Maternal transfer of dechloranes and their distribution among tissues in contaminated ducks

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HIGHLIGHTS

- Relatively serious contamination of DP was found in the e-waste recycling sites, Taizhou.
- Lipid pool, liver sequestration and blood-barrier affect tissue distribution of DP and its analogues.
- The maternal transfer extent of Dec 602 was over one.
- The stereo-selective accumulation of DP occurs among duck tissues.
- The monodechlorinated products in duck likely originated from the exterior environment.

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ABSTRACT

The tissue concentrations of dechlorane plus and its analogues were determined in ducks collected from several e-waste recycling villages of Taizhou, China. Compared with the published literature, the relatively high concentrations of these compounds were detected in ducks, indicating serious DP contamination. Since both the duck meat and eggs were important components for diet, this result reminded us of keeping a watchful eye on human dietary exposure to DP and its analogues in this study area. The wet-weight concentrations of DP and its analogues were significantly related to tissue lipid content ($p < 0.05$), indicating that the lipid pools predominantly impacted the distribution of DPs in ducks. On the basis of lipid adjustment, the significantly lower levels in brain than those in liver and blood, displayed the occurrence of liver sequestration and blood–brain barrier to DP and its analogues in the duck ($p < 0.05$). The maternal transfer of DP and Mirex was not obviously limited, and the transferring extent of Dec 602 was over one. The stereo-selected accumulation of two DP isomers occurred among tissues with preference to *syn*-DP in blood, and to *anti*-DP in brain. The values of lipid-adjusted monodechlorinated products mainly originated from the exterior environment in ducks.

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1. Introduction

Dechlorane plus (DP) is one kind of organic halogenated flame retardants. Since 1960s, DP was produced as a replacement of Mirex. Due to its excellent thermal stability, flame retardancy and low smoke generation, there has been a widespread application of DP in many materials. Currently the annual production of technical DP can be as high as 10 million pounds (Yu et al., 2010), and it has been classified as a high production volume chemical (HPV) in the

United States, also listed on Canada's Domestic Substances Lists (Sverko et al., 2010). Recently, DP is also considered as a possible replacement for decabromodiphenyl ether (Commission, 2011), likely resulting in its more application in the future.

DP has been detected in various environmental matrixes, including the atmosphere (Salamova and Hites, 2011; Yu et al., 2011) surface water (Moller et al., 2010; Wu et al., 2010), soil (Wang et al., 2010a,b,c; Yu et al., 2010) and sediments (Shen et al., 2011; Tomy et al., 2007), also tree bark (Qiu and Hites, 2008). Some studies showed that DP can be well accumulated in wildlife (Sun et al., 2012; Zhang et al., 2011) and human tissue (Ben et al., 2013, 2014; Ren et al., 2009; Siddique et al., 2012; Zheng et al., 2010), and be easily biomagnified across the trophic levels (Sun

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et al., 2012; Tomy et al., 2007; Zhang et al., 2011). The occurrence of DP analogues, for instance, Cl₁₀-DP, Cl₁₁-DP, Mirex, Dec 602, Dec 603 and Dec 604 were also reported in both abiotic and biotic samples (Chen et al., 2011; Guerra et al., 2011; Jia et al., 2011; Li et al., 2014; Peng et al., 2012; Shen et al., 2011, 2009; Sverko et al., 2010; Wang et al., 2010a,b,c; Yang et al., 2011a,b). All these studies imply the potential risk of DP and its analogues impose on the environment and human health.

Tissue distribution plays an important role in toxicology, which can help us understand the migration and transformation among tissues, thus to find the target organ needing further research on the toxic effect of different pollutants (Peng et al., 2012). So far, there were several research papers about tissue distribution of DP in fish (Peng et al., 2012; Zhang et al., 2011), birds (Sun et al., 2012) and frogs (Li et al., 2014). These studies revealed the species-specific migration and transformation pattern of DP among tissues, such as the blood–brain barrier, retention in liver and maternal transfer efficiency. However, there still lies an obvious data gap for the tissue distribution of domestic fowls, which are good indicators of ambient persistent organic pollutants (POPs) levels, considering the intensive contact of the fowls with the environment (Luo et al., 2009). Our aim of this study is to detect the tissue concentrations of DP and its analogues products (including monodechlorinated DP, Mirex and Dec 602, Dec 603 and Dec 604) in contaminated ducks collected from some e-waste recycling villages, and provide a further discussion about the liver sequestration, blood–brain barrier, maternal transfer and stereo-selective bioaccumulation of DP.

2. Materials and methods

2.1. Chemicals

Stock solutions of *syn*-DP (100 µg mL⁻¹), *anti*-DP (100 µg mL⁻¹), ¹³C₁₀ *syn*-DP (100 µg mL⁻¹), ¹³C₁₀ *anti*-DP (100 µg mL⁻¹) and ¹³C₁₂ PCB-208 (40 µg mL⁻¹) were obtained from Cambridge isotope laboratories Inc. (Massachusetts, USA). Stock solutions of *anti*-Cl₁₀-DP (50 µg mL⁻¹), *anti*-Cl₁₁-DP (50 µg mL⁻¹) and Mirex (100 µg mL⁻¹) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Dec 602, Dec 603 and Dec 604 were purchased from Toronto Research Chemical Inc. (North York, ON, Canada). Except for n-hexane and dichloromethane were pesticide grade, other solvents including methanol, ethanol, methyl tertiary butyl ether and isopropanol were LC grade. Dichloromethane and isopropanol were obtained from J.T. Baker (Deventer, The Netherlands); n-hexane, methanol and ethanol were supplied by Fisher Scientific (Pittsburgh, USA); methyl tertiary butyl ether was obtained from Tedia (Fairfield, USA). H₂SO₄ (98%) was supplied by Sinopharm Chemical Reagent Co. Ltd (Beijing, China). Sodium sulfate anhydrous (granular, purity >99.5%) was from Jinke Refined Chemical institutes (Tianjin, China). Silica gel (60–100 mesh) was purchased from Merck (Germany).

2.2. Sample collection

Taizhou City is located at the middle of the coastal area of Zhejiang Province and in the south tip of the Shanghai Economic Zone in China (28° N latitude and 122° E longitude). Dismantling operations for e-wastes in this area have been ongoing for approximately 30 years.

Five villages in Taizhou city, including HMQ, ZG, TS, NW, and LH, were selected as the study sites. Both of HMQ and ZG are typical recycling sites for the obsolete transformers, and both of TS and NW are traditional e-waste dismantling sites for printed circuit boards and cable wires, while LH village was without e-waste recycling

operation. Nine ducks (*Anas platyrhynchos domesticus*), fed about 10–12 months, were selected randomly in nine duck flocks (generally >50 ducks as a flock) from the five villages mentioned above in July 2012. One duck was collected from LH (a low contamination site), and two, respectively, from HMQ, ZG, TS and NW (high contamination sites). The collected ducks were brought to the laboratory and blood samples (about 20 mL) were taken following euthanasia. Then, the liver, pectoral muscle, abdominal adipose, brain and egg tissues were excised. After being homogenized in a tissue homogenizer, various tissues except for blood were freeze-dried, and then kept frozen at –20 °C until analysis.

2.3. Sample extraction, clean-up, and analysis

The extraction, clean-up, and analysis of DP isomers and its analogs in blood and tissue samples were performed as described in our previous study with minor modification (Ben et al., 2014). In brief, after spiking of recovery surrogate ¹³C₁₀ *syn*-DP and ¹³C₁₀ *anti*-DP, tissue samples were homogenized, then ultrasonically extracted 3 times (7 min per time) with methyl tertiary butyl ether: hexane: dichloromethane, 1: 1: 1 (v: v: v). An aliquot of the extract was used for the determination of lipid by gravimetry. The remaining extract was subjected to a chromatography column (30 cm × 10 mm ID) containing 8.0 g sulfuric acid silica (30% acid by weight) and 2.5 g of anhydrous sodium sulphate on top to purify. The injection internal standard (¹³C₁₂-PCB-208) was added prior to the GC/MS analysis.

The quantification of DP and its analogues was performed using an Agilent 6890 GC, coupled with 5973 MSD. The MS analyses were performed in an electron capture negative ionization (ECNI) mode. The separation was performed using a fused silica capillary column (RTX-1614, 30 m × 0.25 mm ID and 0.1 µm film thickness; J&W Scientific, Folsom, CA, USA). The carrier gas used was helium, with a flow rate of 1.0 mL min⁻¹, and methane was used as the reaction gas. The GC oven temperature was programmed as follows: the initial temperature was maintained at 100 °C for 2 min, then increased to 250 °C at a rate of 25 °C min⁻¹, followed by a 1.5 °C min⁻¹ ascent to 260 °C, and finally, the temperature was increased at a rate of 25 °C min⁻¹ to achieve the final temperature level of 315 °C, maintained for 7 min. The injector, transfer line, and ion source temperatures were 250, 280, and 150 °C, respectively. The ion fragments were monitored as follows: *m/z* 617.7 and 619.7 for *anti*-Cl₁₁-DP and *syn*-Cl₁₁-DP, *m/z* 583.7 and 585.7 for *anti*-Cl₁₀-DP, *m/z* 651.7 and 653.7 for *syn*-DP and *anti*-DP, *m/z* 403.7 and 401.7 for Mirex, *m/z* 613.6 and 611.6 for Dec 602, *m/z* 637.7 and 635.7 for Dec 603, *m/z* 79 and 81 for Dec 604, *m/z* 661.7 and 663.7 for ¹³C₁₀ labeled *syn*-DP and *anti*-DP, *m/z* 510 and 508 for ¹³C₁₂-labeled CB-209 and *m/z* 476 and 478 for ¹³C₁₀ labeled PCB-208. *syn*-Cl₁₁-DP is quantified by the relative response factor of *anti*-Cl₁₁-DP.

2.4. Quality control

Laboratory procedure blanks were analyzed for every set of 11 samples. No target compound was found in the blanks. The recoveries of DP and its analogues were estimated by the spiked internal standards, the recoveries of the internal standards were 62.1–117% for ¹³C₁₀ *syn*-DP, 64.6%–113% for ¹³C₁₀ *anti*-DP and 73.9–109% for ¹³C₁₂ CB-209. The limits of detection (LODs) were defined as the concentration of target compounds in sample producing a peak in chromatogram with a signal-to-noise (S/N) ratio of 3, and LODs ranged from 13 (egg) to 181 (blood), 25 to 270, 11 to 111, 18 to 309, 27–190 pg g⁻¹ lw for *syn*-DP, *anti*-DP, *anti*-Cl₁₁-DP, Mirex and Dec 602, respectively. All reported concentrations were corrected by surrogate recovery.

2.5. Data analysis

All the statistical analyses were performed using SPSS 18.0 statistical software. *Spearman* correlation analysis was employed to assess the relevance between the tissue lipid contents and the wet-weight concentrations of DP and its analogues. Two-Related-Sample Tests were employed to compare the tissue concentrations. The fractional abundance of *anti*-DP (f_{anti}) was compared by one-way *Anova*. The significance for all analysis was set at $p < 0.05$.

3. Results and discussion

3.1. Residue levels of DP and its analogues

In this study, DP (*syn*-DP and *anti*-DP) and its related analogues (*anti*-Cl₁₀-DP, *syn*-Cl₁₁-DP and *anti*-Cl₁₁-DP, Mirex, Dec 602, Dec 603 and Dec 604), were determined in five compartments, including whole blood, liver, muscle, fat and brain tissue, from nine domestic ducks collected in Taizhou, China. The target compounds from the matched eggs ($n = 6$) were also determined in order to examine their maternal transfer. Levels of DP and its related analogues were shown in Table 1 as lipid weight (lw).

To date, some studies have been conducted to investigate the tissue levels of DP in birds and their eggs. Similar DP levels were found in water birds from another e-waste recycling region in China, with the DP concentrations ranging from nd–610 ng g⁻¹ lw in the muscle (Zhang et al., 2011). The DP levels were comparable to those observed in herring gulls eggs from the Great Lakes region with the DP production source (<15 ng g⁻¹ ww) (Gauthier and Letcher, 2009), and in terrestrial passerine bird species from Pearl River Delta of China (PRD), a region with burgeoning electronic/electrical manufacturing industries and intensive e-waste recycling activities (3.9–930 ng g⁻¹ lw in muscle; 7.0–1300 ng g⁻¹ lw in liver) (Sun et al., 2012). The comparison indicated relatively serious DP pollution in this study region. However, the DP level in home-produced eggs from other three e-waste recycling sites in South China, varied from hundreds to thousands ng g⁻¹ lw (Zheng et al., 2012), which was two to three orders of magnitude higher than our study. In short, these findings remind us of paying close attention to dietary contamination of DP in e-waste recycling environment, in view that both the duck meat and egg were important components for diet.

There is scarce literature reported the accumulation of dechlorination products of DP in biota. To our knowledge, *anti*-Cl₁₀-DP

was only found in biota in the limited published literature (Guerra et al., 2011; Zhang et al., 2011). However, both *syn*-Cl₁₁-DP and *anti*-Cl₁₁-DP were detected consistently in various biotas. For instance, the concentration of *syn*-Cl₁₁-DP and *anti*-Cl₁₁-DP in liver gathered from terrestrial passerine bird species from PRD of China was nd–41 ng g⁻¹ lw and nd–7.5 ng g⁻¹ lw, respectively, and in muscle was nd–6.5 ng g⁻¹ lw and nd–7.6 ng g⁻¹ lw, respectively (Sun et al., 2012). The levels of *anti*-Cl₁₁-DP were nd to 4.7 ng g⁻¹ ww in chicken tissues collected from Qingyuan county of Guangdong province (Zheng et al., 2014), and nd–1.84 ng g⁻¹ lw in peregrine falcon eggs collected from Canada and Spain (Guerra et al., 2011). In this study, *anti*-Cl₁₀-DP was not found and similar concentrations of *syn*-Cl₁₁-DP/*anti*-Cl₁₁-DP were detected when compared with the Great Lakes region and PRD (industry district) in China. The results from our study and references showed that *anti*-Cl₁₀-DP may not be prone to be accumulated in biota, which was contrary to mono-dechlorinated DP.

In view of other DP-like compounds, both of Mirex and Dec 602 were detected in most of samples, whereas both of Dec 603 and Dec 604 were not found in all samples. The median concentrations of Mirex and Dec 602 in Chinese sturgeon eggs from the Yangze river, was 0.32 ng g⁻¹ lw and 0.02 ng g⁻¹ lw (recalculated on the basis of the lipid content as 35%), respectively (Peng et al., 2012). Guerra et al. (2011) reported the geometric mean value in peregrine falcon eggs collected from the Canadian Great Lakes, was 641 ng g⁻¹ lw for Mirex and 73.2 ng g⁻¹ lw for Dec 602, respectively. The level of Mirex and Dec 602 in our study were much higher than those in Chinese sturgeon (representing the background level). Although the levels of Mirex and Dec 602 were much lower than those in peregrine falcon eggs collected from the Canadian Great Lakes, their existence in human diet (muscle and egg) should not be ignored as for their relatively higher potential of bioaccumulation (Peng et al., 2012; Shen et al., 2011).

There existed great regional variance on the DP concentration in duck tissues. The mean concentration of DP in duck muscle was 6.28 ng g⁻¹ lw, 6.66 ng g⁻¹ lw, 90.2 ng g⁻¹ lw, 291 ng g⁻¹ lw and 1.44 ng g⁻¹ lw from HMQ, ZG, TS, NW and LH, respectively. E-waste recycling operations were not allowable in LH, resulting in its lowest level. Both NW and TS were two typical villages recycling a large amount of DP-containing electric/electrical equipment such as electronic wire/cable and printed circuit boards, whereas both HMQ and ZG had even been two typical transformers/capacitors (containing PCBs) recycling villages. The type of e-waste products recycled may be one of important factors impacted the

Table 1

Levels of dechloranes in tissues of duck collected from the five sites in Taizhou City, Zhejiang Province, Eastern China (ng g⁻¹ lw).

	Blood	Brain	Liver	Fat	Muscle	Egg
Contamination sites ^a						
Dec602	0.27(nd ^b –1.04)	0.24(nd–1.97)	0.48(0.12–1.20)	1.21(0.55–5.49)	1.00(0.11–2.07)	0.60(0.11–1.85)
Mirex	1.49(0.25–9.03)	0.53(nd–2.53)	2.61(0.79–5.72)	5.54(2.56–8.18)	4.94(1.90–8.71)	0.88(0.27–7.85)
<i>syn</i> -Cl ₁₁ -DP	0.19(nd–0.92)	– ^c (nd–0.10)	0.04(nd–13.0)	0.72(nd–2.01)	1.23(nd–4.85)	0.04(0.01–0.08)
<i>syn</i> -DP	2.48(0.36–23.5)	0.36(0.09–2.72)	4.44(0.42–439)	16.9(0.55–51.2)	9.11(1.46–90.0)	1.94(1.12–4.53)
<i>anti</i> -Cl ₁₁ -DP	0.45(nd–1.73)	–(nd–0.59)	0.23(nd–28.0)	1.26(0.11–4.91)	0.41(nd–13.8)	0.10(0.03–0.26)
<i>anti</i> -DP	4.57(1.22–29.1)	3.05(0.41–9.26)	13.1(2.60–783)	43.4(1.85–96.4)	22.1(4.03–210)	3.19(2.28–12.1)
ΣDP	6.97(1.58–52.6)	3.58(0.50–12.0)	17.8(3.32–1221)	60.3(2.40–148)	31.1(5.81–294)	5.13(3.40–16.7)
Low contamination site						
Dec602	0.07	0.48	0.13	0.15	0.08	0.32
Mirex	0.17	0.21	0.75	1.44	1.01	0.79
<i>syn</i> -Cl ₁₁ -DP	0.12	nd	nd	nd	nd	0.01
<i>syn</i> -DP	0.93	0.32	0.51	0.29	0.24	0.73
<i>anti</i> -Cl ₁₁ -DP	0.18	0.11	nd	0.04	nd	0.01
<i>anti</i> -DP	2.20	1.80	1.38	0.88	1.21	1.48
ΣDP	3.13	2.11	1.89	1.16	1.44	2.21

^a Median and range.

^b nd: not detected.

^c –no data.

contamination situation of DP in these study sites.

3.2. Characteristics of tissue distribution

3.2.1. Lipid-dependent tissue distribution

Spearman correlation analysis was employed to assess the relevance between the tissue lipid contents and the wet-weight concentrations of DP and its analogues. There was a significant correlation between the total DP concentration and the tissue lipid content in ducks ($p < 0.001$). Similarly, significant correlation was found for DP-like compounds ($p < 0.001$ for Dec 602, Mirex, and *anti*-Cl₁₁-DP, $p < 0.006$ for *syn*-Cl₁₁-DP). That significant correlation indicated that lipid might play a crucial role in tissue distribution of DP and its analogues. This result was consistent with the tissue distribution of DP in chicken (Zheng et al., 2014), in Chinese sturgeons (Peng et al., 2012) and in European eels (Suhling et al., 2015).

3.2.2. Liver sequestration

As described in Section 2.1, although lipid pool was a major factor affected the tissue distribution of DP and its analogues, it was not the unique factor. The liver sequestration of DP has been found in the northern snakehead and mud carp, with the preferential distribution of DP in liver compared to muscle and brain tissues (Zhang et al., 2011). Peng et al. (2012) also reported that the lipid-normalized concentrations of dechloranes in liver were all higher than in adipose tissue by 1.7 fold for Mirex to 4.9 fold for Dec 602, showing the hepatic sequestration of dechloranes in Chinese sturgeons. In this study, liver/blood ratio together with the liver/muscle ratio and liver/fat ratio was used to explore the liver sequestration of DP, Mirex and Dec 602 in ducks, and the corresponding results of median/mean ratio was listed in Table 2.

In Table 2, the liver/blood concentration ratio (median/mean value) was more than one to DP, Mirex and Dec 602, but their liver/fat concentration ratio or liver/muscle concentration ratios showed closer to one or less than one. Fat or muscle tissue was generally considered as the final sink of hydrophobic compounds in biota, and the pollutants accumulated in fat or muscle may undergo more biological process such as absorption, distribution and metabolism. Different from fat and muscle, the liver tissue is the central compartment with abundant blood perfusion. Therefore, the liver/blood concentration ratio may reflect the occurrence of liver sequestration more than the liver/muscle concentration ratio or liver/fat concentration ratio. Although the dominant liver sequestration of DP was not found when compared to muscle as reported by Zhang et al. (2011) or fat as reported by Peng et al. (2012), the significantly higher level in liver than that in blood demonstrated the occurrence of liver sequestration in ducks (Nonparametric Two-Related Samples Tests, $p < 0.05$).

3.2.3. Blood–brain barrier

Previous studies have shown that blood–brain barrier can effectively prevent a variety of (POPs) into the brain tissue. For example, compared to brain tissue, preferential enrichment of some persistent organic pollutants (POPs) in liver tissue was found, such as PBDEs in birds of prey (Voorspoels et al., 2006) and in fowls

(Yang et al., 2011a,b), PCDD/Fs in wildlife (Wan et al., 2006), PCBs and OCPs in fur seals (Wang et al., 2010a,b,c). For DP and its analogues, Li et al. (2014) reported that DP and DP-like compounds (including DP, Mirex, Dec 602 and *anti*-Cl₁₁-DP) was more prone to be accumulated in liver compared with brain tissue in frogs. Zhang et al. (2011a), (2011b) found the *syn*-DP and *anti*-Cl₁₁-DP were richer in liver when compared to brain, but the result of *anti*-DP in fish was vice versa.

In this study, all of DP and its analogues were detected in the brain tissues of ducks, indicating the potential of these compounds breaking through the blood–brain barrier. However, on the lipid-adjusted basis, the median blood/brain concentration ratios of DP and its analogues ranges from 1.3 for Mirex to 5.1 for *syn*-DP, and the liver/brain concentration ratios varied from 3.2 for Mirex to 11 for *syn*-DP, respectively (Table 2). The lipid-normalized concentrations in brain tissues were significantly lower than those in blood and liver tissues (Nonparametric Two-Related Samples Tests, $p < 0.05$), declaring that the protective blood–brain barrier narrows the passage of these compounds into the brain. The result in the present study was similar to the distribution of DP and its analogues in frogs reported by Li et al. (2014), but was inconsistent with the distribution of *anti*-DP in contaminated fish reported by Zhang et al. (2011a), (2011b). The different blood–brain (liver–brain) accumulation characteristics among ducks, frogs and fish likely implied the species-specific brain uptake of DP in biota.

The blood–brain barrier (BBB) is an important defense mechanism for biota, which could restrict diffusion of large or hydrophilic molecules into the brain (Barrier and Peterson, 2010). Yang et al. (2011a), (2011b) found the great hinder of blood–brain barrier to BDE-209, ascribing to its higher molecular weight. Similar to BDE-209, since DP has the large molecular mass weight and high Kow, the structural-dependent properties may be one of the important factors limiting the brain uptake to these compounds in the duck.

3.2.4. Maternal transfer

The detection of DP and DP-like compounds in the duck eggs indicated their maternal transfer and potential exposure risk to duck reproduction and human health through diet ingestion. Lipophilic organic chemicals are transferred to eggs along with yolk proteins which are formed in the liver of the mother in oviparous organisms (Russell et al., 1999), so that the ratios of lipid-adjusted egg concentration to lipid-adjusted maternal liver concentration (E/L ratios) (Wu et al., 2009) were calculated to assess the extent of maternal transfer to egg in this study. The median/mean of E/L ratios in ducks were listed in Table 2.

Wu et al. (2013) found the existence of species-special maternal transfer in fish. The mean E/L ratio was 0.03 and 0.03 in northern snakehead, and 0.26 and 0.25 in Crucian carp, respectively, for *syn*-DP and *anti*-DP. Nevertheless, the ratio in Chinese sturgeon was 1.3 and 1.4 (recalculated on the basis of lipid content), respectively (Peng et al., 2012; Wu et al., 2013). In this study, the median E/L ratios for DP isomers were higher than those in Crucian carp, and lower than those in Chinese sturgeon. The lipid-normalized DP concentrations in duck eggs were insignificantly different from those in liver tissues (Nonparametric Two-Related Samples Tests,

Table 2
Lipid-adjusted concentration ratio of compounds among duck tissues (median/mean value).

	Liver/blood	Liver/Fat	Liver/Muscle	Blood/Brain	Liver/Brain	Egg/Liver
Dec602	2.0/2.7	0.8/0.6	0.7/0.7	1.6/2.8	4.6/4.1	1.47/1.85
Mirex	2.1/3.5	0.7/0.7	0.7/0.7	1.3/2.8	3.2/4.6	0.69/0.72
<i>syn</i> -DP	1.7/5.5	1.1/2.0	0.6/1.3	5.1/6.3	11/32	0.82/1.35
<i>anti</i> -DP	2.4/8.6	1.2/1.9	0.7/1.1	2.9/2.5	7.0/17	0.72/0.71
ΣDP	2.2/7.3	1.2/1.9	0.6/1.2	3.2/3.2	7.6/21	0.76/0.81

$p > 0.05$). Similar to DP, the median E/L ratio of Mirex was 0.69, which was not significantly different from one ($p > 0.05$). The results indicated little barrier to DP and Mirex during the process of maternal transfer. However, Dec 602 exhibited some difference from DP and Mirex. The median E/L ratios for Dec 602 showed 1.47, ranging from 0.96 to 3.41, implying the possibility of enhanced maternal transfer for Dec 602. It was noticed that the egg samples sizes ($n = 6$) in this study were limited and the results need be assured further.

3.3. Isomeric profiles of DP in tissues

Isomeric profiles of DP in different tissues were examined by the fraction of DP, defined as the concentration of *anti*-DP divided by the total DP concentration. Fig. 1 showed the value of f_{anti} in different tissues in ducks. The mean value of f_{anti} in blood, brain, fat, liver, muscle and egg were 0.65, 0.83, 0.70, 0.73, 0.72, and 0.67, respectively, with the highest value in brain, and the lowest in blood. The difference of f_{anti} value among tissues of ducks were analyzed by one-way *Anova*. The result showed that the f_{anti} value of blood was significantly lower than those of other tissues with the except of egg tissue ($p < 0.05$), implying the prior stereo-selective accumulation of *syn*-DP in blood. It was also found that the f_{anti} value of brain tissue was significantly higher than those in other tissues ($p < 0.05$), indicating the preferential stereo-selective accumulation of *anti*-DP in brain. Sührling et al. (2015) reported the preferred distribution of *syn*-DP into gonads and egg of eels during maturation. Although the f_{anti} value was not significantly different between muscle and eggs in this study ($p > 0.05$), it showed the higher value in the muscle compared with the eggs. Overall, the occurrence of stereo-selective accumulation of DP isomers among tissues warrants their different exposure risk to organs in biota.

Due to the trans-spatial structure of *anti*-DP, *anti*-DP should undergo higher spatial resistance than *syn*-DP when penetrated the blood–brain barrier, resulting in more accumulation of *syn*-DP compared to *anti*-DP. However, it appeared that the structural-dependent theory might not support our result, where *anti*-DP was prone to accumulate in brain tissue compared to *syn*-DP. Sverko et al. (2008) reported that two isomers of DP had different

Table 3

Mean ratio value of monodechlorinated products levels against DP levels in four tissues in ducks.

	Liver	Muscle	Blood	Fat
<i>anti</i> -Cl ₁₁ -DP/ <i>anti</i> -DP	0.034	0.041	0.070	0.060
<i>syn</i> -Cl ₁₁ -DP/ <i>syn</i> -DP	0.029	0.051	0.069	0.039

aqueous solubility, at 207 ng L⁻¹ and 572 ng L⁻¹, respectively. Although it was not referred explicitly to whom with the larger aqueous solubility, *syn*-DP was generally richer in aqueous body than matched sediment in the previous studies (Sverko et al., 2011; Xian et al., 2011), implying higher aqueous solubility of *syn*-DP than *anti*-DP. Likely, when DP isomers were transferred from blood to brain, the more aqueous components in blood might cause more retention of *syn*-DP, resulting in relatively more transfer residual of *anti*-DP in brain tissues. Therefore, the theory of similarity and intermiscibility might explain more in selective bioaccumulation of DP isomers in the process of blood–brain distribution compared with the structural-dependent theory.

3.4. Dechlorinated products of DP

To date, the dechlorination products of DP (including *syn*-Cl₁₁-DP and *anti*-Cl₁₁-DP) have been found in some organism, such as in birds (Mo et al., 2013) and bird eggs (Guerra et al., 2011), fish (Peng et al., 2012; Zhang et al., 2011a,b), frog (Li et al., 2014) and chicken (Zheng et al., 2014). However, data gap still existed on the origin of these compounds in biota.

Liver was considered to be a main metabolic organ in organism, if any dechlorination process occurred, a higher ratio of monodechlorinated products against DP shall be observed in liver compared with other tissues. In this study, the mean values of *anti*-Cl₁₁-DP/*anti*-DP and *syn*-Cl₁₁-DP/*syn*-DP in liver, muscle, blood and fat are listed in Table 3. The mean ratio in liver showed the lowest in the four tissues, suggesting the less likelihood that the *anti*-Cl₁₁-DP/*syn*-Cl₁₁-DP mainly transformed from the parent compound *in vivo*. Previous studies also found the animal liver tissues had low monodechlorination ability in Chinese sturgeon (Peng et al., 2012), rainbow trout (Tomy et al., 2008) and mud carp (Zhang et al., 2011a,b). Considering the larger molecular weight and Kow of DP, this lowest value in liver may be ascribed to the relatively higher liver sequestration capability to DP compared with its monodechlorination products, rather than liver metabolic capability to parent DP.

4. Conclusions

DP and its analogues were generally detected in several tissues of domestic ducks collected from e-waste recycling sites in Taizhou, China, indicating DP pollution in this study area. The tissue distribution of DP might be not only related to tissue lipid pools, but also other mechanisms such as the liver sequestration and blood–brain barrier, which might affect its partitioning within the body. The enhanced efficiency of maternal transfer was found for Dec 602. The stereo-selective accumulation occurred in the duck tissues, indicating the different exposure risk of DP isomers to organs. The monodechlorinated products of DP in duck tissues are likely to be originated from the environment rather than transformed from the parent compound *in vivo*.

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Fig. 1. The value of f_{anti} in different tissues for duck. Box plots are defined as follows: center line, median; box plot edges, the 25th and 75th percentiles; whiskers, range of data values; circle, outliers.

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