-5MS column) coupled with high-resolution mass spectrometry (Waters Micromass Autospec Ultima with a resolution >10,000) by tracing the M^+ , $(\text{M}+2)^+$, or the most intensive ions of the isotope cluster. The data were obtained in the selected ion monitoring (SIM) mode. Additionally QA/QC measures included running a procedural blank, replicate, and initial precision and recovery (IPR).

Results and discussion

The mean recoveries for wastewater were in the range of from 65% to 78%. The results of the sample analyses for the toxic 2,3,7,8-substituted congeners were given in Table 1.

Table 1. Congener levels and profiles of PCDD/Fs in effluents from two paper making mills

Congeners	HT (wheat material)			YY (reed material)				
	Cl ₂ bleaching			Cl ₂ bleaching		ClO ₂ bleaching (ECF)		
	C	E	W	C	W	D ₀	D ₁	W
Σ 2,3,7,8-PCDD/Fs	38.25	35.74	13.51	147.86	25.50	41.44	9.67	48.03
Σ I-TEQ	1.95	2.57	0.81	1.91	0.47	0.32	0.47	0.50

The limit of detection (LOD) for PCDD/Fs in a given sample was defined by a signal to noise ratio greater than 3 times the average baseline variation. TEQs for 2,3,7,8-PCDD/F congeners were calculated for each sample using the International TEFs. When the value of PCDD/Fs congener was less than LOD, total I-TEQ was calculated with 1/2 LOD.

The different patterns of PCDD/Fs in effluents using Cl₂ bleaching process from two different mills could be due to different raw material species. It was observed that the pattern of PCDD/Fs using reeds as raw material is unlike to that in wood kraft pulp. The amount of PCDD/Fs was decreased when chlorine was replaced by chlorine dioxide in mill using reeds as raw material.

References

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