Species- and tissue-specific accumulation of Dechlorane Plus in three terrestrial passerine bird species from the Pearl River Delta, South China

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DP levels positively but $f_{\text{anti}}$ values negatively correlated with trophic level of birds.

**HIGHLIGHTS**

- High DP levels were found in three terrestrial bird species from the PRD.
- DP preferentially accumulated in liver rather than in muscle.
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**ABSTRACT**

Little data is available on the bioaccumulation of Dechlorane Plus (DP) in terrestrial organisms. Three terrestrial passerine bird species, light-vented bulbul, long-tailed shrike, and oriental magpie-robin, were collected from rural and urban sites in the Pearl River Delta to analyze for the presence of DP and its dechlorinated products in muscle and liver tissues. The relationships between trophic level and concentration and isomeric composition of DP in birds were also investigated based on stable nitrogen isotope analysis. DP levels had a wide range from 3.9 to 930 ng g$^{-1}$ lipid weight (lw) in muscle and from 7.0 to 1300 ng g$^{-1}$ lw in liver. Anti-Cl$\text{_11}$-DP and syn-Cl$\text{_11}$-DP, two dechlorinated products of DP, were also detected in bird samples with concentrations ranged between not detected (nd)-41 and nd-7.6 ng g$^{-1}$ lw, respectively. DP preferentially accumulated in liver rather than in muscle for all three bird species. Birds had significantly higher concentrations of DP in urban sites than in rural sites (mean, 300 vs 73 ng g$^{-1}$ lw). The fractions of anti-DP ($f_{\text{anti}}$) were higher in birds collected in rural sites than in urban sites. Significant positive correlation between DP levels and $d^{15}$N values but significant negative correlation between $f_{\text{anti}}$ and $d^{15}$N values were found for birds in both urban and rural sites, indicating that trophic level of birds play an important role in determining DP level and isomeric profile.

1. Introduction

Dechlorane Plus (DP, C$_{18}$H$_{12}$Cl$_{12}$), an additive chlorinated flame retardant, has been used in coating electrical wires and cables, plastic roofing materials, automotive lubricants, and hard connectors in computers and televisions for over 40 years (Tomy \textit{et al.}, 2007). DP was first introduced into the market as a substitute for Dechlorane (C$_{10}$Cl$_{12}$) or Mirex in the 1960s (Ren \textit{et al.}, 2009). DP has three types of commercial products (DP-25, DP-35 and DP-515) classified according to particle size and these products are primarily comprised of two stereoisomers: syn- and anti-isomers (Zhu \textit{et al.}, 2007). The annual production of technical DP is estimated to be as high as 10 million pounds (Yu \textit{et al.}, 2010).

Although DP has been classified as a high production volume chemical by the United States Environmental Protection Agency (Jia \textit{et al.}, 2011) and also listed on Canada’s Domestic Substances Lists (Sverko \textit{et al.}, 2010), it has received little attention until recently. DP was first reported to be found in air, fish, and sediment samples from the Great Lakes region in 2006 (Hoh \textit{et al.}, 2006). Since then, DP has been detected in various environmental matrix in North America, Europe and China, including air (Ren \textit{et al.}, 2008; Wang \textit{et al.}, 2010), indoor dust (Zhu \textit{et al.}, 2007), water (Möller \textit{et al.}, 2010), sewage sludge (De la Torre \textit{et al.}, 2011), soil (Yu
et al., 2010; Ma et al., 2011), sediment (Qiu et al., 2007; Sverko et al., 2008), plant (Qiu and Hites, 2008; Chen et al., 2011), biota (Tomy et al., 2007; Sverko et al., 2010; Wu et al., 2010; Verier and Hites, 2011; Zhang et al., 2011b), and human serum (Ren et al., 2009) and hair (Zheng et al., 2010). These studies have demonstrated that DP was not only environmentally ubiquitous but also bioavailable and potentially bioaccumulative in biota. More recently, the occurrence of degradation products of DP in both biotic and abiotic samples was reported (Sverko et al., 2008; Ren et al., 2009; Zheng et al., 2010; Chen et al., 2011), but the origin of degradation products of DP in environment samples is still indistinct.

Previous studies have shown that biota exhibited species-specific stereoselective enrichment of either syn- or anti-DP. Enrichment of syn-DP was observed in zooplankton, mussels (Tomy et al., 2007), fish (Tomy et al., 2008; Wu et al., 2010; Shen et al., 2011), oyster (Jia et al., 2011) and waterbirds (Zhang et al., 2011b); while selective accumulation of anti-DP was found in wall-eye, goldeye (Tomy et al., 2007), and peregrine eggs (Guerra et al., 2011). A strong negative relationship between the percentage of anti-DP to total DP and trophic level have also been demonstrated in fish and waterbirds collected near an e-waste recycling area in South China (Wu et al., 2010; Zhang et al., 2011b). The underlying reason for the stereoselective bioaccumulation is not clear. Meanwhile, the biomagnification for each DP isomer has also been calculated in different food webs. But the results sometimes were contradictory. For example, both syn- and anti-DP were significantly biomagnified in a freshwater food web from a highly contaminated pond in South China (Wu et al., 2010), while no biomagnifications for the two isomers were found in the Lake Ontario food web (Tomy et al., 2007) and in waterbirds from an e-waste recycling region in South China (Zhang et al., 2011b). The substantial variability in the field-derived bioaccumulation for DP suggested that there is a wide knowledge gap in fully understanding the bioaccumulation behavior of DP.

Birds are sentinel species to monitor the levels and effects of various contaminants in the environment because they are sensitive to environmental changes, occupy a top position in the food chain, and have dietary diversity. Most recently, the bioaccumulation of DP in birds has been reported by a few studies (Gauthier et al., 2007; Venier et al., 2010; Guerra et al., 2011; Muñoz-Arnanz et al., 2011; Zhang et al., 2011b). However, these studies were conducted mostly on aquatic birds and little information was available for terrestrial birds. Terrestrial birds have a diverse living habitat and diet compared to aquatic birds. Recent studies indicated that both habitat and diet of bird play important roles in determining of the level and pattern of organic pollutants (such as PBDEs and HBCD) in birds (Chen and hale, 2010; He et al., 2010; Newsome et al., 2010; Zhang et al., 2011b). Few studies have evaluated whether the bioaccumulation of DP in terrestrial birds is different from that of aquatic birds.

In the present study, three terrestrial passerine bird species, namely light-vented bulbul (LVB), long-tailed shrike (LTS), and oriental magpie-robin (OMR), were collected from rural and urban sites in the Pearl River Delta (PRD), South China. The three species are resident birds with relative small-scale territories and foraging areas (about 2.5 ha), which can serve as bioindicators for monitoring local pollution of DP (Lu et al., 1996; Van den Steen et al., 2009).

The objectives of this study were: (1) to explore the occurrence of DP and its possible degradation products in terrestrial birds from the PRD region; (2) to examine the tissue distribution of DP in birds; (3) to determine differences in bioaccumulation potential of the two isomers in terrestrial bird species and evaluate the potential role trophic level plays on the DP level and isomeric composition.

2. Materials and methods

2.1. Chemicals

Anti-DP, syn-DP (CAS 13560-89-9), anti-C11-DP (1, 6, 7, 8, 9, 14, 15, 16, 17, 18-octadec-7, 15-diene), and anti-C10-DP (1, 6, 7, 8, 9, 14, 15, 16, 17, 17-octadeca-7, 15-diene) standards were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). 13C12-PCB 141 and 13C12-PCB 208 were purchased from Cambridge Isotope Laboratories (Andover, MA).

2.2. Sampling

A total of 54 birds, including 16 LVBs (Pycnonotus sinensis), 19 LTSs (Lanius schach), and 19 OMRs (Copsychus saularis), were collected from seven sites in the PRD, South China between September 2009 and May 2010. The detail of avifaunal sampling method was given in Zhang et al. (2011a). Of the seven sites, the four sites located in the middle of the PRD have highly developed industries and are considered as urban area. The other three sites are characterized by agricultural activities and are considered as rural area. Map of sampling sites are shown in the Appendix (Fig. A1) and detailed information on sample number in rural and urban sites are listed in Table 1. Birds were transported immediately to laboratory and euthanized with N2. The necessary permit was obtained from Forestry Bureau of Guangdong Province for this research under Law of the People’s Republic of China on the Protection of Wildlife. Pectoral muscle and liver were excised from each bird and stored at −20 °C until chemical analysis.

2.3. Sample preparation

The procedure for sample extraction was described in our previous study (Luo et al., 2009). Briefly, a homogenized sample of muscle or liver tissue was mixed with anhydrous sodium sulfate, spiked with surrogate standard (13C12-PCB 141) and Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was determined gravimetrically on an aliquot of the extract. The extract used for chemical analysis was purified by gel permeation chromatography using a glass column (50 cm × 2.5 cm i.d.) packed with 40 g SX-3 Bio-Beads (Bio-Rad Laboratories, Hercules, CA) and eluted with dichloromethane/hexane (v/v = 1:1) for lipid removal. Eluate from 90 to 280 mL containing DP was collected and concentrated to 1 mL, further cleaned up on a column packed with 8 cm neutral silica and 8 cm acidified silica and eluted with 30 mL hexane/dichloromethane (v/v = 1:1). The eluate was concentrated to near dryness under N2 and reconstituted in 50 μL of iso-octane, spiked with known amount of internal standard (5 ng 13C12-PCB 208) before instrumental analysis.

2.4. Chemical analysis

DP was quantified by an Agilent 6890 gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC/MS) using electron capture negative ionization (ECNI) in the selective ion-monitoring mode and separated by a DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. The initial oven temperature was set as 110 °C (held for 1 min), ramped at 8 °C/min from 180 °C (held for 1 min), and then 2 °C/min to 240 °C (held for 5 min), 2 °C/min to 280 °C (held for 15 min), and finally 10 °C/min to 310 °C (held for 10 min). 1 μL of sample was manually injected in the pulsed splitless mode. The temperature of the injection port was set at 290 °C. The monitored and quantitative ions were as follows: m/z 653.8 and 651.8 for DP isomers.
The recoveries of isotopes compositions are expressed as isotope ratio mass spectrometer. The stable nitrogen and carbon elemental analyzer interfaced with a Finigan MAF ConFlo 111 was weighed in tin capsules and analyzed by a Flash EA 112 series isotopes analysis. Approximately 1 mg of the ground samples 2.5. Stable isotope analysis

Approximately 1 mg of the ground samples was weighed in tin capsules and analyzed by a Flash EA 112 series elemental analyzer interfaced with a Finigan MAF ConFlo 111 isotope ratio mass spectrometer. The stable nitrogen and carbon isotopes compositions are expressed as $\delta^{15}N$ and $\delta^{13}C$, with $\delta X = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$, where $\delta X$ is $\delta^{15}N$ or $\delta^{13}C$, and $R$ is the corresponding ratio of $^{15}N/^{14}N$ or $^{13}C/^{12}C$. The precision for this technique is $0.5\%$ (2 SD) for $\delta^{15}N$ and $0.2\%$ (2 SD) for $\delta^{13}C$.

2.6. QA/QC

The procedural blanks were performed in each batch of the samples. Trace amounts of syn- and anti-DP were detected in procedural blanks ($n = 10$) with mean concentrations of 0.43 ng mL$^{-1}$ and 1.14 ng mL$^{-1}$ (accounting for 5.3% and 8.5% of the sample with the lowest DP level), respectively, and they were subtracted from the samples. Recoveries of syn- and anti-DP were evaluated by spiking known concentrations of the target isomers in solutions and matrix, and passing them through the entire analytical procedure. The mean recoveries of syn-DP and anti-DP in three spiked blanks were 87 ± 5.2% and 92 ± 7.8%, respectively, and 96 ± 8.5% and 91 ± 10.2% in three matrix spikes. The mean recoveries of surrogate standard (13C12-PCB 141) in samples were 101 ± 14.3%. Reported concentrations were not corrected by surrogate recovery. Limit of quantifications (LOQs) for syn- and anti-DP were defined as three times the standard deviation of the target value in blanks. For anti-Cl11-DP and anti-Cl10-DP, LOQs were set as a signal of five times the noise level. The LOQs for syn-DP, anti-DP and anti-Cl11-DP/anti-Cl10-DP were 0.35, 2.28 and 0.03 ng g$^{-1}$, respectively.

2.7. Data analysis

Concentrations were expressed on a lipid weight (lw) basis. Concentrations below the LOQs were considered to be zero. Data were not normally distributed and were log transformed before being subjected to Analysis of Variance (ANOVA). The ANOVA test incorporated sampling site, tissue and bird species as fixed factors. Ratio of liver concentrations/[liver + muscle] concentrations was used to evaluate the tissue distribution of DP in bird. Simple linear correlation analysis was used to investigate the relationships between DP concentrations and $\delta^{15}N$ and between $f_{\text{anti}}$ and $\delta^{13}C$ in muscle of the three passerine bird species. All statistical analyses were conducted with SPSS 16.0 (SPSS Inc., Illinois, USA). The level of significance was set at 0.05.

3. Results and discussion

3.1. Levels of DP and its degradation products

Concentrations of DP in muscle and liver of three terrestrial passerine bird species were presented in Table 1. Syn- and anti-DP were detected in all samples. The DP concentrations ranged from 3.9 to 930 ng g$^{-1}$ lw in muscle and from 7.3 to 1300 ng g$^{-1}$ lw in liver, respectively. Birds in urban sites had significantly higher concentrations of DP than in rural sites (mean, 300 vs 73 ng g$^{-1}$ lw, $p < 0.01$), suggesting that DP is linked to industrialization and urbanization.

This is the first study reporting DP concentrations in tissues of terrestrial passerine bird species. To date, only limited studies have reported the DP concentrations in predatory and aquatic birds. Guerra et al. (2011) reported that DP was observed in all peregrine falcon eggs from Canada and Spain, with values ranging from 0.30 to 209 ng g$^{-1}$ lw. Venier et al. (2010) reported DP in plasma of nesting bald eagles from the Great Lakes region with an average concentration of 0.19 ± 0.10 ng g$^{-1}$ ww. DP was detected in eggs of herring gulls from six colonies located in the Laurentian Great Lakes basin of North America at concentrations ranging from 1.5 to 4.5 ng g$^{-1}$ ww (Gauthier et al., 2007). DP was also found in all white stork eggs from Spain at concentrations ranging from 0.003 to 1.4 ng g$^{-1}$ ww (Muñoz-Arnanz et al., 2011). DP concentrations in the present study were much higher than those data reported in North America and Europe. But this comparison must be cautiously treated because different tissues were used and the concentrations were expressed on different manners. Zhang et al. (2011b) reported DP concentrations in muscle and liver tissues of five waterbird species from an e-waste recycling region in the PRD, South China. The concentrations (median from 7.4 to

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Tissue</th>
<th>$\delta^{13}C$ (%)</th>
<th>$\delta^{15}N$ (%)</th>
<th>Lipid (%)</th>
<th>Syn-DP</th>
<th>Anti-DP</th>
<th>Total DP</th>
<th>Anti-Cl11-DP</th>
<th>Syn-Cl11-DP</th>
<th>$f_{\text{anti}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LVB</td>
<td>Rural (n = 9)</td>
<td>Muscle</td>
<td>-25.81 ± 0.17</td>
<td>5.14 ± 0.93</td>
<td>3.54 ± 0.23</td>
<td>0.53 (0.15–0.53)</td>
<td>20 (13.4–52)</td>
<td>15 (3.9–68)</td>
<td>nd (0.34)</td>
<td>nd</td>
<td>0.84 ± 0.02</td>
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<td></td>
<td>Urban (n = 7)</td>
<td>Muscle</td>
<td>-25.48 ± 0.56</td>
<td>6.12 ± 0.78</td>
<td>3.59 ± 0.22</td>
<td>4.4 (2.8–13)</td>
<td>19 (7.5–34)</td>
<td>23 (10–47)</td>
<td>nd (0.85)</td>
<td>nd</td>
<td>0.76 ± 0.02</td>
</tr>
<tr>
<td>LTS</td>
<td>Rural (n = 8)</td>
<td>Muscle</td>
<td>-23.32 ± 0.55</td>
<td>4.60 ± 0.55</td>
<td>3.20 ± 0.44</td>
<td>3.6 (2.6–25)</td>
<td>17 (9.6–100)</td>
<td>21 (12–130)</td>
<td>nd (0.20)</td>
<td>nd</td>
<td>0.80 ± 0.02</td>
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<td></td>
<td>Urban (n = 11)</td>
<td>Muscle</td>
<td>-23.40 ± 0.45</td>
<td>6.39 ± 0.33</td>
<td>4.13 ± 0.21</td>
<td>18 (9.9–150)</td>
<td>63 (25–350)</td>
<td>80 (37–510)</td>
<td>nd (7.6)</td>
<td>nd (nd–2.4)</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>OMR</td>
<td>Rural (n = 5)</td>
<td>Muscle</td>
<td>-23.27 ± 0.39</td>
<td>5.74 ± 1.02</td>
<td>3.57 ± 0.23</td>
<td>5.7 (4.0–8.9)</td>
<td>17 (16–81)</td>
<td>22 (21–90)</td>
<td>nd (1.4)</td>
<td>nd</td>
<td>0.80 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Urban (n = 11)</td>
<td>Muscle</td>
<td>-22.01 ± 0.39</td>
<td>6.66 ± 0.42</td>
<td>3.42 ± 0.30</td>
<td>30 (8.5–280)</td>
<td>77 (30–650)</td>
<td>110 (39–930)</td>
<td>0.15 (nd–7.1)</td>
<td>nd (nd–6.5)</td>
<td>0.73 ± 0.01</td>
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<tr>
<td></td>
<td>Liver</td>
<td>Liver</td>
<td>23.40 ± 0.45</td>
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a LVB = light-vented bulbul, LTS = long-tailed shrike, OMR = oriental magpie-robin.
b Mean ± SE.
c Sum of syn- and anti-DP.
d nd: Not detected.
e Calculated with the relative response factor of anti-Cl11-DP.
600 ng g⁻¹ lw) in these waterbirds were similar to the present study (median from 19 to 350 ng g⁻¹ lw). The relatively high DP levels in bird species from the PRD could be linked to high density of electronic/electrical industries and electronic waste (e-waste) recycling practices in this region (Yu et al., 2010). DP has been reported in air, plant (Chen et al., 2011), soil (Yu et al., 2010), water, sediment, fish (Wu et al., 2010; Zhang et al., 2010), and human serum (Ren et al., 2009) and hair (Zheng et al., 2010) from the PRD in South China. Burgeoning electronic/electrical manufacturing industries and intensive e-waste recycling activities might accelerate the release of DP into the environment. In fact, high DP concentrations were often found near the DP's manufacturing sites and/or accumulated from environment. In fact, high DP concentrations ranging from nd to 7.6 ng g⁻¹ were detected but anti-Cl₁₁-DP in 15 of 108 bird samples (7 LTSs and 8 OMRs). It is believed that the detected frequencies of anti-Cl₁₁-DP in LVB, LTS, and OMR were 28%, 37%, and 55%, respectively. Another dechlorination product was also found in 15 of 108 bird samples (7 LTSs and 8 OMRs). This result is consistent with the previous finding in waterbirds from an e-waste recycling region in South China (Zhang et al., 2011b), in which DP concentrations in liver were also higher than those in muscle.

Considering that the muscle has larger biomass than the liver, DP in muscle was used for inter-species comparison. To avoid the interference of sampling site on the level of DP, birds in rural and urban sites were separately used to perform ANOVA. The result revealed significant differences on DP concentrations among bird species in both rural and urban sites (p < 0.05), increased in the order of LVB < LTS < OMR (Table 1). Concentrations of DP in both rural and urban sites were separately used to perform ANOVA. The result revealed significant differences on DP concentrations among bird species in both rural and urban sites (p < 0.05), increased in the order of LVB < LTS < OMR (Table 1). The relatively high DP concentration in LVB was formed from biotransformation of anti-Cl₁₁-DP and syn-Cl₁₁-DP in bird was derived from in environmental matrix and not formed from e-waste recycling areas (Sverko et al., 2011).

Correlation analysis revealed that anti-Cl₁₁-DP was significantly correlated with anti-Cl₁₁-DP in both muscle (p = 0.001) and liver (p = 0.011) tissues (Fig. 1). This result suggested that anti-Cl₁₁-DP in bird was derived from in vivo dechlorination of anti-Cl₁₁-DP and/or absorbed from food along with anti-Cl₁₁-DP. Zheng et al. (2010) has suggested that anti-Cl₁₁-DP found in the human hair is likely accumulated from environmental matrix and not formed from biotransformation of parent DP because anti-Cl₁₁-DP was significantly correlated with anti-Cl₁₁-DP and the regression lines have the same slope in both human hair and dust sample. Whether anti-Cl₁₁-DP in bird was formed from biotransformation of anti-Cl₁₁-DP and/or accumulated from environment is not clear in the current study. Further research on the origin of dechlorination products of DP in bird species is needed.

3.2. Tissue distribution and inter-species variation

The ratios of liver to muscle (L/M) were used to analyze tissue-specific differences in three passerine bird species. Due to low detected frequencies, the tissue and species distribution of anti-Cl₁₁-DP and syn-Cl₁₁-DP was not discussed in the present study. All collected bird samples except 3 LVBs and 4 LTSs had ratio of L/M > 0.5 (Fig. 2). T-test analysis indicated that ratios of L/M for syn- and anti-Cl₁₁-DP were all significantly higher than 0.5 for the three bird species (p < 0.05), suggesting liver-specific accumulation of DP. This result is consistent with the previous finding in waterbirds from an e-waste recycling region in South China (Zhang et al., 2011b), in which DP concentrations in liver were also higher than those in muscle.

Stable nitrogen isotope ratio, which is affected by dietary exposure, provided independent measurement of trophic level in wildlife (Deniro and Epstein, 1978; Jardine et al., 2006). In the present study, δ¹⁵N values in muscle were measured to demonstrate the differences of trophic level between bird species and to investigate trophic level effects on the DP levels in bird species. Wide ranges of δ¹⁵N were found at values ranged from 1.88‰ to 9.10‰, from 2.57‰ to 8.79‰, and from 3.22‰ to 9.38‰ for LVB, LTS, and OMR, respectively. This result indicated that it was not reasonable to identify the trophic level using an exact numerical value (average or median) for each species, which can be attributed to the largely variability in food items among intra-species individuals. Therefore, individual samples rather than bird species as a whole were used to assess the trophic transfer of DP.

Simple linear correlation analysis showed that positive correlations exist between log normalized concentrations of DP (syn- and anti-Cl₁₁-DP) and δ¹⁵N values in both rural and urban sites (Fig. 3). Since the δ¹⁵N values is related directly to trophic level of bird, the significant positive correlations between δ¹⁵N values and levels of DP in both rural and urban sites (Fig. 3), implied that biomagnifications of DP occurred in these terrestrial passerine bird species. This is different from the results on DP in waterbirds collected in an e-waste
recycling area in South China, in which both syn- and anti-DP showed no biomagnifications (Zhang et al., 2011b). Another two studies have reported the trophic transfer of DP in aquatic food webs. DP (syn- and anti-DP) was significantly biomagnified in a freshwater food web from a highly contaminated pool in South China after excluding the highest trophic level fish species (Wu et al., 2010). In the Lake Winnipeg food web, biomagnifications for anti-DP were observed, while no statistically significant trophic magnification factors (TMFs) for the two isomers were found in the Lake Ontario food web (Tomy et al., 2007). The discrepant results on trophic transfer of DP might be attributed to various factors including the composition of food web, species-specific differences in bio-transformation, limited sample size, or a violation of the steady-state assumption required for calculating TMFs (Sverko et al., 2011).

3.4. Isomeric profiles of DP

The fraction of anti-DP ($f_{anti}$), defined as the concentration of anti-DP divided by the total DP concentration, was calculated for muscle and live tissues of three bird species to evaluate the possible stereoisomer selective enrichment of DP isomers. No significant difference in the $f_{anti}$ values between muscle and liver was observed in the three bird species. Therefore, an overall $f_{anti}$ (muscle and liver) was calculated for the three bird species (Fig. 4). $f_{anti}$ values were 0.828 ± 0.021, 0.803 ± 0.018, and 0.783 ± 0.015 in rural sites and 0.733 ± 0.022, 0.762 ± 0.016, and 0.733 ± 0.014 in urban sites at LVB, LTS, and OMR, respectively. The $f_{anti}$ values in birds from rural sites were significantly higher than those from urban sites ($p < 0.05$). The difference in $f_{anti}$ values between rural and urban sites at least can be attributed to two reasons. The first is the commercial DP used in rural and urban sites might be different. Several $f_{anti}$ values for the commercial mixture were reported in the literatures (Hoh et al., 2006; Wang et al., 2010; Wu et al., 2010). The second reason can be the possible alteration of DP before uptake by the birds. Generally, no direct emission of DP exists in rural sites. The DP in rural sites might undertake long-range atmospheric transport which could alter the DP ratios (Hoh et al., 2006; Möller et al., 2010). In urban sites, the $f_{anti}$ values were reported ranged from 0.70 to 0.76 in sediment and dust samples in previous studies (Wu et al., 2010; Zheng et al., 2010). The mean $f_{anti}$ values in birds collected from urban sites in the present study were consistent with those in abiotic matrix.
In another study which reported DP in terrestrial bird (peregrine falcon eggs) from Spain, the average \( f_{\text{anti}} \) value was 0.77, which is comparable with the present study (Guerra et al., 2011). Gauthier and Letcher (2009) reported that the average \( f_{\text{anti}} \) value was 0.69 ± 0.08 in 101 eggs of the herring gulls from the Laurentian Great Lakes. Muñoz-Arnanz et al. (2011) reported that the average \( f_{\text{anti}} \) values in white stork eggs from Doñana National Park and Madrid in Spain were 0.64 ± 0.07 and 0.66 ± 0.12, respectively. In five waterbird species collected from an e-waste recycling area in South China, Zhang et al. (2011b) reported that the mean \( f_{\text{anti}} \) values were 0.34–0.61. These \( f_{\text{anti}} \) values in aquatic birds were well below those in terrestrial birds from the present and previous studies (Guerra et al., 2011). It seems that there is difference in stereoisomer selective enrichment of DP between terrestrial and aquatic birds. The aquatic bird accumulated more syn- than anti-DP. The two isomers were reported to have different aqueous solubility, at 207 ng L\(^{-1}\) and 572 ng L\(^{-1}\) (Sverko et al., 2008), which may result in selective enrichment of isomer with high solubility for aquatic biota. Currently, no sufficient data is available for researchers to assume the different stereoisomer selective enrichment of DP between terrestrial and aquatic biota. Previous studies have observed that the \( f_{\text{anti}} \) values in fish (Hoh et al., 2006; Tomy et al., 2007; Wu et al., 2010; Shen et al., 2011) and oyster (Jia et al., 2011) were much less than that of commercial DP product, indicating a preferential accumulation of the syn-isomer in these aquatic species. Too many factors may contribute to the confounding \( f_{\text{anti}} \) values measured in biota, such as difference sources, inter-species differences in bioaccumulation, bioavailability, and biotransformation efficiencies between syn- and anti-DP, and the possible alteration of \( f_{\text{anti}} \) values during transport of DP in both terrestrial and aquatic environment (Tomy et al., 2008; Gauthier and Letcher, 2009; Sverko et al., 2011). It remains unanswered which factor is the key role in determination of \( f_{\text{anti}} \) values in the current study.

Previous studies have demonstrated that \( f_{\text{anti}} \) values were associated with the trophic levels of biota. The higher the trophic level, the less the \( f_{\text{anti}} \) (Wu et al., 2010; Zhang et al., 2011b). The correlation analysis in the present study revealed that significant negative correlations between the \( f_{\text{anti}} \) values and \( \delta^{15}\text{N} \) existed in both rural and urban sites (\( p < 0.05 \)) (Fig. 5), although the \( f_{\text{anti}} \) values had spatial difference between rural and urban locations. This result is consistent with the finding for aquatic biota and waterbirds (Wu et al., 2010; Zhang et al., 2011b), confirming that higher trophic organisms may have higher metabolic capacities for anti-DP or preferentially accumulate syn-DP.

### 4. Conclusions

DP and its dechlorinated products (anti-Cl\(_{11}\)-DP and syn-Cl\(_{11}\)-DP) were determined in three terrestrial passerine bird species collected in the PRD, South China. The origin of dechlorinated products in birds is still unclear. Birds from urban sites showed higher concentrations of DP than rural locations, implying that DP is related to industrialization and urbanization. Significant correlation between \( \delta^{15}\text{N} \) values and concentration and isomeric composition of DP in both rural and urban sites indicated trophic level of birds are an important factor in determination of DP level and isomeric composition. The \( f_{\text{anti}} \) values in birds from rural sites were higher than those from urban sites. Further research is needed to understand the cause of dechlorination and the difference in stereoisomer selective enrichment of DP between terrestrial and aquatic birds.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.05.089.

### References


