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Dechlorane plus (DP) in indoor and outdoor air of an urban city in South China: Implications for sources and human inhalation exposure

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ABSTRACT

Dechlorane Plus (DP) is a chemical of emerging concern due to the restrictions on brominated flame retardant formulations. However, very little information is known about the occurrence of DP in indoor and outdoor air and its associated health risk to the exposed human population. In this study, we examined the concentrations and isomer profiles of DP in archived air samples collected from 14 homes, 6 offices, and 10 public microenvironments in Guangzhou, China in 2004–2005. The average (median) value of atmospheric Σ DP (sum of *anti*-DP and *syn*-DP) concentration in the three indoor air was 5.73 ± 5.33 (3.62) for offices, 8.08 ± 5.17 (6.87) for homes, and 57.27 ± 83.08 (32.58) pg/m^3 for public microenvironments, respectively. Σ DP concentration was significantly higher in the public microenvironments than those in homes and offices. The arithmetic mean and median concentrations of Σ DP in outdoor air were 36.00 and 28.76 pg/m^3 , respectively. Spatially and temporally consistent indoor and outdoor samples comparison suggested that outdoor air might be a relevant source of DP for indoor air. Average *anti*-DP fractional abundance ($f_{\text{anti}} = 0.65 \pm 0.04$) in all outdoor samples was similar to those reported in other studies and indistinguishable from that of the commercial mixture ($f_{\text{anti}} = 0.65$). In contrast, a relatively large variation of f_{anti} values was found in the indoor samples, suggesting a complex degradation process of DP existing in these microenvironments. The calculated average daily doses of Σ DP were in the range of 0.38–2.21 ng/day for people intake through air inhalation, which was in the same order of magnitude compared with other exposure pathways for the general publics.

KEYWORDS



Dechlorane plus; air; microenvironment; South China; inhalation

Introduction


Dechlorane Plus (DP) is a kind of chlorinated flame retardant, which was introduced into the market in the 1960s to replace the toxic Dechlorane or Mirex (Hoh et al., 2006). As the flame retardant, commercial DP mixture was commonly used in consumer products such as industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing material (Tomy et al., 2007). DP is an unregulated chlorinated flame retardant, and its annual production was estimated to be over 5000 tons (Ren et al., 2008). With the restrictions on production and usage of some brominated flame retardant such as polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs), the production of DP was supposed to increase as an alternative in some applications. In China, there is only one DP manufacturer, located in Huai'an, Jiangsu Province, which began to produce DP since 2005. Its annual

output is about 300 tons. However, there is little available information about the usage, import, and export of DP in China (Wang et al., 2010).

DP has the typical characteristics of persistent organic pollutants: high lipophilicity, resistance to photo- and biodegradation, and accumulation in fish (Dechlorane Plus Manual, www.oxy.com). This understanding has been corroborated by a series of recent reports. DP had been detected in a wide range of abiotic and biotic samples from North America (Su et al., 2015, Zhu et al., 2007), Europe (L'Homme et al., 2015, Rjabova et al., 2015), and Asia (Kakimoto et al., 2015, Ren et al., 2008). Recent study also demonstrates that DP could be bioaccumulated in the human body and could undergo possible dechlorinated metabolism (Chen et al., 2015, Kim et al. 2016, Ren et al., 2009, Siddique et al., 2011). DP has two isomers, *syn*-DP and *anti*-DP, with different environmental behavior and fates. Stereoselective enrichment

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of DP had been observed in sediment (Hoh et al., 2006), indoor dust (Zhu et al., 2007), biotic organism (Tomy et al., 2007), and human serum (Ren et al., 2009). Nevertheless, available information on the pattern of DP Stereoselective enrichment was inconsistent. Commonly, f_{anti} values in air sample were similar or equal to that of the commercial product (Kakimoto et al., 2015, Moeller et al. 2010, Ren et al., 2008, Yu et al., 2011). However, relatively lower f_{anti} values could be observed and a great variation of these values was found in biotic organism and indoor dust (Tomy et al., 2007, Zhu et al., 2007). In contrast, higher f_{anti} value also could be observed in sediment and sediment core (Ma et al., 2014, Tomy et al., 2007).

Since DP-containing materials and products are primarily used indoors, they may slowly volatilize into the environment during the lifetime of products (Tomy et al., 2007). As a result, there remains the possibility of DP contamination of indoor microenvironments where such items are located. Despite these facts, up to now, a few studies have examined DP concentrations in matrices relevant to human exposure, such as indoor dust and air. DP has been detected in residential indoor dust in the city of Ottawa, with a concentration ranging from 2.3 to 5683 ng/g (Zhu et al., 2007), which was comparable to the level in indoor dust samples collected across China (0.35–1000 ng/g) (Li et al., 2015). DP has been reported in ambient air concentrations around the Great lakes with mean concentration ranging from no detection up to 490 pg/m³ in the air near the Great Lakes (Hoh et al., 2006); the higher DP concentrations and unexpected spatial trend in this study indicated that DP's manufacturing plant may be a primary emission source. A study of airborne DP across 97 Chinese urban and rural areas found that the mean concentration of Σ DP at urban sites (15.6 pg/m³) is higher than that at rural sites (3.5 pg/m³) (Ren et al., 2008), which was clearly an urban effect. In Japan, DP was detected in all samples and Σ DP concentrations ranged from 7.1 to 15.4 pg/m³ (Kakimoto et al., 2014). In Nepalese, DP was identified in 100% of indoor air samples with mean concentrations of Σ DP ranging from 0.67 to 129 pg/m³ (Yadav et al., 2017). The lower DP concentrations and f_{anti} values suggested that the DP level in these studies were essentially affected by the long-range atmospheric transport from remote DP source instead of commercial products.

To our knowledge, only a few studies had reported DP concentrations in the ambient air (Hoh et al., 2006, Ren et al., 2008, Kakimoto et al., 2014) and no previous study was found for DP air concentrations in spatially and temporally consistent indoor and outdoor samples. All of these warranted further study to systematically evaluate the relative significance of human exposure via inhalation of indoor and outdoor air. The objectives of this

study were to determine the DP concentrations in air samples taken from a variety of buildings, compare them with those present in temporally consistent outdoor air, and assess the potential significance of inhalation as a pathway of human exposure to DP. Moreover, the main potential indoor emission sources and distribution of two DP isomers were evaluated.

Experimental section

Chemicals and materials

Individual solutions of the *syn*- and *anti*-DP (50 μ g/mL, in toluene, purity >95%), chlorinated diphenyl congener 209 (PCB-209), and the ¹³C mass labeled PCB-141, PCB-208 were supplied by Wellington Laboratories (Guelph, ON, Canada). All calibration standards and spiking solutions were prepared by serial dilution in n-hexane using volumetric flasks. All of the solvents used for the extraction and cleanup were redistilled using a glass system. Air samples were collected using a high-volume air sampler. Prior to sampling, the quartz fiber filters (QFFs, 20.3 cm \times 25.4 cm, Whatman) were baked at 450°C for 6 hours to remove any organic contaminant, and polyurethane foam plugs (PUFs, 6.5 cm in diameter, 7.5 cm in thickness) were Soxhlet extracted for 48 hours with methanol and for another 48 hours with acetone:hexane mixture (1:1). After sampling, GFFs and PUFs were wrapped with clean aluminum foils and stored at -20°C until extraction.

Sampling location

Detailed sampling sites and the information on microenvironment characteristics were described in reference (Chen et al., 2008) and the supporting information (Figure S1). Briefly, fourteen homes (H1–H14) and 16 workplaces [including 6 offices (OF1–OF6) and 10 other indoor microenvironments (Indoor1–Indoor10)] located in Guangzhou and Foshan cities were selected as indoor air sampling between October 2004 and April 2005. The 10 indoor microenvironments included two ordinary furniture shops, one large electrical appliances shop, two general retail outlets for consumables, two large furniture warehouses, one cloth material warehouse, and two instrument rooms.

Sampling strategy

Air samples were collected at ground level using a high-volume air sampler at 0.4–0.7 m³/min for 8–20 hours. Air was pumped through QFFs to trap the suspended particulate matters and subsequently through PUF to

trap the gaseous matters. To minimize underestimation of concentrations that might occur when the volume of air sampled exceeded the volume of the room, sampling was conducted for a period equivalent to sampling one home volume, allowed to reequilibrate for the same period, and followed by a repeat of the procedure. During sampling the windows of the indoor environment were closed and each yielded sample volumes of 175–385 m³. Outdoor air samples were taken using the same equipment for about 20 hours (approximately 300–840 m³ was taken). On completion of the sampling, we recorded the number of computers and other items of electronic equipment (VCRs, TVs, videos, refrigerators, microwaves etc.) to identify the potential sources of DP. The number of PUF-containing furniture were also recorded. For 8 indoor locations, spatially and temporally consistent outdoor air samples were collected for the convenience of comparison of DP concentrations in indoor and outdoor air. One outdoor air sample (Outdoor8) from the suburban was also included. For ease of reference, a numerical identifier to each indoor and outdoor sample was supplied in the supporting information (Table S1).

Sample Preparation and Cleanup

These samples were primarily used for the determination of polybrominated biphenyl ethers (PBDEs) and a detailed description of the methods used for the extraction and cleanup protocol of air samples has been published elsewhere (Chen et al., 2008). Briefly, surrogate standards (PCB-209 and ¹³C-PCB-141) were added to all samples, the PUF plugs and QFFs were Soxhlet-extracted with acetone:hexane mixture (1:1) for about 72 hours. Concentrated samples were then cleaned and fractionated on acid/basic multilayer silica gel columns with 70 mL of dichloromethane: hexane (1:1) as eluant. The final extracts were concentrated to 200 μL under a gentle nitrogen stream and a known amount of internal standard (¹³C-PCB-208) was added before injection. After analysis of PBDEs by GC-MS, the extracts were sealed and stored at <−20°C as archived samples.

Instrumental analysis

The samples were analyzed for the two DP isomers using an Agilent 7890 series gas chromatograph coupled to an Agilent 5975 C mass spectrometer (GC/MS) with highly purified helium as the carrier gas. Manual injection (1 μL) was made in the pulse splitless mode with a purge time of 2.0 minutes. The injection port and the GC to MS transfer line were held at 280°C and 300°C, respectively. A 15 m DB-5-HT MS column (250 μm i.d;

0.10 μm film thickness; J&W Scientific, Folsom, CA) was used for the DP analysis. The GC oven temperature program was as follows: held at 110°C for 5 minutes, 20°C/min to 200°C, held for 4.5 minutes, and then 7.5°C/min to 300°C, held for 16 minutes. The mass spectrometer was operated in the electron capture negative ionization mode using methane as the reagent gas, and the ion source and the quadpole temperature was 230°C and 150°C, respectively. The following ions were monitored: m/z 475.7 and 473.7 for the internal standard (¹³C-PCB-208), m/z 372.7 and 374.7 for ¹³C-PCB 141, m/z 498 and 500 for PCB-209, m/z 653.7 and 651.7 for DP.

Quality assurance and quality control

DP was analyzed using ¹³C-PCB-208 as internal standards. Since there is no obvious difference in extraction efficiencies between DP and the lesser chlorinated PCB, we choose the PCB surrogate recovery as the indicator of DP recovery, the spiked PCB recoveries averaged 73.5–86.7%, no recovery correction was applied to the DP in the samples. Laboratory blank samples (clean GFFs spiked with PCB surrogate) were treated and analyzed in the same way as the regular samples and constituted about 20% of the total samples analyzed. DP concentrations in the blank samples were undetectable or lower than the method detection limit (MDL) of 0.5 pg/m³. In this paper, concentrations have not been blank or recovery-corrected.

Data analysis

Statistical analysis for DP concentrations in air was performed using SPSS statistical software package, version 19.0 (SPSS Inc., USA). The statistical significance of air DP concentrations between different categories was conducted by independent-sample *t* test. Linear regression analysis was conducted to investigate correlations between DP in air and the number of PUF-containing furniture and electronic equipment. Statistical significance was defined as a *p*-value less than 0.05.

Results and discussion

DP concentrations in different categories of indoor and outdoor air

Most DP isomers were found to be in particle phase, with less than 1% in gas phase; therefore, particle phase was chosen for determining concentrations of these compounds in all samples. The arithmetic and geometric mean, the median, and the minimum and maximum concentrations of DP isomers measured in indoor

(including home, workplace) and outdoor air are summarized in Table 1. As shown in Table 1, DP was detected in all the air samples; the average (median) concentrations of atmospheric Σ DP in the three indoor microenvironments are 5.73 ± 5.33 (3.62), 8.08 ± 5.17 (6.87), and 57.27 ± 83.08 (32.6) pg/m^3 for office, home, and other microenvironment, respectively. No significant difference was found between DP level in the home and office samples ($p = 0.36 > 0.05$). However, the concentrations of DP in other microenvironment were significantly higher than those in home and office ($p < 0.05$), suggesting that point emission sources of DP were likely located in those microenvironments. Specifically, the highest indoor DP air concentration (Σ DP 284.46 pg/m^3) was detected in a large electrical appliances shop (indoor10), which is in accordance with our hypothesis that the shop was a DP hotspot and thus exhibited elevated DP levels. The arithmetic mean and median of DP concentrations in outdoor air are 36.00 ± 31.67 and $28.76 \text{ pg}/\text{m}^3$, respectively. In summary, the mean values of DP concentrations in outdoor are slightly higher than those for indoor air, with a clear cut indoor-outdoor gradient.

A simple comparison based on the reported concentrations of DP in ambient air in China and other different areas in the world was made between our data and the data from these studies. DP has been reported in ambient air concentrations around the Great lakes with mean concentration ranging from no detection up to $490 \text{ pg}/\text{m}^3$ in the air near the Great Lakes (Hoh et al., 2006). Recently, some data were emerging on DP levels in air from urban and rural area in Asia (Kakimoto et al. 2015, Ma et al., 2010, Ren et al., 2008).

Compared to the DP values in these studies, the outdoor DP levels found in this study ($36 \pm 32 \text{ pg}/\text{m}^3$) are similar to those ($34 \pm 24 \text{ pg}/\text{m}^3$) from the site close to a DP-manufacturing plant, but slightly higher than those reported from other urban and rural sites. However, it is unfair to conclude that environmental levels of DP were relatively higher in China than those in other countries. For example, studies had demonstrated that the ambient DP levels in Harbin and Shanghai were similar to those in some rural sites in the Great Lakes area and Global background levels over the Atlantic Ocean, which were all at lower levels (Moeller et al., 2010). The relatively higher DP levels in this study may be attributed to two factors. The first factor may be the degree of contamination. Our sampling sites in Guangzhou and Foshan are important commercial and industrial bases in South China and surrounded by the e-waste (electronic waste) recycling region such as Guiyu and Qingyuan (Xiao et al., 2013). Very high DP concentrations in the environmental samples were reported at the e-waste area. High DP concentrations in the air in this study were likely associated with the practice of e-waste dismantling in the nearby region. The second factor may be associated with the design of this project. Since a part of our study was planned to identify the potential sources of DP, DP outdoor air contamination was determined in several shops selling products potentially containing DP; the values obtained in this study may not represent the actual level in ambient air from Guangzhou. Our previous study has demonstrated high PBDEs concentrations in the same samples (Chen et al., 2008).

Bearing in mind that DP is similar to the highly brominated BDEs (nona- to deca-BDEs) with the high molecular weight and high $\log K_{ow}$ ($\log K_{ow} = 9.3$) and

Table 1. Summary of DP levels (pg/m^3) in indoor (a) and outdoor (b) air samples.

	Workplace											
	Office (n = 6)						Other microenvironment (n = 10)					
	Min	Max	Median	Mean	S.D.	Geo-mean	Min	Max	Median	Mean	S.D.	Geo-mean
(a) indoor air												
<i>syn</i> -DP	0.93	6.25	1.54	2.29	1.98	1.84	1.87	140.06	8.95	24.08	42.35	9.75
<i>anti</i> -DP	1.08	10.10	2.20	3.44	3.36	2.57	6.61	144.41	23.32	33.19	40.85	21.53
Σ DP	2.49	16.35	3.62	5.73	5.33	4.46	10.16	284.46	32.58	57.27	83.08	32.08
Home (n = 14)												
	Min	Max	Median	Mean	S.D.	Geo-mean	Outdoor (n = 8)					
(a) indoor air												
<i>syn</i> -DP	0.53	8.82	3.82	4.13	2.90	3.01	(b) outdoor air					
<i>anti</i> -DP	0.86	10.67	3.80	3.95	2.60	3.26	2.34	30.82	9.30	12.05	10.49	8.39
Σ DP	1.40	19.49	6.87	8.08	5.17	6.48	4.08	58.60	19.46	23.94	21.21	16.10
All indoor (n = 30)												
	Min	Max	Median	Mean	S.D.	Geo-mean	7.09	89.42	28.76	36.00	31.67	24.56
(a) indoor air												
<i>syn</i> -DP	0.53	140.06	4.08	10.41	25.66	4.04						
<i>anti</i> -DP	0.86	144.41	4.19	13.60	26.86	5.84						
Σ DP	1.40	284.46	9.84	24.00	52.27	10.25						

Table 2. Spearman's correlation coefficient among levels of highly BDEs congeners in air samples.

	BDE-208	BDE-207	BDE-206	BDE-209	\sum^{9-10} PBDEs	s-DP	a-DP	\sum DP
BDE-208	1.000	1.000	0.988	0.502	0.800	-0.081	-0.089	-0.086
BDE-207		1.000	0.988	0.499	0.798	-0.081	-0.091	-0.088
BDE-206			1.000	0.613	0.872	-0.066	-0.061	-0.064
BDE-209				1.000	0.921	-0.029	-0.021	-0.002
\sum^{9-10} PBDEs					1.000	-0.056	-0.019	-0.036
syn-DP						1.000	0.950	0.985
anti-DP							1.000	0.990
\sum DP								1.000

**Correlation is significant at the 0.01 level (2-tailed). \sum^{9-10} PBDEs = sum of BDE-208, 207, 206 and 209

they are all distributed in the particle phase of air, we think that a comparison of these compounds' concentration would be pertinent. Clearly, the concentration of DP in the same microenvironment was significantly lower than BDE-209 (data from reference (Chen et al., 2008)), and the average DP levels were about 25 to 180 times lower than those of the BDE-209 in terms of the GM values and 30 to 500 times lower than those in terms of the median values. These discrepancies in concentration were likely due to the differences in production volume and usage patterns between the two flame retardants in China. Correlations between high BDEs and DP isomers in all the air samples were analyzed using spearman's correlation matrices (Table 2). The results showed good correlation coefficients among

nona- to deca-BDEs, and different DP isomers; however, poor correlations were obtained between \sum DP and high BDEs in air samples. This result suggested that these two kinds of compounds may have no coexisting sources. Similar result had been reported in indoor dust sample from Canada (Zhu et al., 2007).

Factors influencing DP levels in indoor air

The detailed concentration of DP in indoor and outdoor air samples from South China are summarized in Table 3. The detailed sampling information is shown in Table S1. As indicated in Table 3, the DP concentrations in indoor air of offices were the lowest in the three different microenvironments studied. Specifically, DP levels in these

Table 3. average DP concentration (pg/m³) in indoor and corresponding outdoor air samples from South China (n = 2 or 3).

indoor concentration level				corresponding outdoor concentration level			
sample code	syn-DP	anti-DP	\sum DP	sample code	syn-DP	anti-DP	\sum DP
Home							
H1	2.05	3.96	6.02	outdoor1	9.80	15.23	25.03
H2	1.95	3.33	5.29	outdoor1	9.80	15.23	25.03
H3	1.50	2.60	4.09	outdoor1	9.80	15.23	25.03
H4	5.37	7.15	12.53	outdoor1	9.80	15.23	25.03
H5	5.94	5.91	11.84	outdoor1'	11.94	24.91	36.85
H6	4.80	4.19	8.99	outdoor1'	11.94	24.91	36.85
H7	3.63	1.69	5.31	outdoor1'	11.94	24.91	36.85
H8	8.58	3.81	12.39	outdoor1'	11.94	24.91	36.85
H9	6.86	4.62	11.48	outdoor1'	11.94	24.91	36.85
H10	2.78	2.40	5.18	outdoor2	2.25	5.35	7.60
H11	0.99	1.73	2.45	outdoor3	3.13	4.97	8.09
H12	2.65	2.99	5.64				
H13	0.53	0.86	1.40				
H14	0.83	1.85	2.67				
Office							
OF1	1.15	1.79	2.94	outdoor1	9.80	15.23	25.03
OF2	1.20	1.98	3.19	outdoor1	9.80	15.23	25.03
OF3	1.27	1.03	2.30	outdoor2	2.25	5.35	7.60
OF4	2.20	3.50	5.70	outdoor2	2.25	5.35	7.60
OF5	0.93	1.56	2.49				
OF6	5.20	6.45	11.66	outdoor5	14.21	28.60	42.81
Other microenvironment							
Indoor1	4.30	6.86	11.16	outdoor1	9.80	15.23	25.03
Indoor2	2.14	8.24	10.38	outdoor4	4.00	8.04	12.03
Indoor3	2.07	8.35	10.42	outdoor5	14.21	28.60	42.81
Indoor4	7.42	18.66	26.08	outdoor5	14.21	28.60	42.81
Indoor5	6.26	16.33	22.58	outdoor5	14.21	28.60	42.81
Indoor6	10.57	24.36	34.93	outdoor6	21.93	44.71	66.64
Indoor7	17.43	25.95	43.38	outdoor6	21.93	44.71	66.64
Indoor8	48.32	47.97	96.29	outdoor6	21.93	44.71	66.64
Indoor9	11.35	27.06	38.41	outdoor7	39.85	72.83	112.68
Indoor10	94.19	103.35	197.93	outdoor7	39.85	72.83	112.68
				outdoor8*	4.87	5.99	10.86

* a suburban sample with no corresponding indoor sample.

office environments were not relevant to the numbers of computer. This is somewhat surprising, as we preliminarily thought the computers used in these offices were one of the most important sources of these contaminants. Although the information indicate that commercial DP mixture was commonly used in consumer products such as industrial polymers used for coating electrical wires and cables, connectors used in computers, our result demonstrated that this flame retardant may not be used in these articles in China.

Concentrations in homes were generally higher than in office environment, though this difference was not statistically significant (t -test, $p > 0.05$). To specify the sources of DP in houses, linear regression analysis was conducted to investigate correlations between DP in air and the number of polyurethane foam plug (PUF)-containing furniture and electronic equipment in homes. No correlation was found between concentrations of DP and the number of PUF-containing furniture; however, weak positive correlation ($r^2 = 0.33$) was found between the numbers of electronic equipment in corresponding individual home. The most likely explanation for this is that the origin of DP in these microenvironments is not related to personal computers or PUF-containing furniture but related to other items of electronic equipment (such as VCRs, TVs, videos, refrigerators, microwaves, etc.). Unfortunately, information on the usage of DP in China is not available, at the same time we did not record the detailed information on the electronic equipment in individual home. To examine within-building variation in concentrations, two buildings from the same community were selected. H1–H4 and H5–H10 were located in the different buildings within the same community. There was a wide variation in concentrations detected in samples within the same building, which indicated that the origin of DP in these microenvironments was not related to the building overall but related to characteristics of individual house.

In an attempt to identify sources and factors that impact the concentrations in various microenvironments, ten samples were collected from other

microenvironments (indoor1-10). Overall concentrations in other microenvironments were highest of the three indoor categories. The much higher concentration of DP could be ascribed to the different functions of these microenvironments. DP levels in the two instrument rooms (only have computers and analytical instruments) were closer to those in office and home environment which was consistent with our extrapolation that computers were not a major source of DP in indoor air. The highest DP level was found in indoor10 which is a large electrical appliance shop. It was possible that there was a large inventory of DP-treated electronic/electrical equipment from all over the world for sale in this shop. I/O (indoor/outdoor) ratios can be an important indicator of pollutants infiltration (Menichini et al., 2007). In this study indoor DP concentrations were compared with the ambient outdoor samples within the same building. As indicated in Figure 1, the I/O ratios are below or closer to 1 for most of the samples, implying that the indoor air may not be a second source to the outdoor. In contrast, in the bedding shop (indoor 8) and electrical appliances shop (indoor 10) with good ventilation, the I/O ratio is 1.44 and 1.75, respectively. The high I/O ratio further verified that these shops are sources of DP to outdoor and outdoor regional environment.

In summary, while there are many different factors influencing DP levels in indoor environment, such as ventilation rate, age of potential sources, extent of usage source items, and so on, our preliminary observations do suggest that the computer and PUF-containing furniture are not major sources of indoor DP pollution; further monitoring of DP sources in all kinds of microenvironment categories are warranted.

DP isomer ratio in indoor and outdoor air

Commercial DP mixture is primarily comprised of two isomers, *syn*-DP and *anti*-DP, with different environmental behaviors and fates. In this study, the relative abundance of *anti*-DP (f_{anti}) was defined as the *anti*-DP concentration

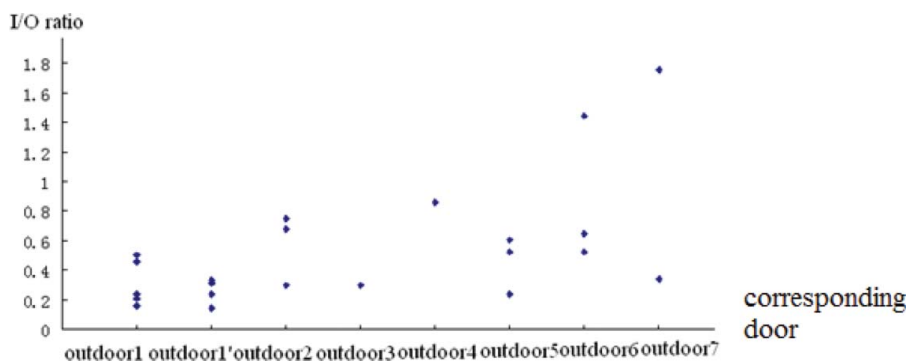


Figure 1. The I/O ratio of DP in indoor air compared with the corresponding outdoor air.

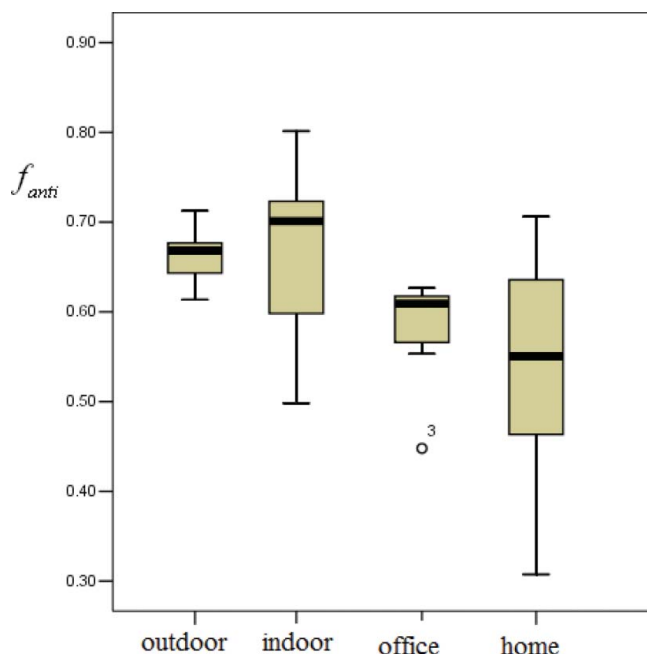


Figure 2. The f_{anti} values for the outdoor, indoor, office, and home samples.

divided by the sum of the *syn*- and *anti*-DP concentrations in the cases where both compounds were detected. These values are presented in Figure 2. As shown in Figure 2, mean values of f_{anti} were 0.65 ± 0.04 , 0.67 ± 0.10 , 0.58 ± 0.06 , 0.53 ± 0.13 for outdoor, indoor, office, and home samples, respectively. Mean values of f_{anti} in outdoor and indoor samples were similar to the values of a commercial mixture, implying that no remarkable stereoselective degradation of DP occurred in these air samples. Similar results were also reported in other studies. Qiu and Hites had demonstrated relatively constant f_{anti} values in the ambient air measured in the Great Lakes (Qiu & Hites 2008). A study on airborne DP across 97 Chinese urban and rural areas found mean f_{anti} values of 0.68 and 0.66, respectively. The similar f_{anti} ratio in these studies suggest that industrial DP products have mainly impacted on these environmental DP levels. Obviously, the mean values of f_{anti} in office and home samples were significantly lower than those of the commercial products ($f_{anti} = 0.65\text{--}0.80$) in other reports. Relatively lower f_{anti} values have also been reported in samples from e-waste area, including soil, dust, and human samples (Ren et al., 2009, Sun et al., 2016, Xiao et al., 2013). A likely explanation for this observation is that, *syn*- and *anti*-DP possess differing physicochemical

Table 4. Calculated human exposure (ng/day/person) to DP through inhalation.

	Min	Max	Median	Mean
<i>syn</i> -DP	0.014	1.05	0.061	0.131
<i>anti</i> -DP	0.023	1.17	0.103	0.164
\sum DP	0.038	2.21	0.162	0.290

properties leading to variation of the stereoisomer profiles, which is supported by Occidental Chemical's test plan. According to that plan, the two isomers had different aqueous solubility at 207 ng/L and 572 ng/L, although no information was given as to which isomer exhibited which solubility. A simple UV exposure study of individual DP also showed that *anti*-DP was degraded more readily than *syn*-DP. In perspective of the photo-degradation and isomerization of *anti*-DP over *syn*-DP, we expect that the DP level in these environments could be fundamentally impacted by local DP emission. In other words, the f_{anti} ratio of commercial DP have been transformed by light or thermo before it is emitted into the surrounding environment. However, available information on the pattern of DP stereoselective enrichment is inconsistent. Stereospecific metabolism of *anti*-DP and/or isomerselective uptake of *syn*-DP can be found in organisms. A trophic transfer study also indicated that organisms with higher trophic positions might have higher metabolic capacities for *anti*-DP (Wu et al., 2010). On the other hand, Sverko et al. (2008) and Qiu et al. (2007) reported stereoselective enrichment of the *anti*-isomer (high f_{anti} values) in surface sediment and sediment cores from Great Lakes. Further work should be carried out to study the environmental fate and transfer of individual isomer.

Exposure to DP via air inhalation

The presence of DP in indoor and outdoor environments could have implications for potential human exposure to this chemical. Using the data obtained from the study, we have estimated the likely range and arithmetic mean of human intake of DP via inhalation. Minimum, mean, and maximum daily exposures via inhalation (assuming 100% absorption of intake) were calculated using the following algorithm:

$$\sum \text{Exposure}_i = ([C_w F_w] + [C_h F_h] + [C_o F_o]) R_r$$

where $\sum \text{Exposure}_i$ is the daily adult human exposure via inhalation (ng of DP person/day), $C_{w/h/o}$ is the concentration in all kinds of microenvironment air, R_r is the adult respiration rate (20 m³/day), $F_{w/h/o}$ is the respective fraction of daily time spent at workplace/home/outdoor. Based on several reports, the typical percentage of time spent outdoor, indoor of working place, and home have been assumed to be 8.3%, 23.8%, and 67.9%, respectively. Using the above algorithm, daily human exposure via gas inhalation was calculated and it is shown in Table 4. The uptake of total DP through inhalation was 0.038–2.21 ng/day, with an average of 0.29 ng/day for a typical

person, which was much lower than those obtained in our previous study for the intake of BDE-209 (Chen et al. 2008). In that study, the calculated mean daily human exposure to BDE-209 is 54.6 ng/day/person (range 2.3–276.6 ng/day/person). At present, a few studies have examined DP concentrations in matrices relevant to human exposure. The estimated DP inhalation (0.29 ng/day) is comparable to that reported for urban areas in Japan with an average of 0.17 ng/day for a Japanese adult (Kakimoto et al., 2014). However, the exposure doses of our DP estimate were higher than those in Nepalese (0.04–0.08 ng/day) (Yadav et al., 2017). Zhu et al. estimated the exposure of adults to DP via dust ingestion in the city of Ottawa, Canada (Zhu et al., 2007). If 100% absorption of intake was assumed, the estimated central values of DP daily intake, derived from the average dust ingestion and the median level of DP in house dust, are 0.46 ng/day for a typical person. In the case of general public, food consumption is another important exposure route. Based on Belgian food habits (L'Homme et al., 2015), a dietary intake was estimated to be 0.14 ng/day. From the comparison of the median daily human exposure to DP with the above-mentioned study, it can be seen that air inhalation contributed equal magnitude of total DP exposure, indicating that exposure through air inhalation was probably one of the important pathways for the background person. Nevertheless, we have to note that an exact comparison has to be made among various routes of exposure, and it should be the same place where the data comes from. Unfortunately, there was a lack of data on DP levels in the same location at present.

Conclusion

This study provided valuable baseline data on the occurrence and potential sources of DP in the Chinese indoor and outdoor environment. DP was detected in all of the air samples, indicating that Chinese residents are exposed to DP in daily life. Σ DP concentration was significantly higher in the public microenvironments than those in homes and offices. Spatially and temporally consistent indoor and outdoor sample comparison suggested that outdoor air might be a relevant source of DP for indoor air. The f_{anti} values for outdoor samples were relatively constant and similar to the values of a commercial mixture. However, relatively lower f_{anti} values with large variation were found in home samples, suggesting a complex degradation process of DP existing in these microenvironment. The estimated daily inhalation dose of DP was in equal magnitude with other exposure pathways, indicating that

exposure through air inhalation may be another important pathway for the background person.

Supplemental data for this article can be accessed on the publisher's website.

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