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PCBs and DDTs in light-vented bulbuls from Guangdong Province, South China: Levels, geographical pattern and risk assessment

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HIGHLIGHTS

- Light-vented bulbul was used as a bioindicator to monitor PCBs and DDTs.
- Geographical patterns of PCBs and DDTs were investigated in Guangdong Province.
- The highest PCB concentration was observed at the e-waste recycling site.
- DDT in light-vented bulbuls was mainly derived from historical residues.
- A significant positive correlation was found between TEQ and PCB levels.

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ABSTRACT

Thirty-two light-vented bulbuls (*Pycnonotus sinensis*) were collected from six sampling sites in Guangdong Province, South China to investigate the geographical variation on the occurrence of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (DDTs). Concentrations of PCBs and DDTs in the pectoral muscle of light-vented bulbul ranged from 140 to 73,000 ng/g lipid weight (lw) and 12 to 4600 ng/g lw, respectively. PCB concentrations were significantly higher in birds from e-waste site compared to other sampling sites (mean, 18,000 vs 290 ng/g lw, $p < 0.0001$), implying that PCBs mainly came from e-waste recycling activities. No significant differences for DDT levels were observed among the sampling sites ($p = 0.092$). Differences in PCB homologue profiles among the sampling sites were found and can be probably ascribed to different local contamination sources. *p,p′*-DDE (>80%) was the most abundant component of DDTs in birds. Compositional pattern of DDTs suggested that historical residue was the main source of DDT. The toxic equivalent (TEQ) concentrations had significant positive correlations with PCB concentrations, indicating that elevated PCB levels may have adverse effects on light-vented bulbuls.

1. Introduction

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), have attracted considerable attention for over 40 years because of their persistence, bioaccumulation, toxicity and susceptibility to long-range transport (Jones and de Voogt, 1999). PCBs and DDTs were added to the list of POPs by the Stockholm Convention in 2001. PCBs were historically used as dielectric and coolant fluids in a variety of industrial products such as transformers, capacitors, electric motors. DDT was extensively used as an agricultural insecticide throughout the 1940s and 1950s. It was estimated that 10,000 t of PCBs (Xing et al., 2005) and 400,000 t of DDTs (Guo et al., 2009) had been produced in China. The production of PCBs and DDT was banned in the 1980s. However, PCBs and DDTs are constantly released from a variety of industrial and agricultural activities into the environment. For example, intensive electronic waste (e-waste) recycling activities have illegally burgeoned in Guangdong Province, releasing large amounts of toxic chemicals into the environment. Remarkable PCB contamination was observed in waterbirds (960–1,400,000 ng/g lipid weight, lw) and fish (18–32,000 ng/g lw) from the e-waste site of Guangdong Province (Luo et al., 2009; Zhang et al., 2010).

Guangdong Province has become one of the most densely urbanized and economically dynamic regions of China since 1980. It is also one of

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the largest manufacturing bases in the world for various products such as electronic/electrical products, toys, garments, textiles, and plastic products (Sun et al., 2012). Meanwhile, Guangdong Province has experienced accelerated environmental deterioration in the past three decades due to rapidly developing industrial, municipal and agricultural activities. PCBs have been widely detected in air, soil, water, sediment and biota from this region (Fu et al., 2003). Unfortunately, extensive e-waste recycling activities have emerged in this region from the 1990s, which resulted in great amounts of PCBs released into the environment (Zhang et al., 2012). Elevated levels of PCBs have been frequently found in various environmental matrices from Guangdong Province (Chen et al., 2009a; Luo et al., 2009). High levels of DDTs have also been detected in water and sediment from Guangdong Province (Fu et al., 2003). New input sources of DDT were present and ascribed to local usage of dicofol and DDT-containing anti-fouling paints (Guan et al., 2009; Yu et al., 2011). Meanwhile, the occurrence of 1-chloro-2,2-bis(4-chlorophenyl)ethene (*p,p′*-DDMU), a secondary metabolite of *p,p′*-DDT, was widely detected in aquatic environmental matrices (Falandysz et al., 1999; Guo et al., 2009; Yu et al., 2011), but information in terrestrial ecosystems is still limited. Therefore, the geographical distribution in concentrations and patterns of these pollutants and their possible sources in Guangdong Province have attracted increasing attention.

Environmental monitoring is needed to evaluate the current levels and risks of different POPs in Guangdong Province. Birds have been successfully used as sentinel species to monitor the levels and effects of POPs in the environment because they are widespread, sensitive to environmental changes, and often high on the food chain (Dauwe et al., 2006; Van den Steen et al., 2010a,2010b; Custer et al., 2012; Sun et al., 2012; Eng et al., 2014). Predatory birds have been widely used as biomonitoring species for POPs (Chen et al., 2009b; Chen and Hale, 2010; Eulaers et al., 2011; Gómez-Ramírez et al., 2014), but most of these birds are less suitable to reflect the local contamination status because they are migratory and live in an extended area with low population densities (Dauwe et al., 2006, 2009). Thus, resident passerine bird species have been successfully used as biomonitoring tools to determine POPs contamination (Dauwe et al., 2009; Van den Steen et al., 2010b; Eens et al., 2013; Morrissey et al., 2013; Eng et al., 2014). In contrast with predatory birds, resident passerine bird species are particularly expected to reflect local pollution with POPs in small study areas because of their small-scale territories and limited foraging areas (Van den Steen et al., 2009, 2010b). Resident passerine bird species, such as great tit (*Parus major*) (Dauwe et al., 2006; Van den Steen et al., 2008, 2009), blue tit (*Cyanistes caeruleus*) (Van den Steen et al., 2010b), and European starling (*Sturnus vulgaris*) (Eens et al., 2013; Eng et al., 2014), have been reported to monitor local contamination with POPs in the environment.

Light-vented bulbul (*Pycnonotus sinensis*) is a polyphagous bird feeding predominantly on berries, soft fruits and vegetables (Wang et al., 2005). Light-vented bulbul is a common resident passerine bird species in Guangdong Province with relatively small home range and foraging areas and readily captured by man-made mist-nets (Wu et al., 2011), making it suitable for monitoring local contamination of OCs. In the present study, 32 light-vented bulbuls from six sampling sites, involving rural, suburban, urban, and e-waste areas, in Guangdong Province of South China were collected and analyzed for PCBs and DDTs. The objectives of this study were to investigate the geographic variation in the levels and profiles of PCBs and DDTs, explore their potential sources, and evaluate their potential effects on light-vented bulbuls.

2. Materials and methods

2.1. Sample collection

Thirty-two light-vented bulbuls were collected from six sampling sites in Guangdong Province, South China from September 2009 to March 2011. Six sampling sites were classified into four categories, rural, suburban, urban and e-waste areas. Liannan (LN) and Maoming (MM), located in the northwest and southeast of Guangdong Province, are two rural sampling sites which are characterized by agricultural activities. Zhaoqing (ZQ) and Heshan (HS), surrounded by the Pearl River Delta region, represent the suburban areas. An urban sampling site is situated in a typical urban area of Guangzhou (GZ) characterized by high population density and heavy industrial and commercial activities. An e-waste sampling site is Qingyuan (QY), where a large amount of e-waste (about 700,000 t) is processed annually using primitive techniques such as open incineration, acid dipping and manual disassembly. The sampling map and sample numbers of each site are given in Fig. 1 and Table 1, respectively. Birds were captured by mist nets of 12 m × 2.6 m × 3.6 cm (length × height × mesh). Eight nets were operated simultaneously at each sampling site for 3–4 consecutive days between 6:30 and 17:30 on days without rain for each period. Nets were checked at intervals of 1 h. Birds were immediately transported to the laboratory and euthanized with N_2. The necessary permit for this study was obtained from the Forestry Bureau of Guangdong Province of China. Pectoral muscles were excised from each bird and stored at −20 °C until chemical analysis.

2.2. Chemical analysis

The extraction procedure for PCBs and DDTs was described in a previous study (Luo et al., 2009). Briefly, approximately 5 g of muscle tissue was homogenized with anhydrous sodium sulfate, spiked with surrogate standards (PCB 30, 65, and 204) and Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was gravimetrically determined from an aliquot of the extract. The remainder of the extract used for chemical analysis was subjected to gel permeation chromatography for lipid removal. Eluate from 90 to 280 mL containing PCBs and DDTs was collected and concentrated to 1 mL, further cleaned up on a multilayer column packed with 8 cm acidified silica, 8 cm neutral silica and 1 cm anhydrous sodium sulfate from bottom to top, and eluted with 30 mL hexane/dichloromethane ($v/v = 1:1$). The eluate was concentrated to near dryness under N_2 and reconstituted in 100 μL of isooctane. Internal standards (PCB 24, 82, and 198) were spiked before instrumental analysis.

Thirty-four PCB congeners (PCB 28/31, 52, 60, 66, 74, 99, 101, 105, 115/87, 118, 128, 130, 137, 138, 146, 149/139, 153, 156, 158, 164/163, 171, 172, 175, 180, 183, 187, 190, 191, 194, 195, 203, 205, 206, 209), DDT (*p,p′*-DDT and *o,p′*-DDT) and its metabolites (*p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDM, *p,p′*-DDMU, *o,p′*-DDE, *o,p′*-DDD) were analyzed in all samples. PCBs and DDTs were quantified by an Agilent 7890 gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC/MS) using electron impact (EI) in the selective ion-monitoring (SIM) mode and separated by a DB-5MS (60 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. The initial oven temperature was set at 120 °C, then increased to 180 °C at a rate of 6 °C/min, further increased to 240 °C at a rate of 1 °C/min, and finally raised to 290 °C at a rate of 10 °C/min (held for 15 min). 1 μL of sample was injected in the pulsed splitless mode. The ion source, quadrupole and interface temperatures were set at 230 °C, 150 °C, and 290 °C, respectively. Detailed information on GC/MS and monitored ions were given elsewhere (Hu et al., 2008).

2.3. Quality assurance and quality control (QA/QC)

Instrumental QC included regular injection of solvent blanks and standard solutions. Procedural blanks, triplicate spiked blanks (20 individual PCB congeners, PCB 8, 18, 28, 44, 52, 66, 77, 101, 105, 118, 126, 128, 138, 153, 170, 180, 187, 195, 206 and 209), and triplicate spiked matrices were analyzed to ensure method QC. Procedural blanks were processed consistently for each batch of 11 samples. Trace levels of PCB 153 and 128 were detected in the procedural blanks (<8% of those in the samples with the lowest levels) and the mean