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Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in 1,4-Dichlorobenzene Mothballs

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Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two of the twelve persistent organic pollutants being addressed in the Stockholm Convention. Exposure to PCDD/Fs is of concern because of their toxicity, which include hormone-dependent cancers and reproductive effects in humans and wildlife. PCDD/Fs are ubiquitous environmental contaminants, and several of the PCDD/Fs congeners, particularly those substituted at 2,3,7,8-positions, are persistent and bioaccumulative. PCDD/Fs can be formed in chemical processes where chlorine is involved. In particular, chemicals such as polychlorinated biphenyls, pentachlorophenol, 2,4-dichlorophenoxy acetic acid, 2,4,5-trichlorophenoxyacetic acid and 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione were found to be contaminated with PCDD/Fs (UNEP 2003). Being product of chlorination of benzene, low concentration of PCDD/Fs in 1,4-dichlorobenzene is possible.

The chemical 1,4-dichlorobenzene usually called p-DCB, and also called paramoth because it is one of the chemicals commonly used to make mothballs. For the past 20 years, p-DCB has been used principally (35-55% of all uses) as a space deodorant for toilets and refuse containers, and as a fumigant for control of moths, molds, and mildews. p-DCB has also been used as an insecticide on fruit and as an agent to control mold and mildew growth on tobacco seeds, leather, and some fabrics. The production volume of p-DCB increased from 1984 to 1994 at a rate of 4% annually and the volume of p-DCB produced in 1994 was 2.82 billion kg in the United States (HSDB 1998). Nevertheless, prior to this study, no reports on PCDD/Fs in p-DCB and the restriction of PCDD/Fs in p-DCB products have been found. In the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, no emission factor of PCDD/Fs in chlorobenzenes products can be given. (UNEP 2003) In this paper, the occurrence and distribution of PCDD/Fs in some commercial p-DCB mothballs are investigated. Except of the toxic of p-DCB, the low concentration of PCDD/Fs in p-DCB mothballs should not be negligible. The results of this article suggest that re-estimation on the risk of using toxic of p-DCB especially for daily use such as mothballs, is expected.

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MATERIALS AND METHODS

The solvents such as n-hexane, toluene and methylene dichloride were pesticide grade. ^{13}C-labelled PCDD/Fs were provided by Cambridge Isotope Laboratory, USA. The samples (20 g) were collected in April 2003 and stored at –20℃ until analysis was performed. 3 brand of p-DCB mothball, which are popular and hold 70% of p-DCB mothball market in China, were selected in this study. 9 samples were collected from the supermarket in Beijing and blended into 3 samples respectively by the brand of mothballs. A big p-DCB mothballs plant, Yanzh Pesticide Co. Ltd, was also selected and 2 samples were collected. The p-DCB contents in the samples were listed in table 1 and the purity of p-DCB in the samples is all above 99%. Samples YZ, YN and XH are produced according to local technical methods, while samples FS and YH are produced with Japanese technical methods.

Table 1. The concentration of p-DCB in 5 samples.

	YZ	YN	XH	FS	YH
P-DCB purity	99.0%	99.0%	99.8%	99.5%	99.0%

YZ: sample No. 1 of Yanzh Pesticide Co. Ltd.; YN: sample No. 2 of Yanzh Pesticide Co. Ltd.; XH: sample of Xinh Chemical Co. Ltd.; FS: sample of Fshi Chemical Co. Ltd.; YH: sample of Yhua Chemical Co. Ltd.

The samples were homogenized and 1 g sample was dissolved into 3 ml n-hexane. 2 μl of nonane solution of 2,3,7,8-substituted ^{13}C-PCDD/Fs was added to the sample solution. The samples were purified by passing through an alumina and a multilayer silica gel column. A 250 mm × 20 mm column was prepared with 8 g alkaline Al_2O_3 and 2 g hydrous Na_2SO_4 and eluted with 50 ml n-hexane initially. Transferred the sample onto the top of the column, and eluted the column with 80 ml 2% (V/V) dichloromethane/n-hexane, and then eluted with 40 ml 50% (V/V) dichloromethane/hexane. Condensed the latter eluate to 1 ml and subjected to the purification by a multilayer silica gel column. In a 250 mm×20 mm column, from bottom to top 1 g silica gel, 1.5 g silica gel coated with $AgNO_3$, 1 g silica gel, 3 g silica gel coated with NaOH, 1 g silica gel, 8 g silica gel coated with H_2SO_4, 1 g silica gel and 2 g $NaSO_4$ were added respectively. Eluted the column with 40 ml n-hexane initially and transferred the sample onto the top of the column. Eluted the column with 80 ml n-hexane, and evaporated the eluate under flow of high purity nitrogen till it became almost dry. At last, 8 μl nonane and 2μl nonane solution containing ^{13}C-1,2,3,4-TCDD and ^{13}C-1,2,3,7,8,9-H_6CDD as recovery standards were added.

The samples were subjected to Agilent 6890 HRGC/5973N LRMS using a 30 m DB-5 fused-silica column for PCDD/Fs analysis. Quantification was performed in selected ion monitoring mode. A blank was run to test for the presence of background contamination.

RESULTS AND DISCUSSION

The processes of the production of p-DCB mothball include several steps of chemical synthesis and purification and are shown in Figure 1.

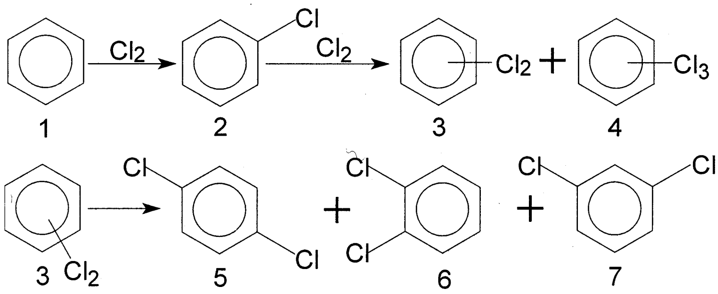

Figure 1. The processes of production of p-DCB mothball.

The process currently used by industry is direct chlorination of benzene (compound No.1) in the presence of a Friedel-Crafts (typically ferric chloride) catalyst to produce monochlorobenzene (compound No.2). The monochlorobenzene reacts with the remaining chlorine to form dichlorobenzenes (compound No.3) and other polychlorobenzenes (such as compound No.4). As chlorination is continued, the tri-, tetra-, penta-, and hexachlorobenzene are formed. Each compound, except hexachlorobenzene, can be chlorinated further; hence, the product is always a mixture of chlorinated benzenes. Pure products are obtained by distillation and crystallization. In addition to the two major isomers of dichlorobenzene, para- (compound No.5) and ortho- (compound No.6), a very small amount of the meta-isomer (compound No.7) is formed. PCDD/Fs maybe synthesize in these processes and low concentration of PCDD/Fs in p-DCB mothballs is possible. To re-estimate the risk of using of p-DCB mothball, it is necessary to evaluate the contamination of PCDD/Fs in them. The analysis results are shown in Figure 2 and Figure 3. The average recovery efficiency was over 75%. The I-TEQ of the 5 mothball samples is shown in Figure 2.

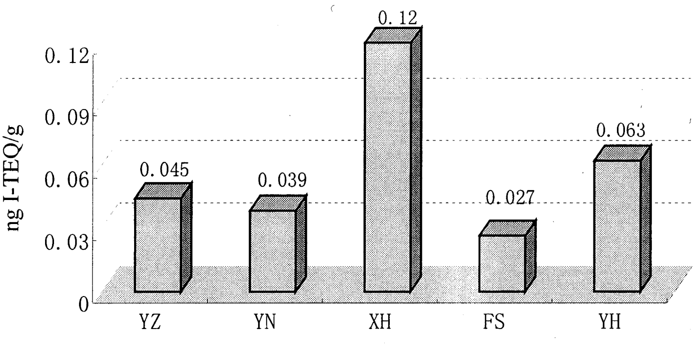

Figure 2. The total I-TEQ of the 5 p-DCB mothball samples.

The I-TEQ of the 5 p-DCB mothball samples was between 0.027 ng/g and 0.126

ng/g. PCDFs were detected throughout all the samples and no PCDDs were detected. P_5CDFs and H_6CDFs were dominated in the PCDD/Fs isomers and only low concentrations of other PCDFs congeners were detected. The I-TEQs of the PCDFs analogues of the 5 samples are given in Figure 3.

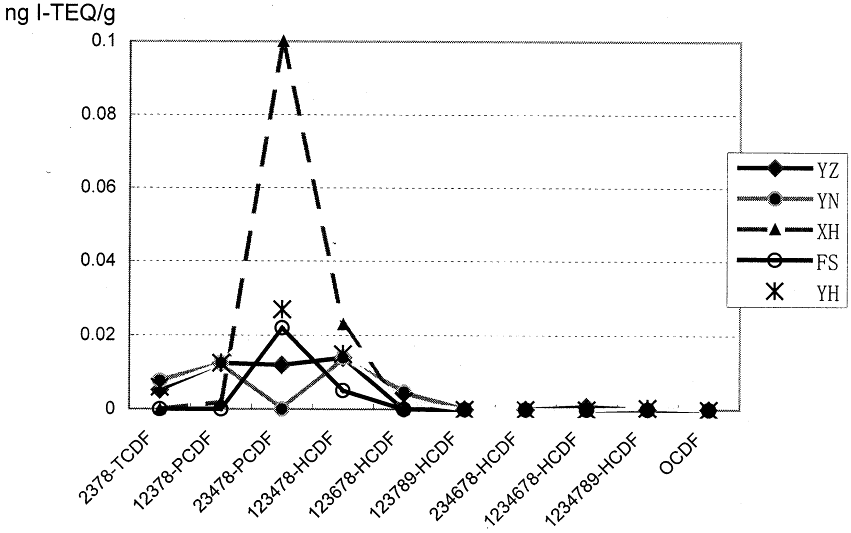

Figure 3. The I-TEQ of the PCDFs analogues of the 5 p-DCB mothball samples.

From Figure 3 it can be seen that 2,3,7,8–T_4CDF, 1,2,3,7,8–P_5CDF, 2,3,4,7,8–P_5CDF and 1,2,3,4,7,8–H_6CDF were the main contributors of I-TEQ in the p-DCB mothball samples. The PCDFs analogue distributing between the samples was similar. The differences of the production techniques maybe influence the analogue distributing of PCDD/Fs in the samples. In the processes of production of p-DCB mothball, polychlorinated biphenyls (PCBs) maybe the intermediate compounds in the formation of PCDD/Fs from benzene. PCBs maybe formed straightforwardly via a radical mechanism in the chlorine present. PCBs can be oxidized and are thus possible precursors of PCDFs (Tuppurainen 1998, Ballschmitera 1983, Sommeling 1994, Peng-Yan Liu 2001).

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