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

Ping-Fan Wu [a, b], Lian-Lian Yu [a, b], Long Li [a], Yun Zhang [a], Xing-Hong Li [b, *]

[a] Hubei University of Technology, Wuhan 430068, China
[b] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, 18 Shuangqing Road, Haidian District, Beijing 100085, China

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.

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

* Corresponding author.
E-mail address: lxhzpb@rcees.ac.cn (X.-H. Li).

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et al., 2012; Tomy et al., 2007; Zhang et al., 2011). The occurrence of DP analogues, for instance, Cl_{10}-DP, Cl_{11}-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}), $^{13}C_{10}$ *syn*-DP (100 μg mL^{-1}), $^{13}C_{10}$ *anti*-DP (100 μg mL^{-1}) and $^{13}C_{12}$ PCB-208 (40 μg mL^{-1}) were obtained from Cambridge isotope laboratories Inc. (Massachusetts, USA). Stock solutions of *anti*-Cl_{10}-DP (50 μg mL^{-1}), *anti*-Cl_{11}-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). H_2SO_4 (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 $^{13}C_{10}$ *syn*-DP and $^{13}C_{10}$ *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 ($^{13}C_{12}$-PCB-208) was added prior to the GC/NCI-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*-Cl_{11}-DP and *syn*-Cl_{11}-DP, *m/z* 583.7 and 585.7 for *anti*-Cl_{10}-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 $^{13}C_{10}$ labeled *syn*-DP and *anti*-DP, *m/z* 510 and 508 for $^{13}C_{12}$-labeled CB-209 and *m/z* 476 and 478 for $^{13}C_{10}$ labeled PCB-208. *syn*-Cl_{11}-DP is quantified by the relative response factor of *anti*-Cl_{11}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 $^{13}C_{10}$ *syn*-DP, 64.6%–113% for $^{13}C_{10}$ *anti*-DP and 73.9–109% for $^{13}C_{12}$ 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*-Cl_{11}-DP, Mirex and Dec 602, respectively. All reported concentrations were corrected by surrogate recovery.