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Contaminants of legacy and emerging concern in terrestrial passerines from a nature reserve in South China: Residue levels and inter-species differences in the accumulation

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ABSTRACT

Knowledge is limited about the bioaccumulation of persistent halogenated compounds (PHCs) in terrestrial wildlife. Several PHCs, including dichlorodiphenyltrichloroethane (DDT) and its metabolites (designated as DDTs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), decabromodiphenylethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and stable isotopes ($\delta^{15}N$ and $\delta^{13}C$) were analyzed in the muscle of four terrestrial passerines, *Parus major*, *Copsychus saularis*, *Pycnonotus sinensis* and *Pycnonotus jocosus*, from a nature reserve in South China. *P. major* had the highest PHC concentrations, with median values of 1060, 401, 92, 25 and 0.3 ng/g lipid weight for DDTs, PCBs, PBDEs, DBDPE and BTBPE, respectively. Fractions of DDT in *P. jocosus* and PCBs 153, 118 and 180 in *C. saularis* were higher compared with the other species. The inter-species differences in PHC concentrations and profiles could be attributed to the differences in trophic level, diet, living habits and metabolic capacity among the birds.

1. Introduction

Persistent halogenated compounds (PHCs), including dichlorodiphenyltrichloroethane (DDT) and its metabolites chlorodiphenyldichloroethylene (DDE) and dichlorodiphenyl dichloroethane (DDD) (the sum of DDT, DDE, and DDD is designated as DDTs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are well-known for their persistence, bioaccumulation, long-range transport potential and toxicity (Lohmann et al., 2007; Kelly et al., 2007). Because of these characteristics, DDTs, PCBs and components of the Penta-BDE and Octa-BDE mixtures have been regulated by the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001, 2010). Deca-BDE has also been phased-out in Europe, and the production and its use in new products in the United States was discontinued in 2013 (USEPA, 2009). In response to PBDE bans or restrictions, some nonregulated brominated flame retardants (BFRs), such as decabromodiphenylethane (DBDPE) and 1, 2-bis (2, 4, 6-tribromophenoxy) ethane (BTBPE), are being used as replacements in some applications (Covaci et al., 2011; de Wit et al., 2010). Given that these alternative BFRs share some physiochemical properties similar to those of PBDEs, one might suspect that they might possibly be bioaccumulated in wildlife and humans, leading to exposure concerns (Covaci et al., 2011; de Wit et al., 2010).

Various studies conducted within the past decade have demonstrated the PHC contamination in South China (Zhang et al., 2002; Lin et al., 2009; Guo et al., 2009; Wu et al., 2010; Mo et al., 2012; Luo et al., 2009; Breivik et al., 2011; Liu et al., 2014; He et al., 2012). Because of the heavily historical use and the newly inputs, DDTs may still pose a threat to wildlife that resident in South China (Guo et al., 2009; Wu et al., 2012). In addition to DDTs contamination, fairly high concentrations of PCBs, PBDEs and some alternative BFRs were reported in wildlife from South China, particularly those from electronic waste (e-waste) recycling sites and electronics manufacturing and assembling centers in this

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region (Wu et al., 2010; Mo et al., 2012; Luo et al., 2009; He et al., 2012). All the bioaccumulation studies were almost exclusively carried out in aquatic ecosystems; studies on these chemicals in terrestrial ecosystems are scarce. Previous studies indicated that bioaccumulation of chemicals with high octanol–water partition coefficient (K_{OW}) and octanol–air partition coefficient (K_{OA}) (log K_{OW} >5 and log K_{OA} >6) may be differed between aquatic and terrestrial animals because of the different ability to absorb and eliminate these chemicals between water-respiring and air-breathing organisms (Kelly et al., 2007). Most of the PHCs fall the K_{OW}/K_{OA} ranges. Therefore, research focusing on accumulation characteristic of PHCs in terrestrial wildlife is essential to better understand the bioaccumulation behavior and impacts of these chemicals. Moreover, few studies have examined the occurrence of the PHCs in wildlife from the sites of ecological concern including nature reserves in this region (Mo et al., 2013). Occurrence of these chemicals in wildlife from key ecosystems is of concern given that most of the PHCs had shown toxicities to organisms (Hellou et al., 2013; George et al., 1988; Darnerud, 2003).

Birds, including terrestrial passerines, have been widely used to study environmental contamination and to evaluate the health of certain ecosystems (Furness, 1993). A few of these species spend their entire adult life in relatively small home ranges, territories and foraging areas. Additionally, they are widespread, sensitive to environmental changes and easily sampled. They are therefore particularly suitable for monitoring local contamination and for assessing the potential effects, often cumulative and non-linear, of many environmental contaminants acting simultaneously (Dauwe et al., 2003; Van den Steen et al., 2009).

The Shimentai National Nature Reserve (SNNR) is the largest nature reserve in South China. It is located in the northern part of the Guangdong Province and is close to some e-waste recycling sites and electronics manufacturing and assembling centers (Fig. 1). The SNNR is home to various kinds of vertebrates including 208 bird species and 68 other vertebrate species, some of which are rare or endangered (Kadoorie Farm and Botanic Garden, 2003). To date, few study have addressed the question of whether the SNNR wildlife have accumulated the PHCs and potentially been affected by these chemicals. The objective of the present study was to examine PHC residue levels and profiles in the muscle tissue of four terrestrial passerine bird species from the SNNR. Nitrogen and carbon stable isotopes in these birds were also analyzed to assess the influences of trophic level and diet on the bioaccumulation of PHCs.

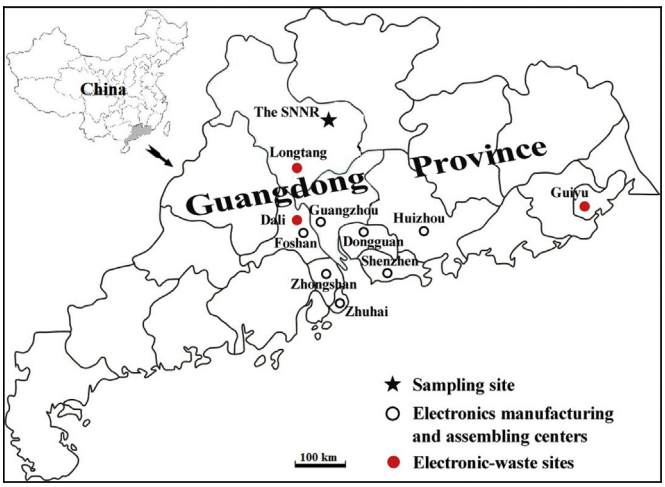

Fig. 1. Map of sampling site. SNNR = Shimentai National Nature Reserve.

2. Materials and methods

2.1. Sample collection

A total of 36 adult (fully grown) terrestrial passerine birds, including the great tit (*Parus major*) (GT) (n = 18), the oriental magpie-robin (*Copsychus saularis*) (OMR) (n = 7), the light-vented bulbul (*Pycnonotus sinensis*) (LVB) (n = 5) and the red-whiskered bulbul (*Pycnonotus jocosus*) (RWB) (n = 6), were collected from the SNNR between June 2012 and October 2013. The four bird species are all sedentary species. GT and OMR are insectivorous (Chen et al., 2012; Viney et al., 1994), while LVB and RWB are omnivorous (Peng et al., 2008). The birds were caught by plastic bird netting, approved by the Forestry Bureau of Guangdong Province, China. These birds were euthanized with N_2 and the pectoral muscle from each bird was excised. The muscle samples were stored at −20 °C until chemical analysis.

2.2. Sample extraction, cleanup, and analysis

The methods for sample extraction, cleanup and analysis were similar to those described elsewhere (Mo et al., 2012, 2013). Briefly, approximately 2–6 g of muscle tissue was homogenized and spiked with surrogate standards (CBs 30, 65 and 204 for DDTs and PCBs; $^{13}C_{12}$-BDE 209 and BDEs 77, 181, and 205 for PBDEs, BTBPE and DBDPE). The samples were then mixed with ashed anhydrous sodium sulfate and extracted in a Soxhlet apparatus for 48 h using 50% acetone in hexane. The extract was concentrated to 10 mL, and an aliquot of 1 mL was used for the determination of lipid content by gravimetry. Another aliquot of the extract was concentrated to 2–3 mL, and was then subjected to gel permeation chromatography (GPC) for lipid removal. The GPC fraction containing the target compounds was concentrated to 1–2 mL and purified by passage through a silica gel packed column (10-mm i.d.) which containing neutral activated silica (8 cm) and 40% sulfuric acid silica gel (8 cm). The final extracts were concentrated to near dryness under a gentle stream of purified nitrogen, and reconstituted in 50 μL of *iso*-octane. Known amounts of internal standards (CBs 24, 82 and 198 for DDTs and PCBs; BDEs 118 and 128 for PBDEs, BTBPE and DBDPE) were added to all extracts prior to instrumental analysis.

The extracts were injected into an Agilent 6890 gas chromatograph (GC) coupled to an Agilent series 5975B mass spectrometer (MS) for the determination of DDTs and PCBs. The MS was operated in an electron impact, selected ion monitoring mode (SIM). A DB-5 MS capillary column (60 m length, 250-μm i.d., 0.25-μm film thickness; J&W Scientific) was used for the separation of individual DDT or PCB isomers/congeners. The measurement of tri-to hepta-BDE congeners (BDEs 28, 47, 66, 85, 100, 99, 153, 154 and 183) was accomplished by use of an Agilent 6890 GC–5975 MS in an electron capture negative ionization (ECNI) mode. A DB-XLB capillary column (30 m length, 250-μm i.d., 0.25-μm film thickness; J&W Scientific) was used for the separation of congeners. The analysis of octa-to deca-BDE congeners (BDEs 196, 197, 202, 203, 206, 207, 208 and 209), DBDPE and BTBPE was performed using a Shimadzu Model QP2010 GC–MS using ENCI in the SIM mode. A DB-5HT capillary column (15 m length, 250-μm i.d., 0.1-μm film thickness; J&W Scientific) was used for separation. Details of the GC conditions and monitored ions have been described elsewhere (Mo et al., 2012, 2013).

2.3. Stable isotopic analysis

Nitrogen and carbon stable isotopes of the samples were analyzed using a previously described method (Wu et al., 2009). Briefly, subsamples of the muscle were freeze-dried, ground with a mortar and pestle and weighed (~1 mg) in tin capsules. Nitrogen