

OCCURRENCE AND CHARACTERISTICS OF PCDD/Fs FROM A RECYCLE PLANT OF CHLOROBENZENE RESIDUES IN CHINA

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Introduction

Chlorobenzenes (CBs) are important chemical products, and mainly used for the synthesis of new chemicals or used as solvents. As the world's largest producer of chlorobenzenes, China established emission inventory of dioxins in 2006 after ratification of Stockholm Convention, and listed chemical production (including chlorobenzenes production industry, CBs) as one of the six most important emission sources for prior actions of dioxins control and reduction in National Implementation Plan of China (NIP).^[5] The industrial production of penta- and hexa- CBs has been banned in China as required by Annex A of Stockholm Convention and its amendment. However, byproduct-POPs such as penta- and hexa-CBs, together with PCDFs and PCBs, are unintentionally formed during the production process.

A pathway of formation of PCBs and PCDD/Fs from precursors such as chlorobenzenes has been suggested in the previous studies,^[1, 2] and therefore CBs industry was recognized as a potential emission source of PCDD/Fs.^[3] A product emission factor of 39 µg I-TEQ/tonne of 1,2-Di-CB, and a residue emission factor of 3000 µg I-TEQ/tonne of 1,2,4-Tri-CB were derived and suggested by UNEP in 2005,^[4] basing on which the dioxins released through products (1,2-Di-CB) and residues (only concern Tri-CB production) from CBs were estimated to be 18.23 g I-TEQ per year in China.

Due to the complexity of CBs industry, there are still great uncertainties in the emission estimation of PCDD/Fs. As far as we know, the researches on the emission of PCDD/Fs from chlorobenzenes industry are still very scarce. The emissions could be affected by factors such as raw materials, productions and technical routes, which need to be further verified and particularized. Besides, PCDD/Fs from Mono-CB production sources have never been concerned. Based on the above situation, a survey of PCDD/Fs from a residue recycle plant was conducted during 2013. The raw materials of this recycle plant were the residues and byproducts from Mono-CB manufacturers. And the concentrations of PCDD/Fs in raw materials, wastewater, product, residue and important intermediates were analyzed. This study would reveal the occurrence and characteristics of PCDD/Fs from Mono-CB production and residue recycle plant in China.

Materials and Methods

Sample Collection

Samples were collected in June 2013. Each sample was obtained through mixture of multiple sampling. The parameters of feedstock and output were also collected during the sampling process. For Mono-CB residue recycling

plant, raw materials, products, residues, wastewater samples were collected. The sampling spots of the plant were demonstrated in Figure 1.

Sample Extraction and Analysis Procedure

Analysis of PCDD/Fs were conducted following the HJ 77.1 and HJ 77.3.^[6,7] All the solvents used for analysis were pesticide residue analysis grades, and were purchased from DUKSAN (Geyonggi-do, South Korea). Samples were spiked with 17 ¹³C-labeled internal quantification standards (CIL, Andover MA., USA) first. Wastewater samples were liquid-liquid extracted with dichloromethane. Products were concentrated and changed to hexane solvents. And residues were diluted by hexane, or soxhlet extracted with 300mL toluene for over 16h if there are insoluble residue. The extracts was changed to hexane and transferred to a separating funnels, and then treated with concentrated sulfuric acid (98%). A multi-layer silica gel (Kanto Chemicals, Tokyo, Japan) column was used to remove interferences. PCDD/Fs were eluted with 200ml of hexane. The analytes were treated with a silica-gel dispersed carbon column to further fractionate PCDD/Fs and PCBs. Finally, PCDD/Fs were eluted with 50 mL toluene. All elution's were concentrated to 30 μ L and spiked with ¹³C-labeled standards (CIL, Andover MA., USA) as syringe spike. 2,3,7,8-substituted PCDD/Fs were quantitatively determined by an HRGC-HRMS (Agilent 6890N, JEOL JMS-800D). Two capillary columns were used for PCDD/Fs, BPX-DXN (SGE, Australia, 60m \times 0.25mm i.d. \times 0.25 μ m film thickness) and RH-12ms (INVENTX, USA, 60m \times 0.25mm i.d. \times 0.25 μ m film thickness). The temperature programs of GC are as follows, the initial oven temperature was set at 130°C, after 1 min, the temperature was ramped at 15°C/min to 210°C, at 3°C/min up to 310°C, and at 5°C/min up to 320°C with a final hold time of 10min. The temperatures of the injector, the interface, and the ion source were set at 300°C. The HRMS was operated in an electron impact (38eV) and selected ion monitoring mode at a resolution R>10000 (10% valley).

Quality Assurance and Quality Control

In this study, procedural blank was conducted during each batch of samples to confirm that there were no interferences. The detection limits of instrument, method, and sample were checked and confirmed regularly. In this survey, the detection limit of sample (SDL) of 2,3,7,8-TCDD was 0.01ng/kg based on a sample weight of 200 grams. Parallel experiments were conducted during each batch of the samples. The results of parallel samples were controlled within 30% of the average when the levels are 3 times higher than SDL. Each sample was spiked with 17 ¹³C-labeled internal standards of PCDD/Fs to validate the performance of the analysis procedure. The recoveries of internal standards were controlled between 50-120%.

Results and discussion

TEQ Concentration of PCDD/Fs

Table 1 presents the TEQ concentrations of PCDD/Fs in the 7 samples. The TEQ concentrations of PCDD/Fs were 32000 and 62000 ng I-TEQ/kg in the two raw material samples, with an average concentration of 47000 ng I-TEQ/kg. These raw materials were remainder mixture of fractionating tower from Mono-CB manufacture plants. And these residues from Mono-CB manufacture plants were recycled because of the valuable components such as Di-CBs. The concentrations of residues in our study were much higher than the former report ^[3], in which study 610 ng WHO-TEQ/kg of PCDD/Fs in remainder mixture was reported. Based on the monitoring results and production data of 2011, the formation of PCDD/Fs from the manufacturer of Mono-CBs were estimated at 470 grams I-TEQ

annually in China. It was confirmed for the first time that large amounts of PCDD/Fs byproducts were formed during the production of Mono-CBs.

Trace concentrations of PCDD/Fs were detected in purified products. Only 0.046 ng I-TEQ/kg of PCDD/Fs were detected in 1,4-DiCB sample (S4), and were less than the reported result 39 ng WHO-TEQ/kg. In the process of distillation and crystallization, most of the PCDD/Fs would enrich in heavy-end residues.

Table 1 TEQ Concentrations of PCDD/Fs in the Recycle Plant

Sample I.D. Unit	S1(1) (ngTEQ/kg)	S1(2) (ngTEQ/kg)	S2(1) (ngTEQ/kg)	S2(2) (ngTEQ/kg)	S3 (pgTEQ/L)	S4 (ngTEQ/kg)	S5 (ngTEQ/kg)
2,3,7,8-TeCDD	81	190	17000	15000	540	0.015	90
1,2,3,7,8-PeCDD	70	23	12000	21000	50	0.0075	41
1,2,3,4,7,8-HxCDD	5.4	8.3	250	500	30	0.001	3.7
1,2,3,6,7,8-HxCDD	11	16	1700	2700	30	0.001	4.3
1,2,3,7,8,9-HxCDD	4.1	11	250	500	30	0.001	2
1,2,3,4,6,7,8-HpCDD	12	23	1200	2000	28	0.00041	2.1
OCDD	3.9	7.9	350	580	8.7	0.00002	0.41
Total PCDDs	190	280	32000	42000	720	0.026	140
2,3,7,8-TeCDF	1100	2100	110000	140000	3800	0.0059	890
1,2,3,7,8-PeCDF	140	290	17000	24000	470	0.0005	42
2,3,4,7,8-PeCDF	20000	39000	2400000	3300000	60000	0.008	5500
1,2,3,4,7,8-HxCDF	6700	13000	650000	990000	16000	0.0015	1200
1,2,3,6,7,8-HxCDF	1000	2200	110000	160000	2800	0.0015	170
1,2,3,7,8,9-HxCDF	58	110	6300	9300	220	0.0005	13
2,3,4,6,7,8-HxCDF	400	850	43000	88000	1200	0.0015	77
1,2,3,4,6,7,8-HpCDF	780	1600	69000	110000	1800	0.00039	100
1,2,3,4,7,8,9-HpCDF	500	960	43000	68000	1100	0.00042	66
OCDF	1400	2400	140000	200000	3500	0.0002	170
Total PCDFs	32000	62000	3600000	5100000	91000	0.02	8200
Total PCDD/Fs	32000	62000	3600000	5100000	92000	0.046	8400

Note: When the concentration was N.D., TEQ of the congener was calculated by 1/2SDL

Because recycle plants only had distillation and crystallization process, the low temperature would not result in the degradation of PCDD/Fs. And there were no further chlorinated reaction at the recycle plants, the regeneration of PCDD/Fs might be ignored. So the PCDD/Fs in the final residues of recycle plants were mainly from the raw materials. Due to the high concentrations of PCDD/Fs in the raw materials, the highest levels of PCDD/Fs were found in the final residues (S2). 3600000 and 5100000 ng I-TEQ/kg of PCDD/Fs were detected in the two samples (S2), which were collected from the waste storage room of this plant. Although the residues of this plant were treated as hazardous waste, the high levels of PCDD/Fs were never concerned until now. High levels of PCDD/Fs were also detected in the wastewater (S3, 92000 pg I-TEQ/L) after setting tank. PCDD/Fs in these residues and wastewater might be discharged into the environment if could not get effective treatment and disposal.

Congener Profiles and Formation Mechanism

PCDFs were the dominant congeners in all of the detected samples, contributed more than 99% of the total PCDD/Fs in raw materials and final residues. Most congeners of PCDDs were not detected. OCDF, 2,3,4,7,8-

PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and 2,3,7,8-TeCDF were the most abundant congeners among the 17 toxic PCDD/Fs. And 2,3,4,7,8-PeCDF was the main contributor to TEQ, accounting for more than 60% of the TEQ except in product sample (S4). In most organochlorinated chemical products, the main congeners of PCDD/Fs was high chlorinated PCDDs, such as OCDD and HpCDD. [8, 9] These patterns in chlorobenzenes industry were quite different from those in other organochlorinated chemicals industry, such as PCP and 2,4-D. Detailed congener profiles of PCDD/Fs in raw products and residues were shown in Figure 2.

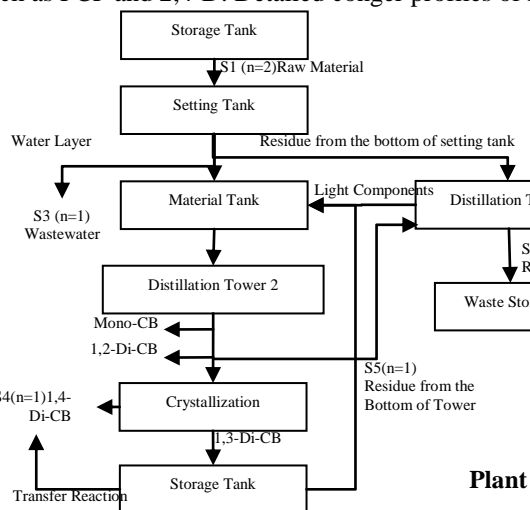


Figure 1 Process Flow Chart and Sampling Spot

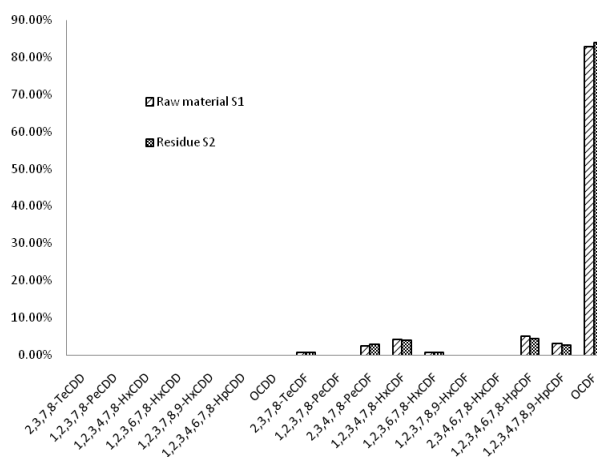


Figure 2 Congener profiles of raw products and residues

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