The Levels of Polychlorinated Biphenyls in 1,4-Dichlorobenzene Mothballs

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Introduction

Polychlorinated biphenyls (PCBs) are known to cause chronic reproductive effects, gastric disorders, and skin lesions in laboratory animals. In addition, the U.S. Environmental Protection Agency suspects that PCBs are probable human carcinogens. Recently, special attention has been focused on a few select PCB congeners which are stereochemically similar to 2,3,7,8-tetrachloro-p-dioxin. The World Health Organization (WHO) has identified 12 of the 209 possible PCBs as being similar in toxicity to the PCDD/Fs. The list of these 12 dioxin-like PCBs includes four non-*ortho* (IUPAC nos. 77, 81, 126, and 169) and eight mono-*ortho* congeners (IUPAC nos. 105, 114, 118, 123, 156, 157, 167, and 189).

PCBs were first manufactured commercially in 1929 and concern about the presence of PCBs in our environment began in the 1960s. After understanding their toxic effects, many of industrialized countries have restricted or banned the production and usage of PCBs, since the beginning of the 1970s. Because of this, there are relatively few ways that people can be exposed to concentrated PCBs. However, the most common exposure routes include: food, surface soils, drinking water and groundwater, indoor air, and workplaces [1].

The chemical 1,4-dichlorobenzene (p-DCB), also called paramoth, is one of the chemicals commonly used to make mothballs. For the more than 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 [2]. The process of production of p-DCB currently used by industry is direct chlorination of benzene or chlorobenzene in the presence of a Friedel-Crafts catalyst (typically $FeCl_3$), and the pure products of p-DCB are obtained by distillation and crystallization from the mixture of polychlorinated benzenes. This process is similar to that of production of PCBs which were manufactured commercially by the progressive chlorination of biphenyl in the presence of a suitable catalyst, e.g., iron chloride.

However, few studies on the formation of PCBs from chlorobenzenes have been published. Buser [3] reported significant quantities of PCDFs and a small amount of PCDDs, PCBs, and chlorophenols were formed in the pyrolysis of chlorobenzenes at 620 ^{o}C. Peng-Yan Liu et al. [4]

revealed that lower chlorinated benzenes produce more PCBs than higher ones. Nevertheless, prior to this study, no reports on PCBs in p-DCB and the restriction of PCBs in p-DCB products have been found. In this paper, the occurrence and distribution of dioxin-like PCBs and total PCBs in some commercial p-DCB mothballs are investigated. Except of the toxic of p-DCB [2], the low concentration of PCBs in p-DCB mothballs should not be negligible.

Methods and Materials

The solvents such as n-hexane, toluene and methylene dichloride were pesticide grade. ^{13}C-labelled PCBs were provided by Cambridge Isotope Laboratory, USA. The samples (20 g) were collected in April 2003 and stored at –20 °C until analysis was performed. 4 brands of p-DCB mothball, which are popular and hold 70% of p-DCB mothball market in China, were selected in this study. 10 samples were collected from the supermarket in Beijing and blended into 5 samples respectively by the brand of mothball. The p-DCB contents in the samples are shown in table 1 and the purities of p-DCB in the samples were all above 99%. Samples XH and YZ are produced according to local technical methods, while samples YH, FS1 and FS2 are produced with Japanese technical methods.

Table 1: The concentrations of p-DCB in 5 samples

	XH	YZ	YH	FS1	FS2
p-DCB purity	99.8%	99.0%	99.0%	99.0%	99.5%

XH: sample of Xinh Chemical Co. Ltd.; YZ: sample of Yanzh Pesticide Co. Ltd.; YH: sample of Yhua Chemical Co. Ltd.; FS1 and FS2: samples of Fshi Chemical Co. Ltd..

After being ground and homogenized three times, about 0.1 g of the sample was dissolved with n-hexane, and ^{13}C-labeled PCB standards were added to the sample solution. The sample was purified by passing through a 250 mm × 12 mm column which was prepared with 8 g alkaline Al_2O_3 and 2 g anhydrous Na_2SO_4. The column was eluted with 50 ml n-hexane initially, and then the sample was transferred onto the top of the column. The column was eluted with 30 ml n-hexane, and then eluted with 40 ml 50% (V/V) dichloromethane/n-hexane. The latter eluate was concentrated finally to near dryness prior to the addition of the recovery standards. At last, the sample was subjected to Agilent 6890 HRGC/5973N LRMS using a 30 m DB-5ms fused-silica column for PCBs analysis. The quantification analysis of PCBs was performed in selected ion monitoring (SIM) mode. At the same time, a blank ran to test for the presence of background contamination.

Results and Discussion

Table 2 summarises the total PCBs and dioxin-like PCBs in the samples. Figure 1 demonstrates a suggested mechanism of the formation of PCBs from polychlorinated benzene. The average recovery of the samples was over 75%.

As seen in Table 1, total PCBs and dioxin-like PCBs were detected in all the samples. Total PCB concentrations ranged from 328 ng/g in sample FS2 to 1798 ng/g in sample YZ, while the levels of WHO-TEQ were between 0. 16 pg/g in sample YZ and 13 pg/g in sample XH. Sample YZ had the highest level of total PCBs followed by XH > YH > FS1 >FS2. Regarding WHO-TEQ, sample XH had the highest value in all the samples, followed by FS1 > YH > FS2 > YZ. Mean concentrations of total PCBs and WHO-TEQ in the samples were 724 ng/g and 3.2 pg/g, respectively. The highest level of PCBs was that of trichlorinated biphenyls (537 ng/g), which maybe due to the relatively low chlorination in the process of p-DCB production.

The process of p-DCB production includes several steps of chlorination and product purification. PCBs may be synthesized in the chlorination reactions and remained in the final products, although the products were purified by some working procedures, such as distillation and crystallization. A suggested mechanism of the formation of PCBs from polychlorinated benzene in the presence of chlorine is shown in Figure 1. PCBs may be formed straightforwardly via a radical mechanism in the chlorine present [4,5]. Cl atom abstracts H from polychlorinated benzene, the resulting polychlorinated phenyl radical reacts rapidly with polychlorinated benzene. This reaction leads to PCBs.

Table 2: The levels of total PCBs and dioxin-like PCBs in some commercial p-DCB mothballs (ng/g)

PCBs	XH	YZ	YH	FS1	FS2	Mean *
Σ MonoCB	ND	ND	ND	ND	ND	ND
Σ DiCBs	26	57	20	9.3	26	28
Σ TriCBs	180	1717	372	206	210	537
Σ TetraCBs	173	24	62	66	76	80
Σ PentaCBs	128	ND	35	40	13	43
Σ HexaCBs	108	ND	7.9	14	3.2	27
Σ HeptaCBs	27	ND	17	ND	ND	8.8
∑ PCBs	642	1798	515	335	328	724
PCB77	3.0	1.6	1.8	1.5	1.1	1.8
PCB105	18	ND	3.4	3.8	1.4	5.3
PCB118	26	ND	5.0	6.9	2.3	8.0
PCB156	15	ND	ND	ND	0.44	3.0
PCB157	2.6	ND	ND	ND	ND	0.52
PCB167	4.8	ND	ND	ND	ND	0.96
WHO-TEQ	0.013	0.00016	0.001	0.0012	0.0007	0.0032

* Note: Mean level of the 5 samples. ND<0.2 ng/g.

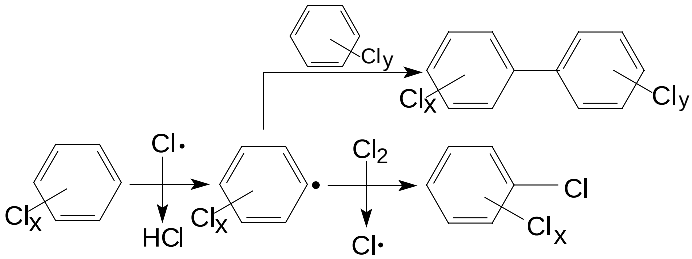

Figure 1: Mechanism of the formation of PCBs. (x, y = 0~6)

The present study is important to provide data on the concentrations of PCBs in p-DCB mothballs in China. Although the levels of WHO-TEQ in the samples were relatively low, the concentrations of PCBs were high in all the samples. The results of this article suggest that re-estimation on the risk of using p-DCB products, especially the products for daily use such as mothballs, is expected.

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