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Species-specific accumulation of halogenated flame retardants in eggs of terrestrial birds from an ecological station in the Pearl River Delta, South China

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HIGHLIGHTS

- Elevated levels of HFRs were determined in eggs of terrestrial passerine bird.
- Interspecific differences in HFR levels may be attributed to differences in diet.
- PBDEs were the predominant HFRs in bird eggs, followed by DBDPE and DP.
- The f_{anti} values were negatively correlated to DP levels in bird eggs.
- *Anti*-Cl_{11}-DP was found in most bird eggs.

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ABSTRACT

Little information is available on the bioaccumulation of halogenated flame retardants (HFRs) in terrestrial ecosystem. Eggs of light-vented bulbul, yellow-bellied prinia, plain prinia, and dark green white-eye were collected from an ecological station in the Pearl River Delta, South China to investigate the occurrence of polybrominated diphenyl ethers (PBDEs) and several alternative HFRs, including decabromodiphenyl ethane (DBDPE), dechlorane plus (DP), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromotoluene (PBT), and 2,3,5,6-tetrabromo-p-xylene (pTBX). Concentrations of PBDEs, DBDPE, DP, HBB, PBEB, BTBPE, PBT, and pTBX ranged from 53–423, 6.1–609, 4.6–268, not detected (nd)-10, nd-1.4, nd-1.7, nd-7.5, and nd-3.2 ng g^{-1} lw, respectively. Light-vented bulbul exhibited significantly lower levels of PBDEs, DBDPE, DP, and HBB than other three bird species due to its phytophagy and the other three bird species' insectivores. PBDEs were the predominant HFRs in bird eggs, followed by DBDPE and DP. Significant negative relationship between the fraction of *anti*-DP and DP concentrations was observed in bird eggs, suggesting that DP levels play an important role in determining the isomeric composition. *Anti*-Cl_{11}-DP, the dechlorinated products of DP, was found in bird eggs with concentrations ranging from nd to 0.86 ng g^{-1} lw and its source is worth further research.

1. Introduction

Halogenated flame retardants (HFRs) have been widely used in electronics, textiles, paints, polyurethane foams, thermoplastics, and building materials to reduce the flammability of many products. Currently, over 75 chemicals have been used as HFRs (Alaee et al., 2003). Among them, polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane have been banned or phased out because of their persistence, bioaccumulation and toxicological effects (Guerra et al., 2012). To meet fire and safety regulations, several non-regulated HFRs, such as decabromodiphenyl ethane (DBDPE), dechlorane plus (DP), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromotoluene (PBT), and 2,3,5,6-tetrabromo-p-xylene (pTBX), have been used as replacements for the restricted HFRs in various products (Covaci et al., 2011; Sverko et al., 2011). Although the information regarding environmental behaviors of these alternative HFRs is limited, available data have suggested that the alternative HFRs might also be persistent, bioaccumulative, and toxic (Covaci et al., 2011).

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Birds have been frequently used as sentinel species to measure the levels and effects of HFRs in the environment because of their sensitivity to environmental changes, top position in the food chain, and dietary diversity (Voorspoels et al., 2006; Sun et al., 2012a). However, ethical and practical reasons impede the sacrifice of free-living birds. Therefore, bird eggs have been successfully used as non-destructive monitoring tools to determine HFRs in the environment. Eggs can not only reflect levels of HFRs in female birds, but also be regarded as a developmental stage which is the most sensitive to HFRs effects (Lam et al., 2008; Gao et al., 2009; Van den Steen et al., 2010). Additionally, eggs of most bird species can be easily collected and the removal of a single egg from a clutch is expected to have a minimal effect on the bird community (Van den Steen et al., 2010). To date, a number of studies have been conducted on PBDE contamination in bird eggs (Jaspers et al., 2005; Chen and hale, 2010; Newsome et al., 2010; Van den Steen et al., 2010), but information on the bioaccumulation of the alternative HFRs in avian eggs, especially terrestrial birds, is scarce.

The Pearl River Delta (PRD) has been becoming one of the manufacturing bases for electronic/electrical products and has also been one of the largest dumping sites of electrical waste (e-waste) in the world. It houses many e-waste recycling areas, such as Qingyuan and Guiyu (Robinson, 2009). It has been estimated that 50–70% of e-wastes from the United States were exported to China for recycling (Puckett et al., 2002) and approximately 145 million electronic devices were disposed using crude recycling techniques in the PRD in 2002 alone, containing up to 2.61×10^8 kg of PBDEs (Martin et al., 2004). Therefore, this region is likely to be a hotspot for HFR contamination. More recently, higher levels of HFRs have been detected in biotic and abiotic samples collected from the PRD (Shi et al., 2009; Zhang et al., 2011; Sun et al., 2012a). Birds living in this region might be exposed to elevated levels of HFRs. However, data on the occurrence of HFRs in bird eggs in this hotspot have not been available yet.

In the present study, eggs of four terrestrial resident passerine birds were collected from an ecological station in the PRD, South China. Concentrations of PBDEs and several alternative HFRs (including DBDPE, DP, HBB, PBEB, PBT, BTBPE, and pTBX) in bird eggs were determined. The objectives of this study were to explore the occurrence of HFRs in the PRD and investigate the accumulation and profiles of HFRs in bird eggs. Species-specific contamination patterns and dechlorination products of DP in bird eggs were discussed in details.

2. Materials and methods

2.1. Sample collection

A total of 33 bird egg samples, including 16 light-vented bulbuls (*Pycnonotus sinensis*, LVB), 9 yellow-bellied prinias (*Prinia flaviventris*, YBP), 4 plain prinias (*Prinia inornata*, PP), and 4 dark green white-eyes (*Zosterops japonicus*, DGW), were collected between 2010 and 2012 at Heshan Hilly Land Interdisciplinary Experimental Station, Chinese Academy of Sciences in the PRD, South China, which is one of the field stations of the Chinese Ecosystem Research Network (Fig. S1, Supporting information). Details of the sampling site can be found elsewhere (Sun et al., 2011). More detailed information on feeding and living habits of each species are given in Table S1. All eggs were nonviable and obtained after the end of the incubation period. The eggs were cleaned with deionized water and then stored at −20 °C until chemical analysis.

2.2. Chemical analysis

The extraction methods were similar to those described in Sun et al. (2012a). Briefly, a homogenized sample of approximately 0.8–3.1 g egg (excluding the eggshell) was mixed with anhydrous sodium sulfate, spiked with surrogate standards ($^{13}C_{12}$-BDE 209, BDE 77, 181 and 205) and then Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was gravimetrically determined from an aliquot of the extract. Another extract used for chemical analysis was purified by gel permeation chromatography using a glass column 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 HFRs was collected and concentrated to 1 mL, further cleaned up on a column filled 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 a gentle nitrogen stream and reconstituted in 100 μL of isooctane. Internal standards (BDE 118 and 128) were spiked before instrumental analysis.

Tri- to hepta-BDE congeners (BDE 28, 47, 66, 100, 99, 85, 154, 153 and 183), DP, HBB, PBEB, PBT, and pTBX were analyzed by an Agilent 6890 gas chromatograph (GC) connected with an Agilent 5975 mass spectrometer (MS) using electron capture negative ionization (ECNI) in the selective ion-monitoring (SIM) mode. A DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific) was used for separation. Octa- to deca-BDE congeners (BDE 202, 197, 203, 196, 207, 206 and 209), DBDPE, and BTBPE were quantified by a Shimadzu model 2010 GC coupled with a model QP 2010 MS (Shimadzu, Japan) using ECNI in the SIM mode and separated by a DB-5HT (15 m × 0.25 mm × 0.10 μm, J&W Scientific). Details on the GC conditions and monitored ions can be found in Luo et al. (2009).

2.3. Quality assurance and quality control

A procedural blank was performed in each batch of the sample analysis. BDE 153 and 209 were detected in the procedural blanks ($n = 4$) and their amounts were less than 5.4% of those in the samples with the lowest levels. The concentrations in the samples were blank corrected accordingly. Recoveries of HFRs were evaluated by spiking the known amounts of 10 PBDE congeners (BDE 28, 47, 66, 85, 99, 100, 138, 153, 154 and 183), DBDPE and DP (*syn*- and *anti*-DP) in solution and matrix, and passing them through the entire analytical procedure. The mean recoveries of the target compounds in the spiked blanks ($n = 3$) and in the spiked matrices ($n = 3$) ranged from 75% to 99% and 76% to 104%, respectively. The relative standard deviations of all targets were less than 15%. The mean recoveries of surrogate standards in all samples were as follows: $^{13}C_{12}$-BDE 209, 89.0 ± 12.5%; BDE 77, 94.1 ± 9.7%; BDE 181, 80.1 ± 9.8%, and BDE 205, 95.2 ± 13.7%. For BDE 153 and 209, method detection limits (MDLs) were set as three times the standard deviation of the target value in blanks. For the undetected compounds in blanks, MDLs were defined as a signal of 5 times the noise level. Based on the mean lipid weight (lw) of the samples, MDLs for PBDEs ranged from 0.019 to 4.75 ng g^{-1} lw. MDLs for DBDPE, DP, HBB, PBEB, BTBPE, PBT, pTBX, *anti*-Cl_{10}-DP, and *anti*-Cl_{11}-DP were 3.67, 3.26, 0.028, 0.018, 0.74, 0.029, 0.007, 0.035, and 0.028 ng g^{-1} lw, respectively.

2.4. Statistical analysis

Concentrations were reported on a lipid weight basis. Data analysis was performed using SPSS 16.0 (SPSS Inc., Illinois). The level of significance was acceptable at $p < 0.05$. For samples with concentrations below MDLs, a value of 1/2 MDLs was used for data analysis. Non-normally distributed data were $\log_{10}$ transformed before being subjected to statistical analysis. One-way analysis of variance (ANOVA) was used to determine interspecific differences in contaminant concentrations of bird eggs. Linear correlation analysis was used to investigate the relationships between PBDEs, DBDPE, DP and HBB levels among the bird species. PBEB, BTBPE,