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Organohalogen contamination in passerine birds from three metropolises in China: Geographical variation and its implication for anthropogenic effects on urban environments

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ABSTRACT

Contamination of organohalogen pollutants (OHPs), including dichlorodiphenyl trichloroethane and its metabolites (DDTs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), decabromodiphenylethane (DBDPE), hexabromocyclododecanes (HBCDs), and dechlorane plus (DP) in three metropolises of China, Beijing, Wuhan, and Guangzhou, and a reference rural site were determined using terrestrial residential passerine species as bioindicator. DDTs dominated in Wuhan whereas flame retardants dominated in Guangzhou and Beijing. No geographical variation was found for PCB levels but it exhibited different homologue profiles among different sites which could be attributed to different dietary sources of birds. Industry characteristics of the sampling location contributed to the geographical differences in the occurrence and contamination profile of OHPs. The transformation of traditional agriculture characterized contamination profiles to industry characterized profiles in Beijing and Guangzhou implicates significantly environmental concern on the flame retardants contamination in non-hot-spot regions of China.

1. Introduction

The occurrence of organohalogen pollutants (OHPs), such as polychlorinated biphenyls (PCBs), dichlorodiphenyl trichloroethane and its metabolites (DDTs), polybrominated dipheny lethers (PBDEs), decabromodiphenylethane (DBDPE), hexabromocyclododecane (HBCDs), and dechlorane plus (DP), has been of great concern because of their persistent, bioaccumulative nature, and their adverse effects on both humans and wildlife. Numerous studies have demonstrated ubiquitous OHP contamination in biota and abiota in China (Law et al., 2008; Ma et al., 2012; Wu et al., 2012). By contrast with the modest growth in the European and North American market, the demand and consumption of flame retardants (FRs), including PBDEs, DBDPE, HBCDs, and DP, is still experiencing a rapid rise with the annual growth of nearly 10% in China (The Freedonia Group, 2011). Legacy pollutants, involving PCBs and DDTs, have been continuously releasing into the Chinese environment due to historical usage and emission (Zhang et al., 2002).

Passerine birds have been successfully used in OHP biomonitoring in terrestrial ecosystems (Eens et al., 2013; Sun et al., 2012a; Van den Steen et al., 2009). Residential passerine species are especially suitable to reflect local contamination because of their small home ranges, territories, and foraging areas (Dauwe et al., 2006; Van den Steen et al., 2008). Moreover, terrestrial passerine birds with large populations are widespread and easily collected, which enables large geographical-scale monitoring and international intercomparison on OHPs pollution (Van den Steen et al., 2009).

The Eurasian tree sparrow (*Passer montanus*, ETS), which is characterized as human commensals (Li et al., 2008), is generally exposed to OHPs via the similar routes (e.g. inhalation and food) as humans. It is also a common bird species with a broad distribution in varieties of environments along urban gradient in China (Zhang and Zheng, 2010). Accordingly, they are particularly suitable model species to study the effects of urbanization closely linked to human

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living environments (Zhang and Zheng, 2010). As for the common magpie (*Pica pica*, CM), it is also a common songbird in most of the northern hemisphere (Jaspers et al., 2008). Throughout its distribution range, the magpie is associated with human activities (Jerzak, 2001). Previous studies have demonstrated synurbanization of this species, owing to its abilities to exploit anthropogenic food resources and to nest near human settlement (Jerzak, 2001).

In the present study, various classes of OHPs, involving DDTs, PCBs, PBDEs, DBDPE, HBCDs, and DP, were determined in two terrestrial passerine bird species, ETS and CM. Beijing, Wuhan and Guangzhou were selected as targeted study areas based on their representativeness in the corresponding geographic position of China from North to South (Fig. S1). The objective of the present study was to investigate the spatial distribution in the occurrence of different OHPs and to obtain the comprehensive contamination profiles in the Chinese urban environment. This study would be significative to extend the database about background levels of OHPs in non-hot-spot regions, i.e. e-waste recycling areas, of China, to explore the local usage and emission of OHPs, as well as to provide a baseline for further long-term biomonitoring in larger geographical scale throughout China.

2. Materials and methods

2.1. Sampling

During the non-breeding season, a total of 76 birds, including 67 ETS and 9 CM, were collected between August 2009 and May 2011 from three regional metropolises and a reference site in China (Fig. S1). Of the three cities, Beijing (BJ), located in the North China Plain, is the capital city of China. 40 ETS were collected from 8 sites located in the downtown areas containing ~7500 people per km^2 of Beijing City. The sampling sites included residential communities, campus, park, and industrial area. Wuhan (WH), situated at the midstream of the Yangtze River, is the largest metropolis in the Central China and has been one of the most important bases of heavy industry and cotton origin over decades. 9 CM were collected from 1 site in the suburb area with the human population density of ~500 people per km^2. Guangzhou (GZ), as the principal capital of Guangdong Province, is a highly industrialized and urbanized city in the Pearl River Delta of South China. 19 ETS were collected from 2 sites in the downtown areas with a mean human population density of ~14 000 people per km^2. One site located in a campus and one site located in a residential community. Shaoguan (SG), located in the northern Guangdong Province, was characterized by agricultural activities with less population density (~100 people per km^2 in the sampling site) and therefore was chosen as a reference site in the present study. 8 ETS were sampled from a rural site located in Shaoguan (Table 1). The details of avifaunal sampling method were given in Zhang et al. (2011). The necessary permit for the sample collection was obtained from the local Forestry Bureau. Birds were transported immediately to the laboratory and euthanized with N_2. Pectoral muscle was excised from each specimen and stored at −20 °C prior to chemical analysis.

2.2. Sample preparation and analysis

Procedures for sample pretreatment have been given in details in our previous study (Yu et al., 2011) with modest modifications. Approximately 1 g muscle tissue was homogenized after lyophilization and Soxhlet extracted with acetone/hexane (1:1, v/v). Surrogates (BDE-77, -181, ^{13}C-BDE-209 for PBDEs, DBDPE and DP, CB-30, -65, and -204 for PCBs and DDTs, ^{13}C-labled α-, β-, and γ-HBCD for HBCD diastereoisomers, respectively) were spiked prior to extraction. An aliquot of the extract was used for gravimetrical determination of lipid content. The remainder was further cleaned through gel permeation chromatography (GPC), followed by cleanup on a 2 g silica gel solid phase extraction column (Isolute®, Biotage AB, Sweden). The fraction containing all target compounds was obtained by 6.5 mL hexane/dichloromethane (60:40, v/v) and another 7 mL dichloromethane. The purified extracts were spiked with internal standards (BDE-118 and -128 for PBDEs, DBDPE and DP, CB-24, -82, and -198 for PCBs and DDTs, d_{18}-labled α-, β-, and γ-HBCD for HBCDs, respectively) before instrumental analysis. PBDEs, DP and DBDPE were analyzed by gas chromatography-electron capture negative ionization mass spectrometry (GC/ECNI-MS) in selected ion monitoring (SIM) mode. For tri- to hepta-BDE congeners and DP isomers, a 30 m × 0.25 mm i.d. × 0.25 μm DB-XLB capillary column (J&W Scientific, CA) was used. For the determination of octa- to deca-BDEs and DBDPE, a 15 m × 0.25 mm i.d. × 0.10 μm DB-5HT capillary column (J&W Scientific, CA) was used. PCB congeners, as well as dichlorodiphenyl trichloroethane and its metabolites (DDTs), were separated on a DB-5MS column (60 m × 0.25 mm i.d. × 0.25 mm, J&W Scientific, CA) installed on an Agilent 6890 GC-5975 MS system equipped with electron impact (EI) ion source. An Agilent 1200 series liquid chromatography (LC) system coupled to an Agilent 6410 electrospray triple quadrupole mass spectrometer operated in electrospray ionization (ESI) negative ion mode was used for HBCDs determination. HBCD diastereoisomers were separated through an XDB-C_{18} column (4.6 mm i.d. × 50 mm, 1.8 μm, Agilent, CA). More details of instrumental analysis were given in the Supplementary Data.

Stable nitrogen and carbon isotope analysis (δ^{15}N and δ^{13}C) were conducted on a Flash EA 112 series elemental analyzer coupled with a Finnigan MAT ConFlo III isotope ratio mass spectrometer using freeze-dried subsamples. Specific analytical approach and the assessment of isotopic ratios were previously given elsewhere (Yu et al., 2011).

2.3. QA/QC and data analysis

Procedural blanks were consistently analyzed and the mean values were used for subtraction. HBCD diastereomers were non-detectable in blanks and only few PBDE congeners, such as BDE-47, -206, -207, -208, and -209, and DP isomers (<10% of that in the samples) were found in blanks. The mean (±standard deviation) recoveries in matrices spiking triplicates ranged from 82.1 ± 1.3% to 104.3 ± 8.0% for individual PBDE congeners, 67.7 ± 16.7% to 94.1 ± 2.4% for seven PCB indicators (CB-28, -52, -101, -118, -138, -153, and -180), and 114.8 ± 7.3%, 90.0 ± 11.7% and 62.3 ± 5.6% for α-, β- and γ-HBCD, respectively. The surrogate standard recoveries

Table 1
Median concentrations and ranges (in parentheses) of the investigated OHPs in the studied samples (ng/g lw).

	Reference site	Urban sites		
	Shaoguan (SG)	Guangzhou (GZ)	Beijing (BJ)	Wuhan (WH)
Species	ETS[a] (n = 8)	ETS (n = 19)	ETS (n = 40)	Common magpie (n = 9)
Lipid (%)[b]	12.0 ± 2.3	11.5 ± 4.4	10.4 ± 4.1	8.1 ± 1.9
δ^{13}C (‰)[b]	−24.7 ± 1.1	−20.2 ± 4.7	−18.7 ± 3.3	−23.8 ± 0.4
δ^{15}N (‰)[b]	8.7 ± 0.4	6.0 ± 1.4	6.8 ± 1.3	5.5 ± 1.2
ΣOHPs[c]	210 (150–3900)	430 (180–5900)	860 (250–13000)	1500 (690–19000)
ΣDDTs[d]	92 (38–3800)	150 (23–880)	340 (89–11000)	1400 (610–15000)
ΣPCBs[e]	44 (24–69)	88 (26–540)	59 (23–720)	87 (25–500)
ΣPBDEs[f]	28 (16–51)	190 (51–3700)	250 (100–2600)	32 (12–2900)
DBDPE	nd[i]	31 (2.8–390)	8.5 (nd–330)	3.6 (0.18–820)
ΣHBCDs[g]	nd	3.4 (0.68–21)	51 (6.5–1100)	2.8 (2.7–14)
ΣDP[h]	24 (8.9–120)	13 (nd–350)	4.9 (nd–31)	4.4 (1.7–18)

[a] ETS: Eurasian tree sparrow.
[b] Mean ± SD.
[c] Sum of ΣDDTs, ΣPCBs, ΣPBDEs, DBDPE, ΣHBCDs, and ΣDP.
[d] Sum of *p,p′*-DDE, *p,p′*-DDD, and *p,p′*-DDT.
[e] Sum of PCB-28/31, -52, -60, -66/95, -74, -99, -105, -118, -128, -130, -137, -138, -146, -149/107, -153/132, -156, -158, -163, -167, -170/190, -178, -180/193, -183, -187, -191, -194, -203, -206, -207, -208 and -209.
[f] Sum of BDE-28, -47, -99, -100, -153, -154, -183, -196, -197, -201, -202, -203, -206, -207, -208, and -209.
[g] Sum of α-, β- and γ-HBCD.
[h] Sum of *syn*-DP and *anti*-DP.
[i] Not detectable or below the MDLs.