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Dechlorane Plus in serum from e-waste recycling workers: Influence of gender and potential isomer-specific metabolism

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ABSTRACT

Dechlorane Plus (DP) and its dechlorinated product, *anti*-Cl_{11}-DP, were measured in serum of 70 occupationally exposed workers in an e-waste recycling region and 13 residents of an urban area in South China. The DP levels were significantly higher in the workers (22–2200 ng/g with median of 150 ng/g lipid) than in the urban residents (2.7–91 ng/g with median of 4.6 ng/g lipid). The DP concentrations in females were found to be associated with their age but such relation was not found for males. Significant differences in DP levels and DP isomer composition were found between genders. The females had remarkably higher DP levels and f_{anti} values (fraction of *anti*-DP to total DPs) in serum than the males. *Anti*-Cl_{11}-DP was significantly correlated with *anti*-DP for both genders but with different slope of regression line. The ratios of *anti*-Cl_{11}-DP to *anti*-DP (mean of 0.017) in males were significantly higher than those (mean of 0.010) in females. Combining with the lower f_{anti} values in males, it is likely that males have higher metabolic potential for DPs than females which resulted in the lower DP loading in serum. However, the different patterns of selective uptake and/or excretion of different compounds between genders cannot be eliminated as a possible reason for the observed gender differences. This study is the first to report on the gender difference in DP accumulation in human, and its mechanism is worth further investigation.

1. Introduction

Dechlorane Plus (DP), a highly chlorinated flame retardant, was first introduced in the 1960s to replace mirex. Consisting of the *syn* and *anti* isomers in a ratio of 1:3, DP technical mixture is produced by the Diels–Alder condensation of hexachlorocyclopentadiene and 1,5-cyclooctadiene in a 2:1 molar ratio. It is widely used in roofing material for commercial buildings, electrical wires and cables, furniture, and other polymeric systems in order to enhance product safety by preventing fire (Betts, 2006). DP is currently classified as a low production volume chemical in the EU, but it has been identified by the U.S. Environmental Protection Agency as a high production volume chemical, meaning that DP is produced or imported into the U.S. in quantities of at least 450000 kg/year (Xian et al., 2011). DP was listed as a potential alternative to decabromodiphenylether (Deca-BDE) in polymer applications by European Commission, and its usage may thus increase in the future (The European Commission, 2007).

Despite its commercial longevity, DP had received little attention on its environmental and health impacts. The two DP isomers were first detected in air, fish, and sediment in the Great Lake (Hoh et al., 2006). Since then, numerous studies reported the occurrence of DPs in biotic and abiotic samples (Sverko et al., 2011; Xian et al., 2011). These studies had demonstrated that DP is environmentally ubiquitous, persistent, and has the potential for bioaccumulation. In a recent study by Möller et al. (2010), DP was found in air and sea water samples from Greenland to Antarctica, indicating that DP is globally spread through atmospheric transport. Moreover, the degradation products of DPs either by dehalogenation or retro-Diels–Alder processes had been detected in various environment compartments such as sediment and dust, and human tissues such as hair and serum (Sverko et al., 2008; Wang et al., 2011; Zheng et al., 2010). However, no hydroxylated, methoxylated and methyl sulfone degradates were found in fish liver extracts following dietary exposure of DP (Tomy et al., 2008).

Little information exists on differences in environment behavior and fate, and human exposure, between the two DP isomers. Studies so far have shown differences based on the matrix sampled and the geographic areas of the studies (Sverko et al., 2011; Xian et al., 2011). For examples, the f_{anti} values, defined as the concentration of *anti*-DP divided by the total DP, were higher in sediment samples from Lake Ontario than that in DP commercial products (Qiu et al., 2007; Tomy et al., 2007). This

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suggests that *syn*-DP is more vulnerable to micro-organism induced degradation in sediments. However, a general trend towards decreasing f_{anti} values in aquatic biota with increasing trophic level was found, indicating that syn-DP seems more bioaccumulative than the anti-isomer in aquatic biota (Wu et al., 2010; Kang et al., 2010). We have been able to identify only three studies of DP levels in humans, including one in which DPs were detected in human serum (Ren et al., 2009), one in hair (Zheng et al., 2010), and one in milk (Siddique et al., 2012). In addition to isomers, degradation products of DPs were detected in human serum and hair (Ren et al., 2009; Zheng et al., 2010). However, the source of these degradation products in human is not known — it could be the result of internal dechlorination of the isomers or the humans could be exposed to the degradation product itself. Finally, little is known regarding the role of some important factors like gender, age, and occupational exposure time on the body burden of the DP isomers.

The purpose of this study was to investigate the serum concentrations of DP and its dechlorination products in e-waste recycling workers and urban residents. We collected serum samples from these two groups in a region in South China. The possible influences of age, occupational exposure time, gender and metabolism on levels of DP were also investigated.

2. Materials and methods

2.1. Sampling population

A total of 83 volunteers participated in this study. Among them, 70 volunteers were occupationally exposed workers who worked in e-waste recycling workshops in Longtang Town, Qingyuan County. The detailed description of this sampling area had been given in a previous report (Zheng et al., 2010). As a control group, the other 13 participants were living in Guangzhou City and they have no occupational exposure experience. Guangzhou city is located approximately 50 km south of Qingyuan County. It is the capital of Guangdong province and the largest urban center in South China. All volunteers in this study provided informed written consent before participation. A short questionnaire was completed by each participant covering information about age, gender, weight, height, and occupational history. The study was approved by the Ethics Committee in School of Life Sciences, Sun Yat-sen University. The volunteers were aged between 20 and 59 years old, and the sex ratio of male to female was 48:52.

2.2. Sample collection

From each subject, approximately 8–10 ml venous blood sample was collected with an anticoagulant-free tube by medical professionals in local hospital between May 2011 and July 2011. The serum was immediately frozen after blood centrifugation, and then transported and kept at −80 °C in laboratory until chemical analysis.

2.3. Chemicals

Standards of *syn*-DP, *anti*-DP, and two dechlorination products of *anti*-DP (1,6,7,8,9,14,15,16,17,17,18-octadeca-7,15-diene, termed *anti*-Cl_{11}-DP; and 1,6,7,8,9,14,15,16,17,17-octadeca-7,15-diene, termed *anti*-Cl_{10}-DP) were obtained from Wellington Laboratories (Ontario, Canada). Surrogate standards (BDE77 and BDE181), and internal standard (BDE128) were obtained from Ultra Scientific (North Kingdom, RI). Organic solvents were redistilled using a glass system.

2.4. Sample cleanup and analysis

The extraction and purification method for DP was similar to that previously published for analysis of DP in serum samples (Ren et al., 2009). The sample extraction, cleanup and analysis of DP and PBDEs were operated together, so the surrogate standards and internal standards used in PBDEs were employed here for DP as well. In brief, 3–4 ml serum of each sample was transferred to a Teflon centrifuge tube and spiked with two surrogate standards (BDE77 and 181) to monitor the recoveries. After incubated overnight in darkness at room temperature to ensure equilibrium of the serum with the standards, the serum was denatured using1.5 ml of 6 M HCl and 8 ml of 2-propanol, and vortexed for 30 s after each addition. The sample was afterwards extracted three times, each time with 10 ml hexane/methyl-tert-butyl ether (MTBE) (1:1, *v*/*v*) and centrifuged at 2500 rpm for 20 min for better separation. The combined extract was then added with 5 ml 1% KCl solution and the mixture was centrifuged at 2500 rpm for 5 min. The organic layer was transferred and the lipid was removed by adding 4 ml of concentrated sulfuric acid. After centrifuging at 2500 rpm for 15 min, the organic layer was transferred to a clean tube. The aqueous fraction was re-extracted twice with 6 ml of hexane in a similar manner. The combined extracts were further cleaned by a multi-layer silica/alumina column using 35 ml of hexane/dichloromethane (1:1, *v*/*v*) as the eluent, and finally condensed to 100 μl under a gentle stream of nitrogen. Before injection, known amounts of internal standard (BDE128) were added. Total lipid content in individual human serum sample was calculated by a pre-reported regression equation using total triglycerides and cholesterol measured in serum (Rylander et al., 2006).

A Shimadzu 2010 gas chromatograph coupled with a mass spectrometer with electron capture negative ionization in a selected ion monitoring mode was used for DP quantification. The target chemicals were separated by a DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. Column temperature was initially set at 110 °C for 1 min, later adjusted to 180 °C at 8 °C/min (kept for 1 min), to 240 °C at 2 °C/min (kept for 5 min), to 280 °C at 2 °C/min (kept for 15 min), and to 310 °C at 10 °C/min (kept for 5 min). Methane acted as a chemical ionization moderating gas at an ion source pressure of 2.4×10^3 Pa. Helium was used as the carrier gas at a flow rate 1 ml/min. Injection of 1 μl sample was conducted with an automatic sampler in the splitless mode, with the injection port temperature set to 280 °C. Ion source and interface temperatures were set to 200 °C and 290 °C, respectively. Ion fragments *m*/*z* 653.8 and 651.8 were monitored for DP isomers; *m*/*z* 618.0 and 620.0 were monitored for *anti*-Cl_{11}-DP; *m*/*z* 584.0 and 586.0 were monitored for *anti*-Cl_{10}-DP; *m*/*z* 79 and 81 were monitored for BDE77, 181 and 128.

2.5. Quality assurance and control (QA/QC)

Milli-Q water was used in procedural blanks, and no target compound was detected. The recoveries of surrogate standards BDE77 and BDE181 were in the range of 74–115% and 73–106%, respectively. Recoveries of *syn*-DP, *anti*-DP, *anti*-Cl_{10}-DP, and *anti*-Cl_{11}-DP in spiked blanks were ranged 80–92%, 89–98%, 85–94%, and 83–91%, respectively. The limit of detection (LOD) was defined to a signal-to-noise ratio of 10. Using an average sample lipid weight of 0.0191 g, the limit of quantitations (LOQs) for *syn*-DP, *anti*-DP, *anti*-Cl_{10}-DP, and *anti*-Cl_{11}-DP were 3.08, 1.29, 0.51 and 0.64 ng/g lipid, respectively. The final results were not recovery corrected.

2.6. Statistical analysis

SPSS 16.0 software package was used for data analysis. Concentrations of all compounds were log transformed to achieve a normal distribution. The differences in DP concentrations between the e-waste workers and the control group, as well as between two genders were analyzed by Student's *t* test. Linear regression analysis was conducted to investigate correlations between *anti*-Cl_{11}-DP and *anti*-DP in e-waste workers. Correlations between concentrations and age, and between concentrations and occupational exposure time were tested using the Spearman's coefficient correlation. For this study, *p*-value less than 0.05 was considered statistically significant.

3. Results and discussion

3.1. Levels of DP in human serum

Anti-DP was consistently detected in all serum samples. *Syn*-DP was detected in all 70 samples from e-waste recycling workers but in only 3 out of 13 from the control group. The low detectable frequency of *syn*-DP in the control group may be partly attributed to its relatively high LOQ value (3.08 ng/g lipid), as well as the low *syn*-DP levels in urban residents. Serum DP concentrations ($\sum$DP, sum of the *syn*- and *anti*-DP isomers) ranged from 22 to 2200 ng/g lipid (median: 150 ng/g lipid) in occupational exposure workers and from 2.7 to 91 ng/g lipid (median: 4.6 ng/g lipid) in urban residents (Table 1). As expected, occupational exposure workers had significantly higher serum DP concentrations than residents in Guangzhou, which could be attributed to the emission of large amounts of DP from e-waste products during e-waste recycling and dismantling activities. It is also in line with our previous studies with environment and biota samples, in which the DP concentrations in this e-waste recycling area were significant higher than those in Guangzhou (Wang et al., 2011; Zheng et al., 2010).

To date, there has been only one report on serum DP concentrations in humans (Ren et al., 2009). DP levels (range of 7.8–470 ng/g with a median of 43 ng/g lipid) in the serum of residents from Guiyu, another e-waste recycling area in South China, were almost four times lower than the e-waste dismantling workers in our study (22–2200 with a median of 150 ng/g lipid). The participants in the study of Ren et al. (2009) were residents who were not categorized by occupation — their levels were closer to our control group (2.7–91 ng/g lipid with a median of 4.6 ng/g lipid) suggesting they may not have been occupationally exposed to DP. Our previous study found that the dust DP levels in e-waste recycling workshops were four times of those in residential area of the same region (Zheng et al., 2010). Thus, the elevation could be explained by their excess exposure to DP during work. The maximum concentration of DP (2200 ng/g lipid) was detected in a 48 year old female e-waste dismantling worker, which was also the highest reported concentration so far in biota and human samples.

No significant correlation was observed between serum DP concentrations and age in the e-waste recycling workers. When occupational exposure time rather than age was used to perform correlation analysis, there was still no significant correlation (Fig. 1). This result is in line with the observation in human serum in the research by Ren et al. (2009). However, when we present results in age ranges, <40, 40–49, and ≧50, by sex, results come to be different. For females, the DP concentrations were highest in the age group greater than 50, followed by the age group of 40–49, with the lowest concentrations found in the age group less than 40. A simple linear regression analysis showed that the DP concentrations in females were significantly correlated to age (Fig. 2). However, no differences between age groups and no relationships with age were found for men (Fig. 2). The different age effects between the genders might reflect the fact that DP half-lives are different between males and females. Males may have lower DP half-lives than females, which would result in the DP concentrations in males being more susceptible to short-term exposures than long-term exposure, and for DP concentrations in males generally being lower than in females. These are also consistent with our results that male might have higher metabolic potential than female, and thus DP are easier to be excreted out in male, which will be discussed later. In a previous study on hair DPs in residents living in the same sampling area as the present study (Zheng et al., 2010), seniors (aged more than 60) were found to have significantly higher hair DP levels than other age groups. Significant differences, however, were not observed between hair DP levels in children (aged below 6), adolescents (7–18), and adults (19–60). In the present study, all donors were less than 60 years of age, making it impossible to determine whether seniors would have higher serum DP lever than the other age groups.

3.2. Isomer profiles of DP

The two stereoisomers of DP, *syn*- and *anti*-, have different physical and chemical properties which lead to the variations in their persistence in the environment (Zhu et al., 2007). Therefore, isomer ratios can be used to trace the sources of DP and to explore the differences in environment behaviors between the two isomers. The fraction of *anti*-DP (f_{anti}) was defined as the concentration of *anti*-DP divided by the total DP. The f_{anti} in the serum from the e-waste recycling workers varied from 0.48 to 0.76, with a median of 0.66 (Table 1). Meanwhile, given that the concentrations of *syn*-DP were only detectable in three serum samples from the residents in the control group, f_{anti} could only be calculated using these three samples, with the values of 0.60, 0.71 and 0.56, respectively. It is, therefore, meaningless to compare the values of f_{anti} in control group with e-waste workers.

Although there are three industrial formulations of the technical mixture of DP which differ only in the particle sizes of the final products, several values of f_{anti} for commercial DP products were reported in the literature from 0.65 to 0.8 (Gauthier and Letcher, 2009; Hoh et al., 2006; Qiu et al., 2007; Sverko et al., 2008; Tomy et al., 2007; Wu et al., 2010), suggesting that the isomer ratio could vary from lot to lot during production of DP. The f_{anti} values in current study from

Table 1
Summary of characteristics, serum DP concentrations (ng/g lipid), and f_{anti} values of occupational exposed workers from an e-waste dismantling region (Qingyuan) and residents from a nearby urban region (Guangzhou), given as the median (range).

	E-waste dismantling workers			Controls		
	Male (n = 33)	Female (n = 37)	Total (n = 70)	Male (n = 7)	Female (n = 6)	Total (n = 13)
Age (years)	43 (22–57)	45 (20–59)	44.5 (20–59)	27 (25–40)	26 (24–46)	27 (24–46)
Occupational exposure time (years)	6 (1–20)	7 (2–20)	6.5(1–20)	0	0	0
BMI[a] (kg/m^2)	23.1 (18.3–28.7)	23.6 (17.5–30.8)	23.4 (17.5–30.8)	24.3 (19.1–26.3)	20.1 (18.2–22.5)	22.6 (18.2–26.3)
Syn-DP	45.3 (7.44–204)	80.7 (12.4–578)	52.7 (7.44–578)	3.01[b]	5.33 and 36.3[b]	nd (nd–36.3)[b]
Anti-DP	73.9 (14.2–495)	180 (15.0–1640)	103.6 (14.2–1640)	4.07 (2.66–7.50)	6.00 (3.15–54.9)	4.63 (2.66–54.9)
$\sum$DP[c]	121 (21.7–699)	265 (27.4–2220)	153 (21.7–2220)	4.07 (2.66–10.5)	8.66 (3.15–91.3)	4.63 (2.66–91.3)
Anti-Cl_{11}-DP	1.03 (nd–4.75)	1.68 (nd–9.93)	1.47 (nd–9.93)	nd	nd	nd
f_{anti}[d]	0.64 (0.48–0.73)	0.70 (0.52–0.76)	0.66 (0.48–0.76)	0.71[e]	0.56 and 0.60[e]	0.60 (0.56–0.71)[e]

nd = nondetected.
[a] BMI is a person's weight in kilograms divided by that person's height in meters squared.
[b] *Syn*-DP was only detectable in one male and two females in control group.
[c] The sum of *syn*-DP and *anti*-DP.
[d] *Anti*-DP/(*anti*-DP + *syn*-DP).
[e] f_{anti} could only be calculated in three samples in control group.

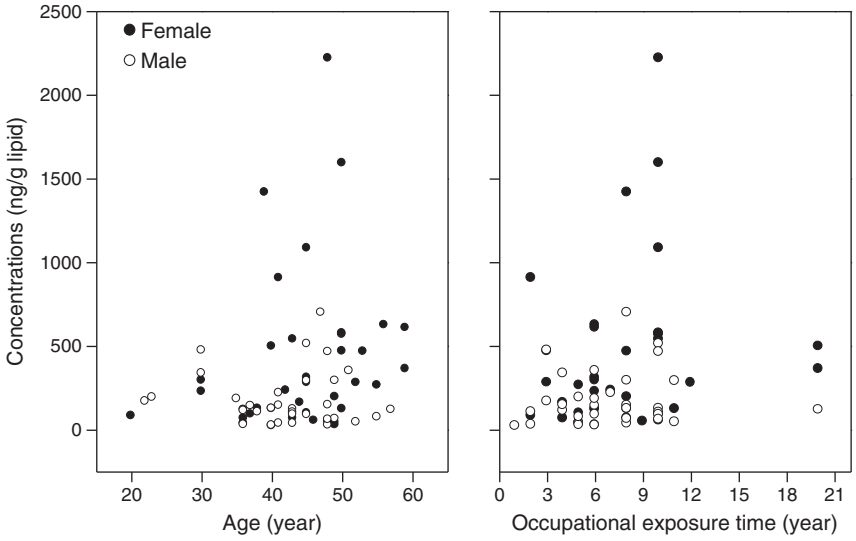

Fig 1. Relationships between serum DP concentrations and age or occupational exposure time in e-waste dismantling workers.

e-waste recycling workers ranged from 0.48 to 0.76, most of which were lower than the reported technical f_{anti} values. In the meantime, the range of f_{anti} values in the current study was similar with those (0.40–0.77) from the residents in another e-waste recycling area reported by Ren et al. (2009), while the mean from the two studies (0.65 and 0.58, respectively) appeared different. The differences in environmental DP isomer composition between the two sampling areas and in sex structure between the two sampling populations, may contribute to the observed divergence. In the present study, 47% participants were male compared to 73% in Ren et al. (2009), and it was found that the f_{anti} were significantly different between male and female. This will be discussed later in the last section.

The f_{anti} value in serum (0.65 ± 0.07) was higher than those (0.55 ± 0.11) in human hair of occupational workers from the same sampling region (Zheng et al., 2010). The lower f_{anti} values found in human hair of e-waste recycling workers may be attributed to the

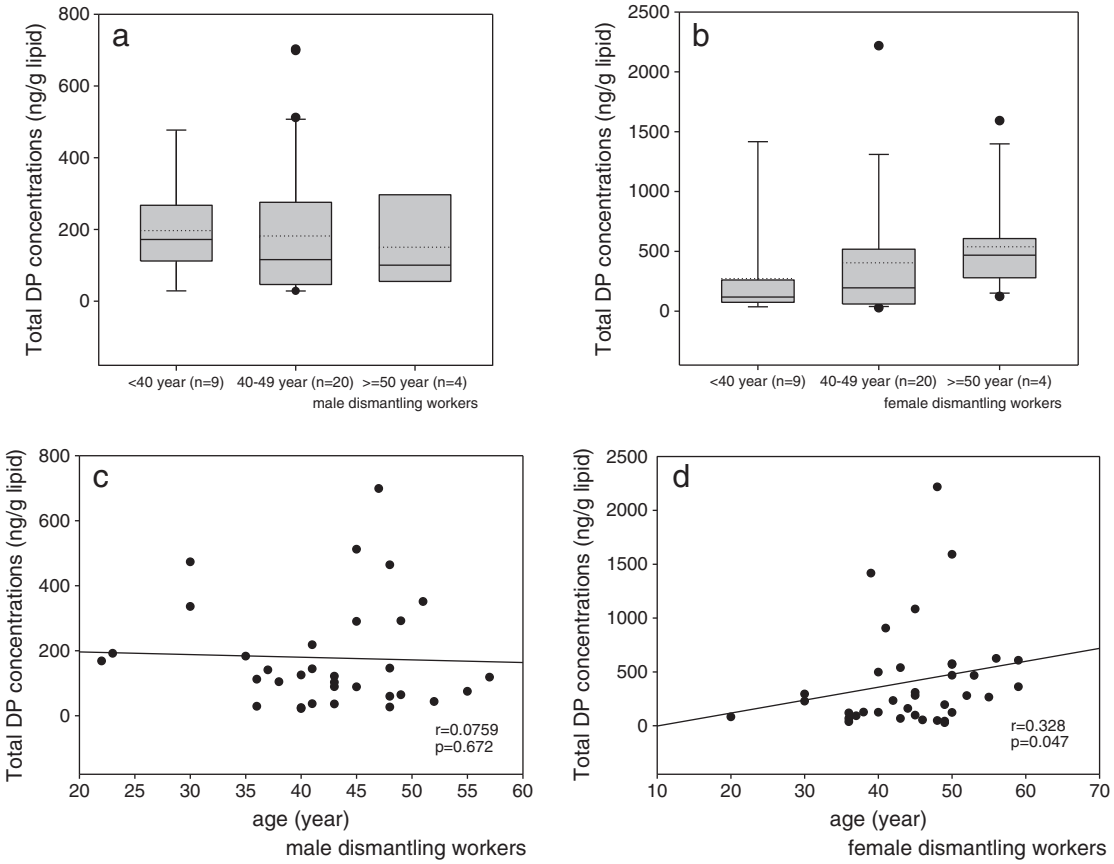

Fig 2. Boxplots of serum DP concentrations grouped by age as well as correlations between serum DP concentrations and age in (a, c) male and (b, d) female e-waste recycling workers. In the boxplots, the solid lines from the bottom to upper were 5th, 25th, 50th, 75th, and 95th percentile, respectively. The dot lines were the mean.

DP metabolic process in human body before incorporation into hair, the different transport rates for the isomers, and the stereoselective enrichment of DP in human hair.

3.3. Dechlorination products in human serum

Dechlorinated DP products were first detected by Sverko et al. (2008) in sediments from Niagara River, Canada. Since then dechlorinated DP products were detected in various environmental compartments e.g., air, dust, sediment (Chen et al., 2011; Sverko et al., 2008; Zheng et al., 2010), and plant (Chen et al., 2011), and in human hair (Zheng et al., 2010). Ren et al. (2009) detected a dechlorination DP tentatively identified as a −1 Cl dechlorination product in serum from the residents of e-waste dismantling area, but no quantitative data were provided due to the lack of authentic standard. In the present study, two dechlorinated *anti*-DP compounds, *anti*-Cl_{10}-DP and *anti*-Cl_{11}-DP, were measured in the human serum. None of the samples displayed *anti*-Cl_{10}-DP. Meanwhile, *anti*-Cl_{11}-DP was detected in 51 of the 70 samples from e-waste recycling workers, but in none of the 13 samples from the control group, which could be due to its levels being lower than the LOQ. The concentrations of *anti*-Cl_{11}-DP in serum of e-waste recycling workers ranged from nondetectable (ND) to 9.93, with a median of 1.47 ng/g lipid (Table 1). The degradation of DP could be caused by photolysis (Sverko et al., 2008) and/or thermal degradation, such as the e-waste burning processes (Chen et al., 2011). However, whether *anti*-Cl_{11}-DP is a product of in vivo dechlorination of *anti*-DP is still not clear.

3.4. Influence of serum DP from gender and potential metabolism

The gender effects on serum DP concentrations were examined for e-waste recycling workers but not for control group due to the limited sample number. The concentrations of *syn*-DP, *anti*-DP, $\sum$DP and *anti*-Cl_{11}-DP presented a normal distribution after log transformed in both genders. Therefore, Student's *t*-test was used to determine the differences between male and female. The results indicated that females had significantly higher serum concentrations of *syn*-DP, *anti*-DP, $\sum$DP and *anti*-Cl_{11}-DP ($p = 0.018$, 0.009, 0.010, 0.018, respectively) than males (Fig. 3a, b, c, d). The f_{anti} values in the females (median of 0.70) were also found to be significantly higher than those (median of 0.64) in the males ($p < 0.05$, Fig. 3e). Given that this is the first known study of gender effect on serum DP levels, comparison with other studies is not possible.

As shown in Table 1, no significant differences in demographic characteristics, including age, body mass index (BMI) and occupational exposure time, were found between the two genders, and the number of males (n = 33) was well balanced with the number of females (n = 37). Since the study samples share the same geographical region, occupation and similar incomes, exposure background difference is therefore not expected. Hence, it is likely that difference in serum DP levels between genders may attribute to selective absorption and elimination, and distinct rates of metabolism.

Previous reports in the literature suggested that *anti*-DP would be more reactive and susceptible to biological attack based on its less hindered spatial conformation (Hoh et al., 2006). Thus, the higher f_{anti} values in females may reflect that females have a lower DP metabolism capacity than males. *Anti*-Cl_{11}-DP is an important degradation product of *anti*-DP. The concentration ratio of *anti*-Cl_{11}-DP to *anti*-DP and the correlation between these two compounds in serum may reflect possible gender difference in metabolism of the isomers. The ratios of *anti*-Cl_{11}-DP to *anti*-DP in the females (ranging from 0.0047 to 0.0229 with median of 0.0086) were significantly lower than those in the males (ranging 0.0093–0.0337with median of 0.0157) ($p < 0.001$, Fig. 3f). Meanwhile, the linear regression

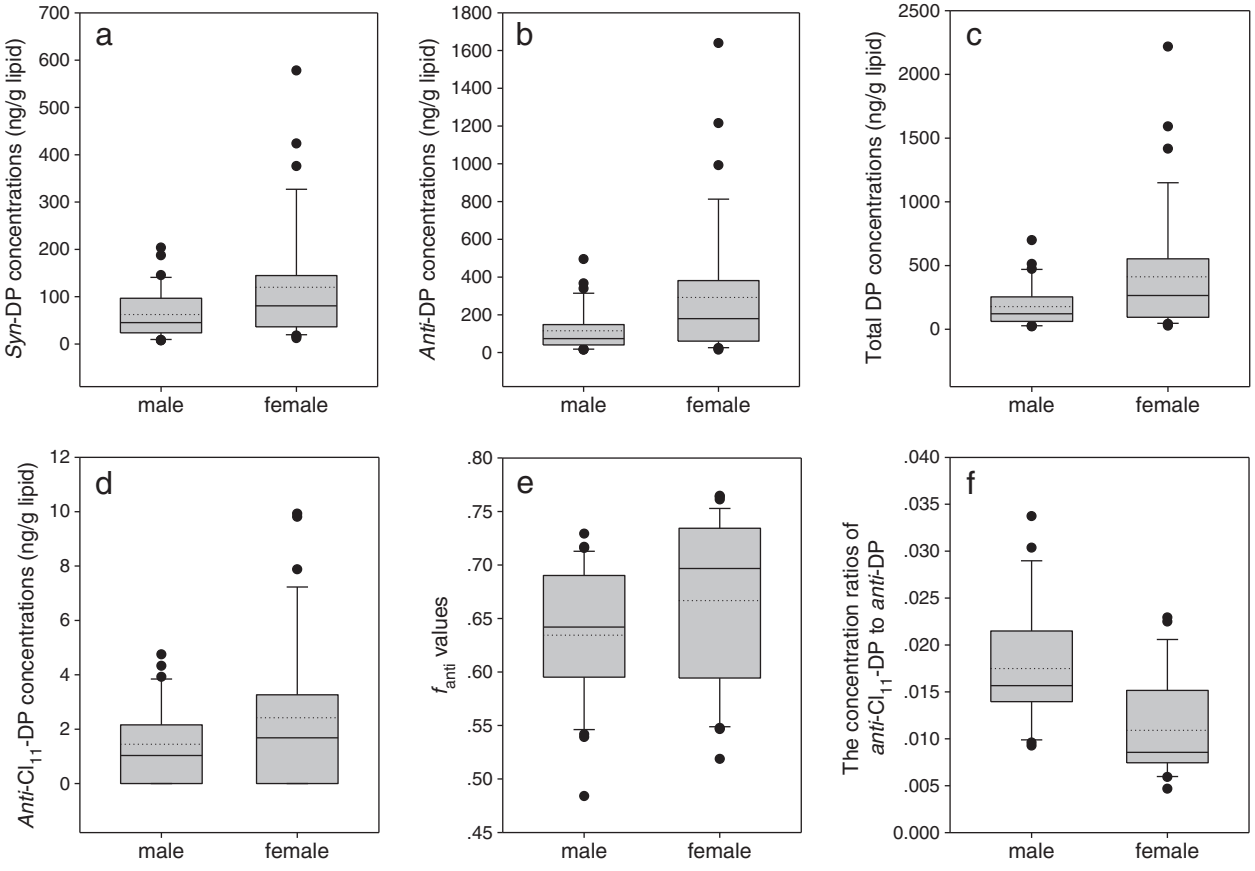

Fig. 3. Boxplots of (a) *syn*-DP, (b) *anti*-DP, (c) total DP, (d) *anti*-Cl_{11}-DP, (e) f_{anti} values, and (f) ratios of *anti*-Cl_{11}-DP to *anti*-DP in male (n = 33) and female (n = 37) e-waste recycling workers. The solid lines from the bottom to upper were 5th, 25th, 50th, 75th, and 95th percentile, respectively. The dot lines were the mean.

analysis revealed significant correlation ($p<0.001$) between *anti*-Cl_{11}-DP and *anti*-DP in both genders, but the slope of the regression line (0.725) was greater for males than that (0.693) for females (Fig. 4). These results, combined with the higher f_{anti} values in females, suggested that *anti*-Cl_{11}-DP in human body may be partly formed from in vivo dechlorinated metabolism of *anti*-DP, and the metabolism capacity for DP is greater in male than that in female. Otherwise, a similar ratio of *anti*-Cl_{11}-DP to *anti*-DP values and a similar slope of the regression line between genders would be expected. The high metabolic potential in male can also partially explain the low DP concentrations of their serum.

So far, very few information is available on the metabolism of DP in organisms. Zhang et al. (2011b) reported a possible hepatic dechlorination of *anti*-DP in northern snakehead according to its significantly greater ratio of *anti*-Cl_{11}-DP to *anti*-DP in liver compared to muscle. Meanwhile, further decrease in the fraction of *anti*-DP with higher trophic levels were observed in fresh water food web (Wu et al., 2010) and avian species (Zhang et al., 2011a), which could be associated with the increased metabolism of *anti*-DP or selective absorption of *syn*-DP by the high trophic level biota. These results combined with the finding in the present study strongly hint that *anti*-Cl_{11}-DP could be formed via in vivo biotransformation in biota and human.

However, Zheng et al. (2010) suggested that the *anti*-Cl_{11}-DP in human is likely to accumulate from environmental matrix rather than from in vivo biotransformation by comparing DP in human hair and indoor dust. But it should be noted that human blood and hair are different tissues which may lead to distinct outcomes. Other than endogenous exposure, exogenous exposure from dust could also contribute to the burden of pollutants in hair, which could influence the result. Additionally, other unknown factors in the process of pollutant transfer from blood to hair could also alter the pollutant profile. A dietary exposure to DP isomers using juvenile rainbow trout showed no evidence for dechlorinated metabolites of DP (Tomy et al., 2008), which may be caused by distinct metabolism systems in different species, as well as different exposure levels.

We cannot exclude the possibility that the differences on DP profile between two genders may be caused by selective uptake and excretion alone. Apparently, further researches are needed to assess the sex-dependent DP concentrations, isomer ratios and metabolism in other populations with larger sample size.

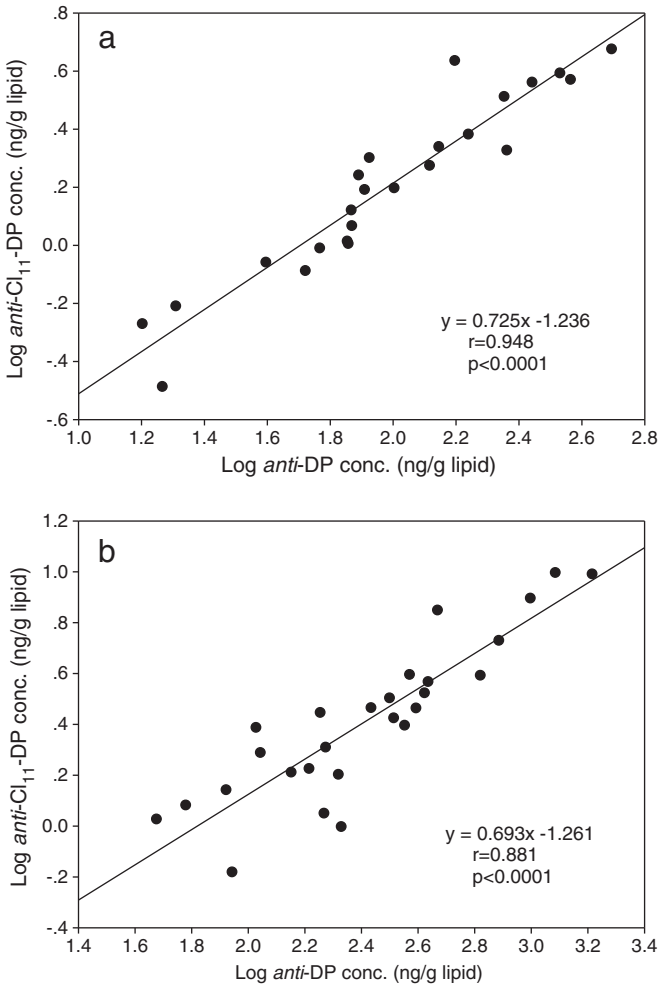

Fig 4. Correlations between serum concentrations of *anti*-DP and *anti*-Cl_{11}-DP in (a) male (n = 33) and (b) female (n = 37) e-waste recycling workers.

4. Conclusions

Current measurements of DP in the serum of e-waste recycling workers revealed high DP burden. The DP concentrations were found to be related to their age in female workers, while such relationship was not seen for male workers. In this study, we presented the first reported gender difference in DP accumulations. For e-waste recycling workers, the higher f_{anti} values and lower ratios of *anti*-Cl_{11}-DP to *anti*-DP in females suggested that they might have lower metabolic rate of DP than males. This result also hinted the possibility that *anti*-Cl_{11}-DP is at least partly formed by in vivo metabolism. Based on the evidence gathered at the current stage, a definitive explanation for the gender different accumulation levels of DP cannot be drawn. The present study highlights the needs for further studies on the behavior and metabolism of DP in human body, and evaluation of potential adverse impacts of DP on human health.

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References

Betts KS. A new flame retardant in the air. Environ Sci Technol 2006;40:1090–1.
Chen SJ, Tian M, Wang J, Shi T, Luo Y, Luo XJ, et al. Dechlorane Plus (DP) in air and plants at an electronic waste (e-waste) site in South China. Environ Pollut 2011;159:1290–6.
Gauthier LT, Letcher RJ. Isomers of Dechlorane Plus flame retardant in the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes of North America: temporal changes and spatial distribution. Chemosphere 2009;75:115–20.
Hoh E, Zhu L, Hites RA. Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes. Environ Sci Technol 2006;40:1184–9.
Kang JH, Kim JC, Jin GZ, Park H, Baek SY, Chang YS. Detection of dechlorane plus in fish from urban-industrial rivers. Chemosphere 2010;79:850–4.
Möller A, Xie Z, Sturm R, Ebinghuas R. Large-scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica. Environ Sci Technol 2010;44:8977–82.
Qiu X, Marvin CH, Hites RA. Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario. Environ Sci Technol 2007;41:6014–9.
Ren GF, Yu ZQ, Ma ST, Li HR, Peng PG, Sheng GY, et al. Determination of Dechlorane Plus in serum from electronics dismantling workers in South China. Environ Sci Technol 2009;43:9453–7.
Rylander L, Nilsson-Ehle P, Hagmar L. Asimplified precisemethod for adjusting serum levels of persistent organohalogen pollutants to total serum lipids. Chemosphere 2006;62:333–6.
Siddique S, Xian QM, Abdelouahab N, Takser L, Phillips SP, Feng YL, et al. Levels of Dechlorane Plus and polybrominated diphenylethers in human milk in two Canadian cities. Environ Int 2012;39:50–5.
Sverko E, Tomy GT, Marvin CH, Zaruk D, Reiner E, Helm PA, et al. Dechlorane Plus levels in sediment of the lower Great Lakes. Environ Sci Technol 2008;42:361–6.
Sverko E, Tomy GT, Reiner EJ, Li YF, McCarry BE, Arnot JA, et al. Dechlorane Plus and related compounds in the environment: a review. Environ Sci Technol 2011;45:5088–98.
The European Commission report on potential alternatives to deca-BDE. http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE. (accessed January 16, 2011).

Tomy GT, Pleskach K, Ismail N, Whittle DM, Helm PA, Sverko E, et al. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. Environ Sci Technol 2007;41:2249–54.

Tomy GT, Thomas RC, Zidane MT, Murison EK, Pleskach K, Hare J, et al. Examination of isomer specific bioaccumulation parameters and potential in vivo hepatic metabolites of *syn*- and *anti*-Dechlorane Plus isomers in Juvenile Rainbow Trout (Oncorhynchus mykiss). Environ Sci Technol 2008;42:5562–7.

Wang J, Tian M, Chen SJ, Zheng J, Luo XJ, An TC, et al. Dechlorane Plus in house dust from e-waste recycling and urban areas in South China: sources, degradation, and human exposure. Environ Toxicol Chem 2011;30:1965–72.

Wu JP, Zhang Y, Luo XJ, Wang J, Chen SJ, Guan YT, et al. Isomer-specific bioaccumulation and trophic transfer of Dechlorane Plus in the freshwater food web from a highly contaminated site, South China. Environ Sci Technol 2010;44:606–11.

Xian Q, Siddique S, Li T, Feng YL, Takser L, Zhu J. Sources and environmental behavior of Dechlorane Plus — a review. Environ Int 2011;37:1273–84.

Zhang XL, Luo XJ, Liu HY, Yu LH, Chen SJ, Mai BX. Bioaccumulation of several brominated flame retardants and Dechlorane Plus in waterbirds from an e-waste recycling region in South China: associated with trophic level and diet sources. Environ Sci Technol 2011a;45:400–5.

Zhang Y, Wu JP, Luo XJ, Wang J, Cheng SJ, Mai BX. Tissue distribution of Dechlorane Plus and its dechlorinated analogs in contaminated fish: high affinity to the brain for *anti*-DP. Environ Pollut 2011b;159:3647–52.

Zheng J, Wang J, Luo XJ, Tian M, He LY, Yuan JG, et al. Dechlorane Plus in human hair from an e-waste recycling area in South china: comparison with dust. Environ Sci Technol 2010;44:9298–303.

Zhu J, Feng YL, Shoeib M. Detection of Dechlorane Plus in residential indoor dust in the city of Ottawa, Canada. Environ Sci Technol 2007;41:7694–8.