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Occurrence, behavior and human health risk assessment of dechlorane plus and related compounds in indoor dust of China

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HIGHLIGHTS

- Dechlorane compounds were measured in indoor dust across China.
- Higher concentrations of DP were found in urban and public samples.
- Sources of DP and "DP-like" compounds were different in indoor dust.
- Health risk of exposure to DP and related compound were acceptable.

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ABSTRACT

Levels of dechlorane plus (DP) and "DP-like" compounds were measured in indoor dust samples collected across China. The concentrations of ΣDP and "DP-like" compounds ranged from 0.35 to 1000 ng g^{-1} and < 0.21 to 2.4 ng g^{-1}, respectively. The total DP concentration in urban sites were significantly higher than those of rural sites, while no significant difference was found for "DP-like" compounds, suggesting different sources of these compounds. Significant positive correlations were found between f_{syn} and latitude, and between f_{syn} and longitude. The deleterious risk associated with DP exposure via indoor dust for the general population in China was low and safer than expectation. For estimating human exposure via indoor dust, sensitivity analysis showed that more attention should be given to the influential variables such as the level of pollutants, body weight, and the amount of ingestion and adsorption.

1. Introduction

Dechlorane plus (DP) is a highly chlorinated flame retardant primarily used in cable coating, plastic roofing material, computer monitors and furniture (Betts et al., 2006; Sverko et al., 2011). It was initially known as a possible replacement for mirex around the 1970s (Hoh et al., 2006), and had been used as an alternative to decabromodiphenyl ether flame retardant according to the European Commission (The European Commission Report, 2011). Their occurrence in environment were firstly reported in the North American Great Lakes Basin (Hoh et al., 2006). To date, DP has been consistently detected in the environment worldwide (Venier and Hites, 2008; Hites et al., 2010; Möller et al., 2010; Xiao et al., 2012), indicating its long-range atmospheric transport. It was reported that DP exposure altered the hepatic alkoxyresorufin O-dealkylase activity and contributed to the biological effect in a 90-day oral exposure study in quail (Li et al., 2013).

Dechlorane 602 (Dec 602), dechlorane 603 (Dec 603), and dechlorane 604 (Dec 604) are "DP-like" compounds used as substitutes for mirex (Feo et al., 2012), which was banned in the 1970s due to their environmental effects (Kaiser, 1978). These "DP-like" compounds were also shown the similar properties with flame retardants (International Programme, 2009). According to the Nondomestic Substances List issued by Environmental Canada, Dec 602 and 604 are still in use (CEPA Environmental Registry, 2009). Dec 604 was considered as an impurity in a commercial product of mirex (National Toxicology Program, 1990), which has been used for termite control in China (Jia et al., 2011). Dec 602, 603, and 604 were firstly identified in the sediment of the Laurentian Great

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Lakes (Shen et al., 2009), and thereafter in a canal near the DP manufacturing plant in Huai'an, China (Wang et al., 2010b), in the suspended sediments of Niagara River in relatively low concentrations (Shen et al., 2011), and in the coastal environment of Northern China (Jia et al., 2011).

In China, DP has been detected in China's air (Ren et al., 2008; Yang et al., 2012), soil (Ma et al., 2011a; Yu et al., 2010), sediment (Qi et al., 2010), oyster (Jia et al., 2011), and water recently (Qi et al., 2010; Ma et al., 2011b). Anpon Electrochemical Co., Ltd, a major DP manufacturer in Huai'an, China, was recently held responsible for the high concentration of DP in the surrounding environment (Wang et al., 2010a; Xian et al., 2011). Accordingly, identifying the potential environmental impact and adverse health effects due to the production and/or use of Dechlorane compounds necessitated their study through measurements.

Indoor environment quality is critical for human health. It was found that direct occupational exposure could lead to higher DP levels in the blood and hair of exposure groups than those in control groups (Zhang et al., 2013). House dust serves as a repository and concentrates of several persistent organic pollutants (Sjödin et al., 2003). For example, evidence showed that ingestion and dermal contact with house dust contributed to 82% of polybrominated diphenyl ethers (PBDEs) exposure for Americans (Lorber, 2007). The exposure to house dust accounted for 56–77% of the total PBDE intakes in five different age groups in the USA (Johnson-Restrepo and Kannan, 2009). Another similar study revealed that house dust was a major exposure pathway for DP in China (Zheng et al., 2010). However, there was limited information on the occurrence of DP in indoor dust across China. Therefore, the objectives of the present study are to investigate the pollution patterns of dechlorane compounds in Chinese indoor dust, and to study their behaviors and sources as well as to estimate their potential health risk.

2. Methods

2.1. Sample collection, preparation and analysis

The detail of sample collection, preparation and analysis can be found in Supplementary Material. A total of 81 dust samples, including 45 from home house and 36 from public buildings, were collected across China between January and March in 2010. According to the sampling location, 55 of samples can be considered as urban samples and 26 as rural samples. Therefore, in this study all the samples were divided into 2 groups for comparison, urban vs. rural, and public vs. home. More detailed description of sample compositions was given in our previous study (Qi et al., 2014). Dust samples were collected by volunteer participants with a pre-cleaned brush that was used to sweep the floor under desks, shelves, beds, and so on. The dust was packed in aluminum foil and combined as one sample from different locations in each site. Large debris and particles were removed from the samples such that all of the dust samples can be considered as fine fraction of indoor dust, which is suitable for chemical analysis. After being spiked with surrogate CB-155, 0.2 g of dust sample was ultrasonic extracted 3 times with hexane/acetone (1:1, v/v). The extracts were purified with a silica gel column. A known amount of internal standard (octachloronaphthalene) was added to the extracts before the final volume was adjusted to 1.0 mL with isooctane. The samples were analyzed by Agilent 6890 GC-5975 MS under negative ion chemical ionization conditions.

2.2. Quality assurance and control

Precleaned sodium sulfate powder was prepared as a surrogate for dust in the method blank samples ($n = 8$) and spiked blank samples ($n = 8$), which were treated as real samples in the whole procedure for blank checking and recovery testing. All the target chemicals were negligible in the method blank samples. The average recoveries of DP in the spiked blank samples and CB-155 in the real samples were 83.4 ± 12.1% and 89.2 ± 10.5%, respectively, which were in the acceptable range from 70% to 130%. Values of the minimum amount of analyte which produced a peak with a signal to noise ratio of 10 were used as the method detection limit (MDL). The MDLs were in the range of 0.05–0.11 ng g^{-1} for the target compounds. The reported concentrations were not recovery and blank corrected. Values below MDLs were replaced with half of MDLs for data analysis.

3. Results and discussion

3.1. DP and Dec in the indoor dust

3.1.1. Levels and spatial distribution of DP

As presented in Table 1, the concentrations of these two major isomers, syn-DP and anti-DP, ranged from < 0.08 to 610 ng g^{-1} and 0.35 to 690 ng g^{-1}, respectively. The median concentration of anti-DP (2.8 ng g^{-1}) was almost 3 times higher than that of syn-DP (1.0 ng g^{-1}), which was close to the isomer ratio of 3:1 in their technical products (Zhu et al., 2007). As expected, syn-DP was positively and significantly correlated with anti-DP ($p < 0.0001$, $r = 0.88$).

DP was prevalent in indoor dust with high detection rates in the present study (Table S2). Similarly, it was detected in all the dust sample (median: 7.3 ng g^{-1}) in Vancouver, Canada (Shoeib et al., 2012). The levels of ΣDP in the present study ranged from 0.35 to 1000 ng g^{-1} with a median concentration of 4.0 ng g^{-1}. Consistent DP levels (median: 4.5 ng g^{-1}) have been reported in house dust samples collected in California during 2011 (Dodson et al., 2012). Compared to other studies in China, these values were 3 times lower than those of dust samples collected in Guangzhou, China in 2008–2009 (Wang et al., 2011). The highest levels of these contaminants were formerly reported to be related to e-waste recycling activities. For instance, a median concentration of 540 ng g^{-1} (Wang et al., 2011) and a mean concentration of 1500 ng g^{-1} (Zheng et al., 2010) had been reported in some e-waste recycling regions in China, which were approximately 2–4 orders of magnitude higher than those in the present study. It should be pointed out that the present study collected the reservoir dust rather than recently settled dust, which may overestimate the concentration. Furthermore, our sampling technique for indoor dust was different from those of previous studies (Table S2), which should be also considered for the direct comparison.

Spatial distribution of DP concentrations showed higher levels in the Northern China (Fig. 1). However, our previous study on outdoor air across China showed higher concentration and detection

Table 1
Summary statistics for dechlorane compounds concentrations in house dust (ng g^{-1}).

Compound	N[a]	Range	Mean(SD)	Median
Dec 602	38	<0.05–0.64	0.06(0.09)	<0.05
Dec 603	6	<0.05–0.20	0.02(0.03)	<0.05
Dec 604	2	<0.11–2.0	0.03(0.22)	<0.11
ΣDec	38	<0.21–2.4	0.08(0.27)	<0.21
syn-DP	80	<0.10–610	14(76)	1.0
anti-DP	81	0.35–690	19(80)	2.8
ΣDP	81	0.35–1000	33(140)	4.0
f_{syn}	80	0.07–0.84	0.29(0.14)	0.26

[a] Number of samples above detection limit.