DETERMINATION OF PCDD/FS AND DL-PCBS AS IMPURITIES IN CHINESE PENTACHLORONITROBENZENE PESTICIDES

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Introduction

Pentachloronitrobenzene (PCNB, $C_6Cl_5NO_2$, CAS No. 82-68-8), also known as quintozene or terrachlor, is a fungicide commonly used in many countries including China. PCNB is included neither in the USEPA list of pesticides with the potential to contain dioxin impurities, nor in the UNEP Toolkit[1]. However, a survey conducted by the Ministry of Agriculture, Forestry and Fisheries (MAFF) of Japan in 2002 revealed that 3.7 and 0.86 ng TEQ/g Active Ingredient (AI) of PCDD/Fs and DL-PCBs, respectively, where present in Japanese PCNB formulations, which is also consist of another academic report[2]. Also PCDD/Fs in three PCNB formulations collected in Australia were found at average lower bound concentrations of 3.9, ranging from 1.7 to 4.2 ng TEQ/g, respectively[3]. Such facts have led to the ban in Japan and the suspension of registration in Australia for PCNB. Today, PCNB is still produced and used in China. Actually China has ever issued product specification standards for two types of PCNB product, i.e. HG2460.1-93 for PCNB raw pesticide, and HG2460.1-93 for 40% PCNB powder. According to the Registered Pesticide Information System maintained by the Chinese Ministry of Agriculture, there are 2 records of raw pesticides and 21 records of formulations (http://www.chinapesticide.gov.cn/ , accessed on May 2, 2012) in China. To the best of our knowledge, so far there's no data about unintentionally produced POPs contained in Chinese PCNB products, which prevents a comprehensive risk assessment of these chemicals still in-use. In the present study, five Chinese PCNB products were tested for the concentrations of PCDD/Fs and DL-PCBs. The results were then compared with the data reported for PCNB products in other countries and also compared with the limit defined by Japanese MAFF as a reference.

Materials and methods

Five PCNB product including 2 raw pesticide products and 3 formulations were collected for analysis, detailed information about the producers and AIs are shown in Table 1. These products were purchased individually from the producers during the period of 2010 to 2011.

Table 1: Information on the five PCNB samples assessed in this study

Sample	Content of AIs	Formulation	Producer
#R1	95% PCNB	Raw pesticide	Shanxi Sanli Chemical Co., Ltd
#R2	95% PCNB	Raw pesticide	Shandong Dezhou Tianbang Agrochemical Co., Ltd
#F1	40% PCNB	Powder	Sichuan Guoguang Agrochemical Co., Ltd
#F2	30% PCNB, 15% Bromothalonil	Powder	Jiangsu Tuoqiu Agrochemical Co., Ltd
#F3	20% PCNB, 20% Thiram	Powder	Shandong Dezhou Tianbang Agrochemical Co., Ltd

Aliquot of each sample (0.1-0.2 g) was firstly extracted for 16 h in Soxhlet extraction using dichloromethane (DCM) as the solvent. The extraction was spiked with 0.5-1 ng $^{13}C_{12}$-labeled 2,3,7,8-PCDD/Fs and DL-PCBs internal standards, corresponding to 7 PCDDs, 10 PCDFs, 12 DL-PCBs as target analytes. The extraction above was concentrated and then sequentially subjected to sulfuric acid treatment and multi-layer silica gel column chromatography with hexane as an eluent. Further treatment with silica-gel dispersed carbon column chromatography using toluene as the eluent resulted in the fraction used for the determination of PCDD/Fs and 4 non-ortho DL-PCBs. This fraction was concentrated and spiked with 0.5 ng of four $^{13}C_{12}$-labeled PCDD/Fs and four $^{13}C_{12}$-labeled PCBs internal standards as syringe spike, then filled up with nonane to 50 µL. However for the other fraction of the dichloromethane/hexane fraction (1:3, V/V) as the eluent originally designed for the determination of the other 8 mono-ortho DL-PCBs, significant interferences from the sample matrix have been observed. Therefore, the mono-ortho DL-PCBs had to be determined additionally. For this purpose, a part of the hexane extraction from the multi-layer silica gel column chromatography was stepwise diluted. The dilution was spiked with 0.5-1 ng $^{13}C_{12}$-labeled PCBs internal standards as cleanup spike, and then subjected to multi-layer silica gel column chromatography with hexane as an eluent. The fraction was concentrated and spiked with 0.5 ng of 5 $^{13}C_{12}$-labeled PCBs internal standards as syringe spike, then filled up with nonane to 50 µL. To get a better understanding about the congener profile of PCBs in the samples, 13 other PCB congeners were also included in the clean spike added. Quantification and identification were performed with an Agilent 6890N high resolution gas chromatography coupled with JEOL JMS-800D high resolution mass spectrometer (HRGC/HRMS). An autosampler (Agilent 7683 Automatic Liquid Sampler) was used for injection (1 µL, splitless). The details of the instrumental operational parameters are described in a previous paper[4].

The minimum detection limit (DL) and the minimum quantification limit (QL) were determined according to the Chinese standard HJ 77 method. The variability of analytical procedures was assessed by replicate analysis of all samples. Analytical blanks were included to assure that no contamination had occurred during extraction, cleanup and analysis.

Results and discussion

TEQ concentrations of PCDD/Fs and DL-PCBs in Chinese PCNB products

The detected TEQ concentrations of PCDD/Fs and DL-PCBs in five Chinese PCNB product samples are shown in Table 2. Duplicate analysis was conducted for each sample, and both low bound and upper bound TEQ values were calculated.

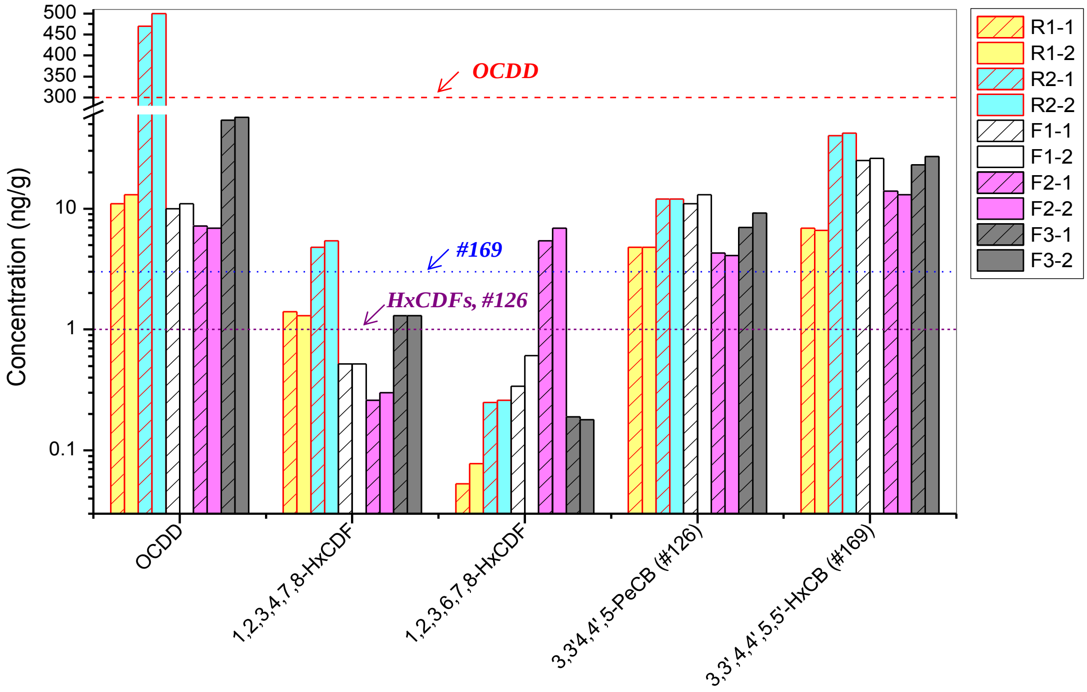
Table 2: TEQ (WHO_{2005}) levels of PCDD, PCDF and PCB in the investigated PCNB samples

Sample	#R1-1	#R1-2	#R2-1	#R2-2	#F1-1	#F1-2	#F2-1	#F2-2	#F3-1	#F3-2
Low bound (ng TEQ/g)										
TEQ_{PCDDs}	0.0059	0.0068	0.15	0.16	0.0042	0.0046	0.010	0.0086	0.023	0.024
TEQ_{PCDFs}	0.26	0.25	0.78	0.86	0.16	0.19	0.65	0.79	0.36	0.36
$TEQ_{PCDD/Fs}$	0.27	0.26	0.93	1.0	0.16	0.19	0.66	0.8	0.38	0.39
$TEQ_{DL\text{-}PCBs}$	0.69	0.68	2.4	2.5	1.9	2.1	0.85	0.8	1.4	1.7
Total TEQ	0.96	0.94	3.3	3.5	2	2.3	1.5	1.6	1.8	2.1
Upper bound (ng TEQ/g)										
TEQ_{PCDDs}	0.06	0.06	0.22	0.23	0.031	0.032	0.026	0.028	0.039	0.042
TEQ_{PCDFs}	0.27	0.26	0.78	0.86	0.17	0.20	0.66	0.81	0.36	0.36
$TEQ_{PCDD/Fs}$	0.33	0.32	1.0	1.1	0.21	0.23	0.69	0.84	0.4	0.41
$TEQ_{DL\text{-}PCBs}$	0.69	0.68	2.4	2.5	1.9	2.1	0.85	0.80	1.4	1.7
Total TEQ	1.0	1.0	3.4	3.6	2.1	2.3	1.5	1.6	1.8	2.1

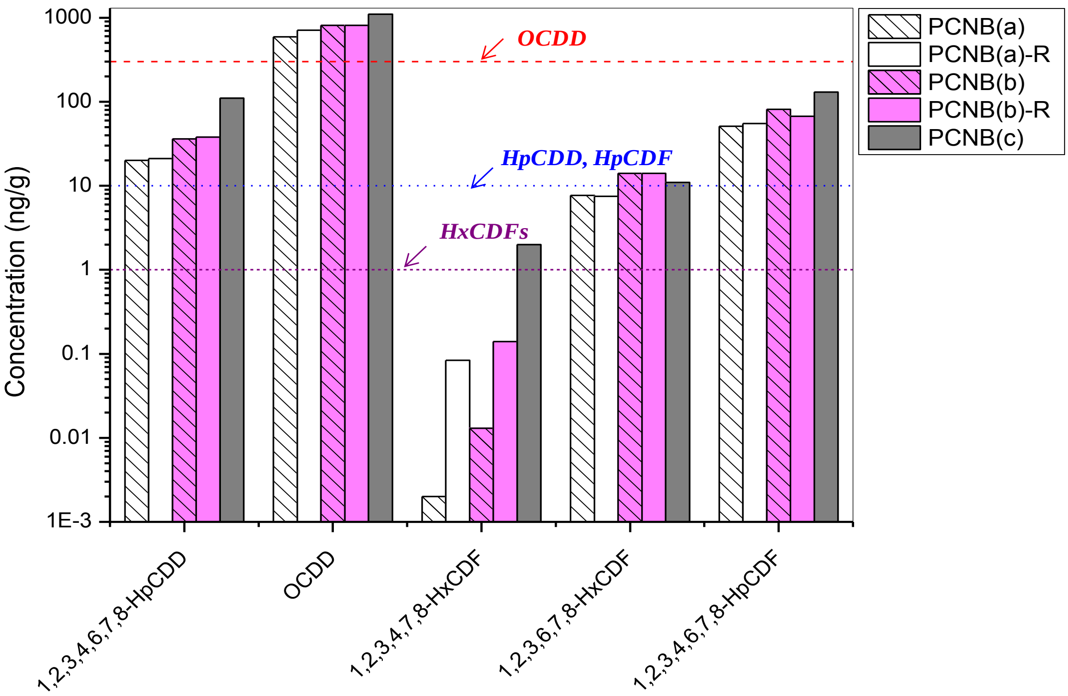
It needs to be highlighted that 50 to 95% of the total TEQ was contributed by the DL-PCBs and that the PCDD/Fs had a lower contribution to the total TEQ. This highlights that for an appropriate assessment of dioxin-like toxicity from unintentionally produced POPs impurities in PCNB pesticides the DL-PCB need to be included in the measurement. Only then an appropriate risk assessment can be conducted.

Congener profiles of PCDD/Fs and DL-PCBs in Chinese PCNB products

The main congeners detected in five Chines PCNB product samples are shown in Figure 1(a), including one PCDDs congener (i.e. OCDD), two PCDFs congeners (i.e. 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF), and two DL-PCBs congeners (i.e. #126 and #169).



(a)



(b)

Figure 1: (a) Main congeners of PCDD/Fs and DL-PCBs detected in the investigated Chinese PCNB products and (b) main PCDD/F congeners detected in PCNB on the Australian market by Holt et al. in 2010[3]; The dashed lines represented the limit defined by the Japanese MAFF standard.

There's no regulatory limit for dioxins as impurities in pesticides in China, therefore the limit issued by Japanese MAFF was used here for comparison as a reference. As shown in Figure 1(a), all five PCNB products exceeded the Japanese limit for one or more congeners. These results indicate risk might be caused by the PCDD/F and in particular DL-PCB as impurities in these products.

Comparison of PCDD/Fs concentrations with the data of Australian study

In the Australian study reported by Holt et al. [2], PCDD/Fs concentrations in PCNB product samples collected in Australia have been described in detailed previously, however no data of DL-PCBs were reported. When comparing the lower bound TEQ values in the Australian study with the present study, it's obvious that the TEQ caused by PCDD/Fs in Chinese PCNB product samples were basically one order of magnitude lower than those reported in the Australian study. The main detected 2,3,7,8-PCDD/Fs congeners in the Australian study (Figure 1(b)), included two PCDDs congeners (OCDD and 1,2,3,4,6,7,8-HpCDD) and three PCDFs congeners (1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF) and therefore a similar pattern as in our study. Also all three samples exceed the Japanese limit for four or more congeners (Figure 1b). The significant difference of PCDD/Fs concentrations (and the similar PCDD/Fs congener profiles) in the Australian study compared to our Chinese study is probably caused by difference in the production process. For the production of Chinese PCNB raw pesticides, the flowchart is illustrated in Figure 2.

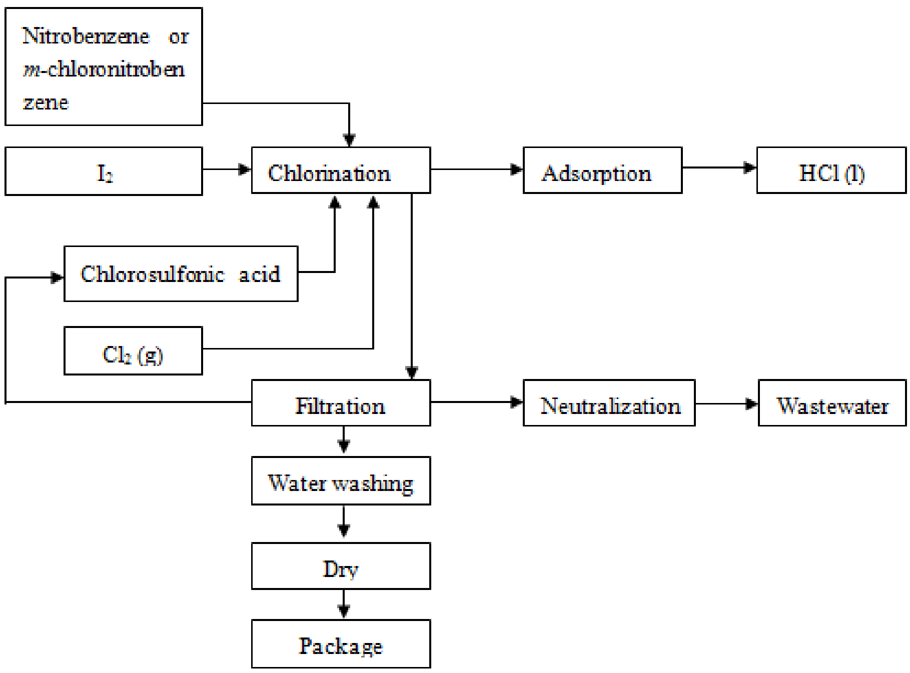


Figure 2: Production processes of the Chinese PCNB raw pesticide manufacturing

Acknowledgements

This research was financially supported by the National High-Tech Research and Development Program (No. 2009AA064001; 2010AA065105) and the National Natural Science Funds (No. 51078212; 50838002).

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