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# Habitat- and species-dependent accumulation of organohalogen pollutants in home-produced eggs from an electronic waste recycling site in South China: Levels, profiles, and human dietary exposure☆

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ABSTRACT

Organohalogen pollutants (OHPs) including chlorinated paraffins (CPs), polybrominated diphenyl ethers (PBDEs) and other halogenated flame retardants (OHFRs) (dechlorane plus (DP), decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), hexabromobenzene (HBB), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA)) originating from an e-waste recycling area in Guiyu, southern China were investigated in chicken and goose eggs. As expected, OHP concentrations were higher in chicken eggs collected from the location (site 1) approaching the e-waste recycling center than from the location (site 2) far from the e-waste recycling center. Also, much higher OHP levels were observed in goose eggs foraging in residential area (site 2) than that in agricultural area (site 1), suggesting a clear habitat dependent OHP bioaccumulation pattern both concerning distance from e-waste activities and type of foraging habitat. Goose eggs exhibited higher short chain chlorinated paraffins (SCCPs) concentrations but lower PBDE and OHFR levels than chicken eggs. The proportion of high brominated PBDEs (hepta-to deca-BDEs) was lower in goose eggs than that in chicken eggs and showed a clear decrease from site 1 to site 2. DP isomeric composition $f_{anti}$ values (the ratio of the *anti*-DP to the sum of the *anti*- and *syn*-DP) in goose eggs were significantly lower than those in chicken eggs ($p < 0.001$). These differences are likely a reflection of factors such as the species-specific differences in habitat preference and the differing environmental behaviors of the pollutants owing to their inherent properties (such as solubility and vapor pressure). Our findings suggested a high dietary intake of OHPs *via* home-produced eggs. For BDE99 there is a potential health concern with respect to the current dietary exposure *via* eggs.



## 1. Introduction

Organohalogen pollutants (OHPs) are generally brominated or chlorinated chemicals that are widely found in e-wastes (Robinson, 2009). Polybrominated diphenyl ethers (PBDEs) are typical brominated pollutants, and have been banned or restricted in some regions of the world (Betts, 2008). Other brominated pollutants, e.g., decabromodiphenyl ethane (DBDPE), tetrabromobisphenol A (TBBPA), hexabromocyclododecanes (HBCDs), hexabromobenzene (HBB), and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), were used in plastics, textiles, electronic circuitry and some of them used as alternatives for the legacy OHPs, such as PBDEs (Covaci et al., 2011). Chlorinated paraffins (CPs) and dechlorane plus (DP) belong to the class of chlorinated pollutants and are extensively used in many types of polymers (Boer et al., 2010; Xian et al., 2011). Recently, toxicological research indicated that CPs are carcinogenic (Boer et al., 2010), and DP may induce apoptosis in the liver of juvenile Chinese sturgeon (Liang et al., 2014). These studies provide further concerns on the potential threat of CPs and DP to human health and ecosystems. Available data on these halogenated flame retardants (HFRs) indicated that these chemicals might also be persistent, bioaccumulative, and toxic (Covaci et al., 2011). So far, numerous studies have reported high concentrations of both legacy OHPs and newer-generation chemicals in various environmental

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media and biological samples at e-waste recycling sites (Ben et al., 2013; Zhang et al., 2011).

Guiyu, located in Guangdong Province, on the southern coast of China, is one of the largest e-waste recycling centers in the country. Nearly 80% of the families residing here have members involved in e-waste operations (Li et al., 2008). Primitive e-waste processes like manual separation, open burning, and strong acid digestion were adopted by the locals, which have caused severe OHP pollution in Guiyu (Gao et al., 2011; Labunska et al., 2013a). It is expected that most of these contaminants, once in the environment, can accumulate in living organisms (Covaci et al., 2011). The species-specific nature of bioaccumulation of OHPs has been reported in various field studies (Chen et al., 2010; Sun et al., 2014), with bioavailability and biotransformation being suggested as the likely reasons for this. The differing living and feeding habits of animals are also highlighted as important factors in determining the OHP profiles. However, little is known about the OHP compositional differences of biotas occupying different habitats. Moreover, dietary intake is a significant pathway of human exposure to OHPs, largely attributed to consumption of dairy products with a relatively high fat content. Thus, the possible adverse effects of OHPs from these hot spots (e-waste recycling sites) on local animals and residents have become particularly concerning.

Both chickens and geese are poultry, but their life habits are different. Chickens are essentially terrestrial fowls while geese are a kind of water fowl and often have open grazing access to both land and water bodies. Since eggs are a high-fat component of the daily human diet and are considered to be a good indicator of ambient persistent organic contaminant levels (Windal et al., 2009), chicken and goose eggs are a good option for investigating the bioaccumulation characteristics of OHPs in biotas in different habitats. Therefore, in the present study, home-produced chicken and goose eggs were collected from families living in the e-waste recycling areas in Guiyu. The primary aim of this study was to investigate the residual levels and compositional patterns of OHPs in chicken and goose eggs affected by e-waste recycling, in order to determine the possible differences in species living in different habitats around the e-waste disposal center and to estimate the daily dietary intake of OHPs *via* consumption of these eggs by the local residents.

## 2. Materials and methods

### 2.1. Sampling

A total of 40 samples, including 17 chicken eggs and 23 goose eggs, were collected from two sites (site 1, N 23°19′38″ E 116°21′39″; and site 2, N 23°19′4″ E 116°21′23″) in an e-waste recycling region in Guiyu in December 2013 (Fig. S1). Site 1 was located in an industrial park at a distance of about 2 km from the e-waste recycling workshops. Chickens at site 1 foraged around the residential areas, while geese at site 1 spent the daytime in local paddy field or watercourses and rested at a farmhouse during the night. Site 2 is located in at a distance of about 2.5 km from the e-waste recycling workshops. Both chickens and geese at site 2 foraged exclusively in residential areas (Fig. S2). Eggs freshly laid by the free-range poultry were collected from site 1 (8 chicken eggs and 9 goose eggs) and site 2 (12 chicken eggs and 11 goose eggs). The eggs were cleaned with deionized water and the egg contents were transferred to clean glass jars, which were then stored at −20 °C until chemical analysis.

### 2.2. Sample preparation

All the samples were freeze-dried and homogenized into powder, weighed (1.0 g) and spiked with the surrogate standards ($^{13}C_{10}$-*trans*-chlordane, PCB30, PCB65, PCB204, BDE77, BDE181, BDE205, $^{13}C_{12}$-BDE-209, $^{13}C_{12}$-labeled α-, β-, γ-HBCD and $^{13}C$-labeled TBBPA) prior to extraction. The lipid content was determined gravimetrically on an aliquot of the extract (one tenth of the extract), while the rest of the extract was divided into two equal parts for further purification. One part was used for the determination of CPs, PBDEs, DBDPE, DP, BTBPE, and HBB. The other part was used for the determination of TBBPA and HBCDs. Detailed sample preparation procedures are described in the Support Information (SI).

### 2.3. Instrumental analysis

For the CP ($C_{10}$–$C_{17}$ with $Cl_5$–$Cl_{10}$) analysis, an Agilent 6890 gas chromatograph (GC) connected to an Agilent 5975C mass spectrometer (MS) operated in electron capture negative ionization (ECNI) mode was equipped with a DB-5HT (15 m × 0.25 mm i.d., 0.10 μm film thickness) capillary column. The injector temperature was set to 250 °C, the transfer line temperature was 280 °C, and the ion source temperature was 200 °C. The oven temperature program is detailed in the SI. All monitored ions of short chain chlorinated paraffins (SCCPs) and medium chain chlorinated paraffins (MCCPs) were divided into four groups: 1) $C_{10}$ and $C_{11}$, 2) $C_{12}$ and $C_{13}$, 3) $C_{14}$ and $C_{15}$, and 4) $C_{16}$ and $C_{17}$ to improve the instrument sensitivity. Therefore, for each sample, four individual injections were needed in order to analyze all the selected CP congeners. Congener groups were identified by the retention time range, the signal shape, and the correct isotope ratio. The quantification of SCCP ($C_{10}$–$C_{13}$ with $Cl_5$–$Cl_{10}$) and MCCP ($C_{14}$–$C_{17}$ with $Cl_5$–$Cl_{10}$) was conducted according to the CP carbon chain length and the degree of chlorination as described previously (Reth et al., 2005).

PBDEs, DBDPE, DP, BTBPE, and HBB were analyzed using a GC/MS (Agilent 6890N/5975C MSD; Agilent Technology, CA) in ENCI mode. Di-through hepta-BDEs, DP, and HBB were separated with a DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. For octa-through deca-BDEs, BTBPE, and DBDPE, a DB-5HT (15 m × 0.25 mm i.d., 0.10 μm film thickness) capillary column was used. The oven temperature programs are detailed in the SI.

For the analysis of TBBPA and HBCDs, an Agilent 1200 series liquid chromatography (LC) system coupled to an Agilent 6410 electrospray triple quadrupole mass spectrometer equipped with a XDB-$C_{18}$ column (50 mm × 4.6 mm i.d., 1.8 μm, Agilent, CA) was used. Details of the analytical methodology used for separation and quantification of TBBPA and HBCDs have been published previously (Feng et al., 2012).

### 2.4. Quality assurance and quality control (QA/QC)

In order to avoid any interference and contamination, all glassware was rinsed with solvents (acetone, dichloromethane and hexane) and heated at 450 °C prior to use. Spiked samples were analyzed to validate the sample preparation method. During the sample analysis, each batch of 11 samples included one procedural blank. Trace amount of a few PBDEs were detected in the procedure blanks, but the levels were less than 1% of the analyzed concentration in the samples. The average recoveries of the spiked surrogate standards ranged from 63 to 98%, 72–117%, 50–108% and 66–107% for CPs ($^{13}C_{10}$-*trans*-chlordane), PBDEs (BDE77, BDE181, BDE205 and $^{13}C_{12}$-BDE-209), TBBPA ($^{13}C$- TBBPA) and HBCDs ($^{13}C$-α-, β-, γ-HBCD), respectively. Instrumental QC was performed by regular injection of solvent blanks and standard solutions. The method detection limit (MDLs) was defined as a signal to noise (S/N) ratio of 10. The MDLs were in the range of 0.2–1.8 ng/g lipid weight (lw) for CPs, 0.2–0.4 ng/g lw for PBDEs and OHFRs, and 0.7–1.7 ng/g lw for HBCDs and TBBPA.