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Unintentional formed PCDDs, PCDFs, and DL-PCBs as impurities in Chinese pentachloronitrobenzene products

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Abstract Pentachloronitrobenzene (PCNB) products have been reported to contain relatively high levels of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) as impurities. No data was available for Chinese PCNB products which are still produced and used in China. Therefore, we analysed Chinese PCNB products, including two raw pesticides and three formulations available on the market. In all samples, PCDDs, PCDFs, and dioxin-like polychlorinated biphenyls (DL-PCBs) were detected at levels exceeding Japanese regulation limits. The concentrations of PCDDs and PCDFs (0.16 to 0.93 ng TEQ g^{-1}) were lower than the PCNB formulations measured from the Australian market (3.9 ng TEQ g^{-1}). However, the Toxic Equivalent (TEQ) contribution from DL-PCBs (0.7 to 2.5 ng TEQ g^{-1}) to total TEQ was higher compared to PCDDs and PCDFs. This discovery demonstrated that it is necessary to consider the DL-PCBs impurity in organochlorine pesticides and other organochlorine chemicals in particular chlorinated aromatic compounds for adequate risk assessment. In addition to DL-PCBs, other unintentionally POPs—hexachlorobenzene (HCB) (3.7 to 52 ng g^{-1}) and pentachlorobenzene (PeCBz) (0.04 to 0.3 ng g^{-1}) which are listed in the Stockholm Convention—were detected in the PCNB samples. The PCNB production steps were assessed for their unintentional POPs formation potential. Thermolysis of the aromatic compounds using iron chloride ($FeCl_3$) as catalyst is suggested as relevant production step for (DL-)PCBs formation. Since the levels in the formulated PCNB recalculated to active ingredient were higher compared to the raw pesticide, the formulation process (e.g., milling) may also have had an influence on additional PCDD/Fs and PCBs formation.

Keywords Pentachloronitrobenzene · PCDDs · PCDFs · DL-PCBs · HRGC/HRMS · TEQ

Introduction

Humans can be exposed to pesticides and their impurities through direct handling, occupational exposure using pesticides, entry of treated areas, contact with environmental residues and dietary and drinking water intake (Fantke et al. 2012; Hamilton and Crossley 2004; Vida and Moretto 2007). Furthermore, the environment is exposed to pesticides primarily by reaching non-target organisms via wind drift, leaching, and runoff (Coats and Yamamoto 2003; Stenersen 2004).

Technical pesticides, although by definition being "pure active ingredient", also may contain complex mixtures of other minor chemical impurities such as unintentionally produced persistent organic pollutants (POPs) due to process variables, side reactions and impurities in starting materials (Ambrus et al. 2003). The most prominent unintentionally produced POPs are polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs). PCDD/Fs and DL-

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PCBs cause major environmental concern due to their adverse effects on the human health and the environment, and have been included in the Stockholm Convention initial list of "dirty dozen" POPs.

The release of PCDD/Fs from chlorinated pesticides has been identified as a major source of environmental contamination from historic use (Masunaga et al. 2003; Weber et al. 2008). Recently, it was also revealed that all of a total of 23 tested contemporary pesticides used in Australia contained PCDD/Fs (Holt et al. 2010). In addition, large PCDD/F reservoirs exist at former pesticide production sites and related landfills (Goetz et al. 2013; Weber and Varbelow 2013; Torres et al. 2013).

A range of pesticides have been investigated for containing unintentional POPs, and emission factors for PCDD/Fs have been summarized in the Standardized Toolkit for Identification and Quantification of Dioxins and Furans Release (UNEP 2013). These include, e.g., pentachlorophenol (PCP), sodium pentachlorophenate (PCP-Na), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), 2,4,5-trichlorophenol, 2,4-D and other chlorophenol derivatives, 2,4,6-trichlorophenyl-4'-nitrophenyl Ether (CNP), triclosan and chlorobenzenes. However, DL-PCBs emission factors have not been listed in the Toolkit for any pesticide yet.

Due to the challenging matrix of pure organochlorine compounds (i.e., the pesticide active ingredient), the isotope dilution technology using high resolution gas chromatography/high resolution mass spectrometer (HRGC/HRMS) has been utilized for an accurate congener-specific analysis in other studies assessing PCDD/Fs in organochlorine compounds (Holt et al. 2010; 2012; Liu et al. 2004; Masunaga et al. 2001).

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 has been extensively used for the prevention and control of certain soil-borne diseases on golf courses, sod farms, home lawns, and institutional areas where turf is grown (Li et al. 2011). PCNB was not included in the USEPA list of pesticides with the potential to contain dioxin impurities (USEPA 2005) and was not included in the former UNEP Toolkit (UNEP 2005), but was recently added to the updated toolkit version (UNEP 2013). A survey conducted by the Ministry of Agriculture, Forestry and Fisheries (MAFF) of Japan in 2002 revealed that the contents of PCDDs, PCDFs and DL-PCBs were at 3.7 and 0.86 ng TEQ g^{-1} active ingredient (AI) in the PCNB formulations produced in 1987 and 1997, respectively (MAFF 2002). Similar levels of dioxins were also found in Japanese PCNB samples at 0.78 and 1.2 ng TEQ g^{-1} AI (Horiguchi et al. 2007). Realizing the importance of controlling the PCDD/Fs impurities in pesticides, the Japanese MAFF issued the Notice No.1456 in 2005, which regulate the limit of 0.1 ng TEQ g^{-1} AI for every congener of 7 PCDDs, 12 PCDFs, and 12 DL-PCBs. Based on this regulation, PCNB and three other pesticides (CNP, PCP, and 2,4,5-T) have been banned for production or use in Japan.

In the study conducted by Holt et al. (2010), the contents of PCDDs and PCDFs as impurities in 23 current use and 4 obsolete pesticide formulations in Australia were determined. PCNB samples were found to contain the highest levels among the current use pesticide formulations, with the average concentration of 1,500 ng g^{-1} AI, ranging from 1,100 to 2,000 ng g^{-1} AI (n=3 formulations). TEQ levels in the three PCNB formulations were also elevated with average lower bound concentrations of 3.9 ng g^{-1} AI, ranging from 2.4 to 5.6 ng g^{-1} AI, respectively. PCNB was widely produced and used in many countries over the past decades. For instance, the total production of PCNB in China was about 1,000 t a^{-1} (Wang 2010), and the usage of PCNB in the USA was estimated at 349–454 t a^{-1} (EPA 2006). The high volume use of such a pesticide may represent an important dioxin source to the environment in particular when considering that PCDD/Fs and TEQ levels increased when PCNB (and 2,4-D) are exposed to sunlight (Holt et al. 2012). As indicated by the Australian Pesticides and Veterinary Medicines Authority (APVMA), a risk to health for workers applying the PCNB products in some situations will be caused by these impurities. APVMA then suspended the approvals for quintozene and all products containing quintozene in April 2010, which has been extended in April 2011 (APVMA 2010, 2011). Due to the same reason, recently the Environmental Risk Management Authority of New Zealand has revoked the approvals for the quintozene after a reassessment (ERMA 2010, 2011). Also in the USA, the sale of PCNB products was suspended by the Environmental Protection Agency (EPA) in 2010.

Unlike the Japanese survey, the DL-PCBs have not been included in the Australian or other studies assessing unintentional POPs in pesticides.

Despite of its ban in many countries, PCNB is still produced and used in China. According to the Registered Pesticide Information System maintained by the Ministry of Agriculture, there are 2 records of raw pesticides and 25 records of formulations in China (China Pesticide Information Network 2014). Shanxi Sanli Chemical Co., Ltd and Shandong Dezhou Tianbang Agrochemical Co., Ltd are producers of registered raw pesticide products of PCNB. All registered formulations are produced using the raw pesticide products from these two companies with annual production of PCNB products in China of about 1,000 t a^{-1} (Wang 2010). China has issued product specification standards for two types of PCNB products, i.e., HG2460.1-93 for PCNB raw pesticide and HG2460.2-93 for 40 % PCNB powder formulation.

In the present study, the concentration levels and congener profiles of PCDDs, PCDFs and DL-PCBs were analysed in five Chinese PCNB products and the corresponding TEQ levels were calculated. The results are compared with the levels reported for PCNB products in other countries and also compared with the limit defined by Japanese MAFF as a reference. In addition, the concentrations of PeCBz, HCB, and 13 non-dioxinlike-PCBs (ndl-PCBs) including the 7 indicator PCBs were investigated.

Materials and methods

Samples and chemicals

Five PCNB products including two raw pesticide products and three pesticide formulations were collected for analysis. These products were purchased individually from the producers during the period of 2010 to 2011. The products were selected due to their large volume of production and consumption in China. Detailed information about the producers and content of AIs are shown in Table 1

All organic solvents used for extraction and cleanup were pesticide residue analysis grade or HPLC grade, and purchased from J. T. Baker (New Jersey, USA). Silica gel (0.100–0.210 nm in diameter) was obtained from Kanto Chemicals Co., Inc. (Tokyo, Japan). $^{13}C_{12}$-labeled and unlabeled native standard solutions of PCDD/Fs and PCBs were purchased from Cambridge Isotope Laboratories (Massachusetts, USA).

Sample pretreatment

The main purpose of pretreatment is to improve the concentration of the target compounds and reduce the matrix interference. All of the steps were made to achieve this purpose. The flowchart of the analytical procedure is shown in Fig. 1. Aliquots of each sample (0.1–0.2 g) was firstly extracted for 16 h using Soxhlet extraction with dichloromethane (DCM) as the solvent, based on the methodology for extracting of solid pesticide samples by Masunaga et al. (2001). The extraction was spiked with 0.5–1 ng $^{13}C_{12}$-labeled 2,3,7,8-PCDD/Fs and $^{13}C_{12}$-labeled PCBs internal standards as the cleanup spike, corresponding to 7 PCDDs, 10 PCDFs, 12 DL-PCBs, and 13 other PCBs as target analytes. Details about the spiked internal standards are shown in Table S1 in supporting information.

The extract was concentrated and then sequentially subjected to sulfuric acid treatment and multi-layer silica gel [anhydrous Na_2SO_4 (6.0 g), 10 % (*w/w*) $AgNO_3$-silica (3.0 g), silica (0.9 g), 22 % (*w/w*) H_2SO_4-silica (6.0 g), 44 % (*w/w*) H_2SO_4-silica (4.5 g), silica (0.9 g), 2 % (*w/w*) KOH-silica (3.0 g), silica (0.9 g)] 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 the 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 DL-PCBs internal standards as syringe spike, then filled up with nonane to 50 μL. A second fraction eluted with dichloromethane/hexane (1:3, *v/v*) as the eluent was carried out for the determination of the other 8 mono-ortho DL-PCBs. However, significant interferences from the sample matrix were observed in this fraction. Therefore, the mono-ortho DL-PCBs had to be determined additionally. For this purpose, an aliquot 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 five $^{13}C_{12}$-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 including the 7 indicator PCBs were also included in the cleanup spike added.

Instrumental analysis

Quantification and identification was 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 have been described in a previous paper (Huang et al. 2011).

Quality assurance and quality control

The minimum detection limit (DL) and the minimum quantification limit (QL) were determined according to Chinese

Table 1 Information about five samples determined

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

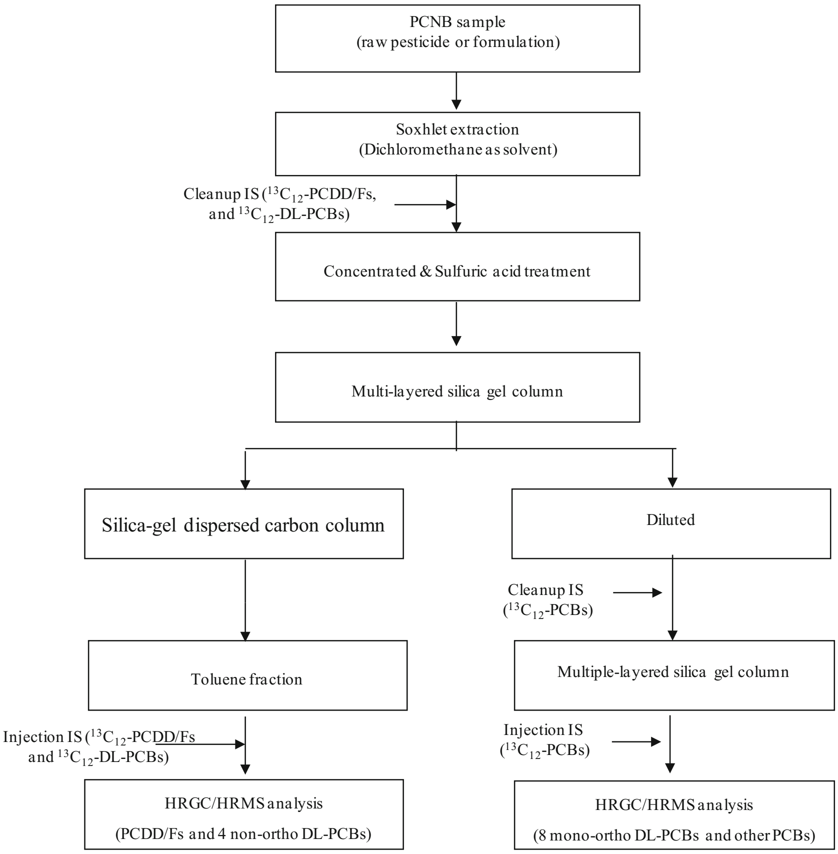


Fig. 1 Flowchart of the analytical procedure

standard HJ 77.3-2008 method. Briefly, each compound in the standard solution for calibration curve of the minimum concentration was quantified 5 times, and then the standard deviation (SD) was calculated. Threefold of the SD was taken as DL for the instrument (IDL) and tenfold of the SD was taken as QL for the instrument (IQL). In addition, blanks containing threefold of the IDL concentrations were analysed five times, and the SD was calculated for each compound. Threefold of the blank SD was taken as DL for the method (MDL) and tenfold of the SD was taken as QL for the method (MQL). DL for the sample (SDL) and QL for the sample (SQL) were calculated from MDL and MQL, respectively. The variability of analytical procedure was assessed by replicate analysis of all samples. Analytical blanks were included to assure 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 (0.26 to 0.93 ng TEQ g^{-1}) and DL-PCBs (0.68 to 2.5 ng TEQ g^{-1}) in five Chinese PCNB product samples are shown in Table 2 (more detailed results are shown in Table S2 and Table S3 in supporting information). Levels of total TEQ ranged between 0.94 ng TEQ g^{-1} and 3.6 ng TEQ g^{-1}. Duplicate analysis was conducted for each sample, and both lower bound and upper bound TEQ values were calculated and showed good consistency (Table 2) indicating that the analytical method used was robust and reliable.

The levels in the formulated PCNB recalculated to active ingredient were higher compared to the raw pesticide. For example, the raw pesticide from one producer contained 3.5 ng TEQ g^{-1} while the TEQ content in the formulation was approximately 10 ng TEQ g^{-1} AI. This might be explained by a formation of PCDD/Fs and PCBs in the formulation process (e.g., milling, other mixing procedures). Further additional studies are needed to assess this possibility. Also, components other than the active ingredients of the pesticide formulations might be assessed for possible contamination.

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 demonstrates that for an appropriate assessment of dioxin-like toxicity from unintentionally produced POPs impurities in PCNB pesticides, the DL-PCBs need to be included in the measurement. The same is possibly true for other pesticides and organochlorine chemicals based on chlorinated aromatic compounds. For

Table 2 TEQ (WHO2005) levels of PCDD/Fs and DL-PCBs in the investigated PCNB samples (ng TEQ g^{-1})

	Compounds	#R1	#R1 (replication)	#R2	#R2 (replication)	#F1	#F1 (replication)	#F2	#F2 (replication)	#F3	#F3 (replication)
Lower bound	TEQ (PCDDs)	0.006	0.007	0.150	0.160	0.004	0.005	0.010	0.009	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	0.80	0.38	0.39
	TEQ (DL-PCBs)	0.69	0.68	2.4	2.5	1.9	2.1	0.85	0.80	1.4	1.7
	Total TEQ	*0.96*	*0.94*	*3.3*	*3.5*	*2.0*	*2.3*	*1.5*	*1.6*	*1.8*	*2.1*
	TEQ (DL-PCBs)/Total TEQ (%)	*72*	*72*	*73*	*71*	*95*	*91*	*57*	*50*	*78*	*81*
Upper bound	TEQ (PCDDs)	0.060	0.060	0.220	0.230	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	0.40	0.41
	TEQ (DL-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*
	TEQ (DL-PCBs)/Total TEQ (%)	*69*	*68*	*71*	*69*	*90*	*91*	*57*	*50*	*78*	*81*

In the present study, one of the highlights is 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 demonstrates that for an appropriate assessment of dioxin-like toxicity from unintentionally produced POPs impurities in PCNB pesticides, the DL-PCBs need to be included in the measurement. However, in the study conducted by Holt et al. (2010), they only determined the contents of PCDDs and PCDFs in PCNB pesticide formulations. They did not report data on DL-PCBs. It is possible or most likely that the PCNB formulations in Australia also contained relevant DL-PCB levels and that the PCDD/Fs TEQ and inventory considerations from the Australian study considerably underestimated the total TEQ burden. Based on this reasons, we want to highlight the total TEQ levels including both TEQ (PCDD/Fs) and TEQ (DL-PCBs) and the contribution from DL-PCBs.

example, DL-PCB have also been detected as impurities in chlorinated pigments (Anezaki and Nakano 2014; Hu and Hornbuckle 2010). Therefore, appropriate risk assessment with respect to dioxin-like toxicity can be conducted only by considering both PCDD/Fs and DL-PCBs contamination in organochlorine pesticides and other organochlorine compounds.

When comparing the lower bound TEQ values in the Australian study (Holt et al. 2010) with those of the present study, the TEQ levels caused by PCDD/Fs in Chinese PCNB product samples were approximately one order of magnitude lower. Since for all Chinese PCNB samples (including sample #R2 dominated by OCDD and therefore similar to the Australian congener pattern), DL-PCBs were the major TEQ contributors. It is possible or most likely that the PCNB formulations in Australia also contained relevant DL-PCB levels and that the PCDD/Fs TEQ and inventory considerations from the Australian study considerably underestimated the total TEQ burden.

Based on the current study results, the total TEQ from the total Chinese production volume of approximately 1,000 tonnes of PCNB per year (Wang 2010) can be roughly estimated between 1.0 g and 10 g TEQ a^{-1}. The total release of TEQ to the environment may be even higher considering the increase of PCDD/Fs and TEQ concentrations during sunlight exposure of PCNB (Holt et al. 2012).

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

The main congeners detected in five Chinese PCNB product samples were highly chlorinated compounds (Table 3; Table S2 and S3). For some samples, the OCDD dominated total PCDD/Fs concentration while in other samples the PCDFs were present at higher levels.

There is currently no regulatory limit for dioxins as impurities in pesticides in China (and almost all other countries!). Therefore, the limit issued by Japanese Ministry of Agriculture, Forestry and Fisheries was used here for comparison as a reference. The congeners responsible for exceedance of the Japanese regulations are shown in Fig. 2a, including OCDD and two PCDFs congeners (1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF) and two DL-PCBs congeners (PCB #126 and PCB #169). As shown in Fig. 2a, all five PCNB products exceeded the Japanese limit for one or more congeners. These results indicate that the use of these products may result in unacceptable risk, due to the PCDD/Fs and in particular DL-PCBs as impurities.

The study of Holt et al. (2010) described PCDD/Fs concentrations in contemporary PCNB pesticide samples collected in the Australian market without mentioning on the origin of production. Holt et al. (2010) also did not report data on DL-PCBs. The main detected 2,3,7,8-PCDD/Fs congeners in the Australian market study (Fig. 2b), included two PCDDs congeners (OCDD and

Table 3 Concentration of PeCBz, HCB, PCDD/Fs and DL-PCBs in the investigated PCNB samples (ng g^{-1})

	Compounds	#R1	#R1 (replication)	#R2	#R2 (replication)	#F1	#F1 (replication)	#F2	#F2 (replication)	#F3	#F3 (replication)
PeCBz	–	–	–	0.29	0.30	0.12	0.12	0.09	0.10	0.04	0.04
HxCBz	–	–	–	50	52	12	13	13	14	4.2	3.7
PCDDs	TeCDDs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	PeCDDs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	HxCDDs	ND	ND	0.11	0.11	ND	ND	0.1	0.1	0.11	0.1
	HpCDDs	0.45	0.48	1.9	2.1	0.23	0.25	0.46	0.37	1.7	1.8
	OCDD	11	13	470	500	10	11	7.2	6.9	54	57
	Total PCDDs	11	13	472	502	11	11	7.8	7.4	56	59
PCDFs	TeCDFs	1.0	0.48	0.65	0.84	0.17	2.0	0.13	0.70	0.19	0.38
	PeCDFs	0.8	0.66	4.6	5.2	0.42	0.59	0.37	0.40	2.2	2.2
	HxCDFs	3.0	2.9	16	17	1.9	2.3	6.6	8.1	5.2	5.2
	HpCDFs	8.3	8.3	24	26	5.6	5.9	6.8	6.1	14	15
	OCDF	37	36	93	100	31	31	30	27	76	80
	Total PCDFs	50	48	138	149	39	42	44	42	98	103
DL-PCBs	Non-ortho PCBs	12	12	64	68	37	40	19	18	35	42
	Mono-ortho PCBs	9.2	7.5	55	59	4.9	4.8	3.9	3.3	32	42
	Total DL-PCBs	21	19	110	120	41	44	23	21	67	84

ND not detected (i.e., lower than the reporting limit)

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 had a similar pattern as in our study. All three samples of Holt et al. (2010) would also have exceeded the limit of the Japanese standard, even for four or more congeners (Fig. 2b).

The significant difference of PCDD/Fs concentrations in the Australian study compared to our Chinese study is probably caused by differences in the production process. This might indicate that the measured PCNB from the Australian market have been produced by other producers (e.g., PCNB is/was also produced in the USA and Mexico) or that within the time of pesticides sampling from the Australian market (2008) and the sampling of the Chinese products (2011) the Chinese producer might have modified their production as a response to publication of the impurity data (Holt et al. 2010); including a conference in China (Holt et al. 2009) and the resulting ban of quintozene in several countries.

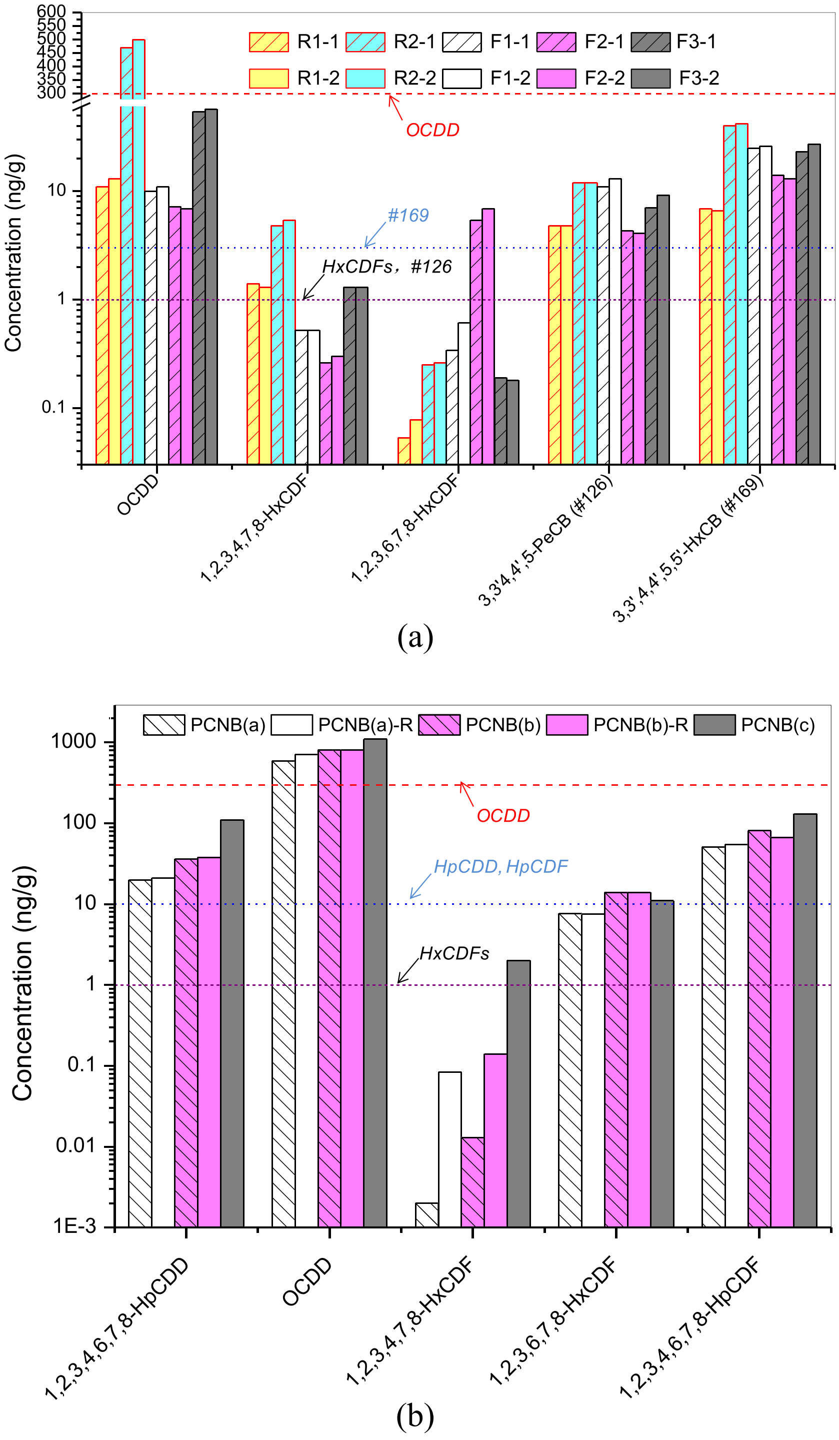
In addition to PCDD/Fs and DL-PCBs, we also assessed the concentrations of 13 ndl-PCBs including the seven indicator PCBs in Chinese PCNB products (Table S2 and S3). High levels of DecaCB (240 to 2,700 ng g^{-1}) and lower levels of NonaCB (110 to 410 ng g^{-1}) and OctaCB (37 to 270 ng g^{-1}) were detected. However, the seven indicator PCBs were below the detection limits of around 10 ng g^{-1}. For the HeptaCBs, the PCB 189 (3.9 to 43 ng g^{-1}) was the dominant congener while the indicator HeptaCB 180 was not detected. This demonstrates that the formation of the PCBs is largely triggered by condensation of chlorobenzenes and that the chlorination of biphenyl resulting in the formation of high levels of indicator PCBs had not a measurable relevance in PCNB production.

Hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) which are listed as POPs in the Stockholm Convention were also detected in Chinese PCNB samples and therefore formed unintentionally in the production process (see Table 3). The HCB levels were 3.7 to 52 ng g^{-1} (18 to 55 ng g^{-1} AI) and PeCBz levels were two orders of magnitude lower at 0.04 to 0.30 ng g^{-1} (0.20–0.32 ng g^{-1} AI). Based on the production volume and the measured concentrations, the total release of HCB and PeCBz were 18 to 55 g a^{-1} and 0.20 to 0.32 g a^{-1}, respectively.

Some considerations regarding formation of PCBs and PCDD/Fs in the production process

PCNB can be produced by either the chlorination of nitrobenzene or the nitration of chlorinated benzenes (EHC41 1984). According to the information provided by the producers, the production processes for the two Chinese PCNB raw pesticides were similar, as shown in Fig. 3. Briefly, the autoclave was filled with chlorosulfonic acid as solvent, and then nitrobenzene (in Shandong Dezhou Tianbang Agrochemical Co., Ltd.) or *m*-chloronitrobenzene (in Shanxi Sanli Chemical Co., Ltd.) was used as the raw material and iodine as the catalyst (typically 0.3 %). After heating to 60–100 °C, the chlorine gas (Cl_2) was introduced while stirring the mixture continuously. The hydrogen chloride (HCl) generated was bumped into the adsorption kettle by a water injector. After the chlorination was completed, the mixture was educed and filtered. The chlorosulfonic acid

Fig. 2 **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. (2010)



(a)

(b)

was returned to the recycling kettle. The filter cake was water-washed to be neutral and reclaimed, and the washing water was sent to the neutralization tank for treatment.

Dorrepaal and Louw (1978) and Sommeling et al. (1993) suggested a pathway of PCBs formation from chlorobenzene (CBz) radicals as shown in Fig. S1 in supporting information. Liu et al. (2001) confirmed by experiments that PCBs are formed by pyrolysis of CBz in an HCl atmosphere at 250 to 340 °C. However, in the production of Chinese PCNB product, the temperature is considerably lower (95–105 °C) with still significant amount of PCBs formed. The reaction involving elemental chlorine with aromatic compounds is however triggering radical reactions. The recombination of aromatic radicals can result in the formation of bi-aromatic molecules like PCBs. Since the levels of chlorobenzene are relatively low (low ppb level), a direct recombination of chlorobenzenes radicals seems unlikely. The

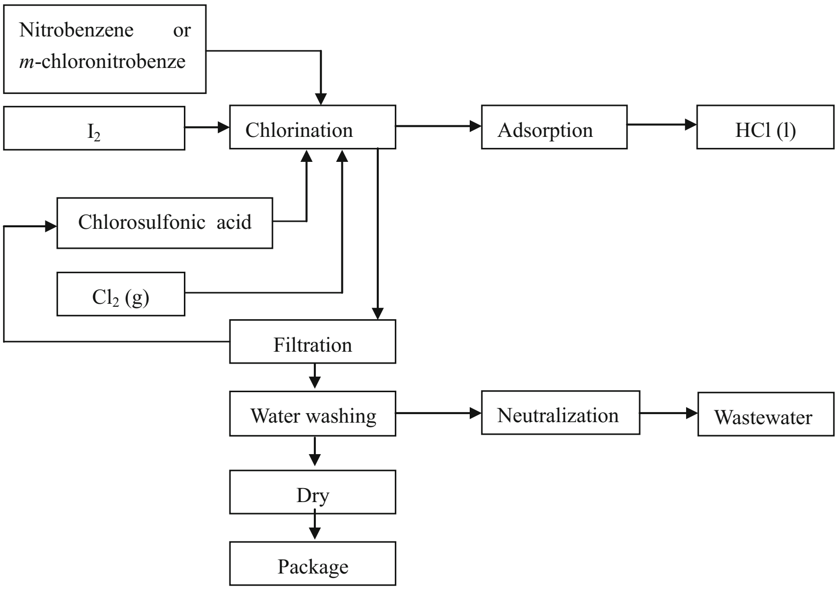


Fig. 3 Production process for Chinese PCNB raw pesticides

main precursor molecules are most likely chlorinated nitrobenzene. An initial step might be the formation of chlorobenzene radicals by elimination of the nitro-group. For a detailed understanding, the behavior of the nitro-group in radical reactions in the presence of chlorine needs to be further elucidated which is however out of the scope of this paper.

The dimerization of chlorinated aromatic compounds including chlorobenzene or chlorophenol by radical mechanisms has been documented as important precursors of PCDD/Fs (Chen et al. 2011; Weber and Hagenmaier 1999). Liu et al. (2004) proposed the formation pathway of PCDD/Fs from CBz based on their synthesis study of 1,4-DiCBz, as illustrated in Fig. S2 in supporting information. In the production of Chinese PCNB product, there are conditions favoring PCDD/Fs formation similar to those described in the study of Liu et al. (2004). Therefore, analoguous dimerization pathways via radical mechanisms can be considered for PCDFs and PCDDs formation. For a detailed elucidation of the actual formation mechanism, the role of the nitro-group needs to be elucidated. It should also be assessed if the difference in PCDD/F concentration between the two producers depends on the different educts (*m*-chloronitrobenzene and nitrobenzene).

Conclusions

According to the present study, DL-PCBs need to be included when assessing PCNB formulations for their dioxin-like toxicity. Furthermore, when considering the relatively few data in literature and in the UNEP toolkit, it is necessary to pay more attention to unintentionally formed DL-PCBs in organochlorine pesticides and other aromatic organochlorine compounds.

Considering the significant difference of PCDD/Fs concentrations found in Chinese products and products on the Japanese and Australian market, differences in production processes and probably refining processes exist between the different producers (and time of production). The significant difference of PCDD/Fs concentrations found in Chinese products and products on the Japanese and Australian market suggests that production of PCNB could be optimized towards low PCDD/F and PCB content by modifying or refining processes (BAT/BEP). However, optimized PCNB formulation still has the problem that PCNB itself is persistent in the environment and additionally can form PCDD/Fs under sunlight with related TEQ increases that exceed even the provisional low POPs content of the Basel Convention for waste of 15 μg TEQ g^{-1} (Holt et al. 2012). Furthermore, PCNB degradation is considered the largest source of global pentachlorobenzene release (UNEP 2010). Relevant environmental management measures, such as establishing environmental standards for products, should be established to eliminate dated production technology. The best approach in our opinion is the phase in of alternatives including integrated pest management to reduce or even eliminate the use of PCNB products.

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