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Phosphate flame retardants and novel brominated flame retardants in home-produced eggs from an e-waste recycling region in China

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HIGHLIGHTS

- EH-TBB, BEH-TEBP and PFRs were measured in free-range chicken eggs.
- Chlorinated PFRs had higher detection frequencies than non-chlorinated PFRs in eggs.
- TPHP had a higher detection frequency in albumen; BEH-TEBP was higher in yolks.
- Dust ingestion is a more important pathway than egg intake in human exposure to PFRs.

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ABSTRACT

Phosphate flame retardants (PFRs) and novel brominated flame retardants (NBFRs) (2-ethylhexyl-2,3,4,5-tetrabromo-benzoate (EH-TBB) and bis-(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP)) were measured in free-range chicken eggs from three e-waste recycling sites and a negative control site located in Guangdong province, Southern China. BEH-TEBP, tris-(chloroethyl)-phosphate (TCEP), tris-(chloropropyl)-phosphate (∑TCPP, two isomers) and tris-(1,3-dichloroisopropyl)-phosphate (TDCIPP) were detected in more than 50% of eggs samples with low concentrations. The median values of BEH-TEBP and total PFRs were 0.17–0.46 ng/g ww (wet weight) and 1.62–2.59 ng/g ww in eggs from the e-waste sites, respectively. The results indicate that EH-TBB, BEH-TEBP and PFRs are less persistent and bioaccumulative than polybrominated diphenyl ethers (PBDEs) in chicken eggs, and possibly also in other bio-matrices. Triphenyl phosphate (TPHP) were identified in albumen with higher frequencies, but at similar concentrations compared to yolk, while BEH-TEBP was mainly detected in yolk. The estimated daily intake (EDI) of BEH-TEBP and total PFRs from consumption of chicken eggs ranged from 0.03 to 0.09 and 0.32–0.52 ng/kg bw/day for adults, and 0.20–0.54 and 1.89–3.02 ng/kg bw/day for children in e-waste sites, respectively. Indoor dust ingestion seems to be a more important pathway for the intake of these FRs, while egg consumption is probably a more important exposure pathway for PBDEs.

1. Introduction

With the ban of polybrominated diphenyl ethers (PBDEs) in Europe and the United States (European Court of Justice (2008); UNEP, 2009), the usage of alternative flame retardants (FRs), like 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis-(2-ethylhexyl)- 3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and phosphate flame retardants (PFRs), has significantly increased in recent years (Covaci et al., 2011; van der Veen and de Boer, 2012; Wei et al., 2015). As novel brominated flame retardants (NBFRs), EH-TBB and BEH-TEBP have been used as alternative of Penta-BDE (Covaci et al., 2011; Roberts et al., 2012). They have been reported as major components of Firemaster 550, a commercial fire safety additive, with a ratio of 4:1 (Stapleton et al., 2008), while another additive FR product, BZ-45, was also found to contain them (Davis and Stapleton, 2009). PFRs, such as tris-(1-chloro-isopropyl)-

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phosphate (TCIPP), triphenyl phosphate (TPHP) and tris-(2-butoxyethyl)-phosphate (TBOEP), have been widely used in commercial products such in textures, cable coating, paints, foams and electronic products, and also being applied as plasticizers or additives in lubricant (van der Veen and de Boer, 2012). EH-TBB, BEH-TEBP and PFRs contain ester bonds in their chemical structures, given them less persistent properties and different bioaccumulation characters comparing with persistent FRs, such as PBDEs, dechlorane plus (DPs), decabromodiphenyl ethane (DBDPE), or 1,2-bis-(2,4,6-tribromophenoxy) ethane (BTBPE).

The occurrence of NBFRs and PFRs has been frequently reported in environment, including air, indoor dust, soil, and sediment (Brandsma et al., 2015; Cequier et al., 2014; Kim et al., 2014; Liu et al., 2014), but limited studies investigated their levels in biota, such as fish, wild birds, mammals or humans (van der Veen and de Boer, 2012; Wei et al., 2015). Sundkvist et al. (2010) detected TCIPP (0.4–16 ng/g ww, wet weight), TPHP (0.04–2.3 ng/g ww) and TBOEP (0.86–4.2 ng/g ww) in fish tissues, which had similar PFR levels with those in fish from Netherland (Brandsma et al., 2015). Tri-ethylhexyl phosphate (TEHP) (6 ng/g ww) and 2-ethylhexyl diphenyl phosphate (EHDPHP) (3.5 ng/g ww) were reported as main PFRs in fish from Philippines (Kim et al., 2011a, b). PFR values in fish tissues from the Dutch North Sea were not correlated with lipid percentage (Brandsma et al., 2015), suggesting that PFRs do not follow the same distribution as lipids like other PBDEs (Brandsma et al., 2015; Malarvannan et al., 2015). Based on the limited studies on PFRs in creatures, the bioaccumulation of PFRs seemed to be different from PBDEs (Brandsma et al., 2015; Kim et al., 2011a, b; Malarvannan et al., 2015; Sundkvist et al., 2010). EH-TBB and BEH-TEBP might undergo hydrolysis in gastrointestinal tract, with 70% degradation of BEH-TEBP being reported in a gastrointestinal absorption model (Fang and Stapleton, 2014). The rapid hepatic elimination of tris-(1,3-dichloroisopropyl)-phosphate (TDCIPP) was reported in an *in vitro* study using chicken hepatocytes, where TDCIPP was all transformed into bis-(1,3-dichloroisopropyl) phosphate (BDCIPP) in 36 h (Farhat et al., 2014).

Qingyuan is one of the largest e-waste recycling areas in China. However, the improper handling process during e-waste recycling leads to terrible pollution to regional environment and seriously threatens the health of on-site workers and local residents. The environmental contamination in e-waste recycling regions could further pass down to local agriculture and eventually threaten food safety (Song and Li, 2014).

Dietary intake has been considered as an important human exposure pathway for persistent FRs, but data about less persistent FRs in food is still limited (Domingo, 2014; Xu et al., 2015). Eggs from free-range chicken were recognized as to have higher level of organic pollutants than eggs from caged chicken and other food, due to the (more) intensive contact of hens with the environment (Covaci et al., 2009; Domingo, 2014). In our previous studies, intakes of persistent FRs (including PBDE, DPs and DBDPE) via local home-produced free-range egg consumption were proved to be a great threat to health of the locals in e-waste recycling area (Zheng et al., 2012). As a follow-up study, we aimed (1) to investigate the extent of contamination of EH-TBB, BEH-TEBP and PFRs in free-range chicken eggs from e-waste recycling region; and (2) to assess the human exposure risks of these FRs via egg consumption for local residents. To the best of our knowledge, this is the first study on human dietary exposure of PFRs in e-waste recycling sites.

2. Methods and materials

2.1. Sampling

Free-range chicken eggs (N = 45) were collected from three villages that rely on e-waste recycling business (Site 1, N 23°32′ E 113°03′; Site 2, N 23°36′ E 113°04′; and Site 3, N 23°34′ E 113°02′) and a negative control site (N 23°34′ E 113°03′) in Qingyuan (Guangdong Province, China) in July, 2010. The free-ranged hens were raised on the recycling sites where the e-waste was primitively dismantled and extracted. The control site is about 5 km away from other three recycling sites and free of e-waste recycling activities. More details about sampling areas were provided in our previous study (Zheng et al., 2012). The collected egg samples were transported to our laboratory within 12 h. The albumen of eight eggs was separated from yolk, and analyzed individually, while the remains of each egg were homogenized. All samples were then lyophilized individually, and the water content of each sample was gravimetrically determined. Dry samples were packed with aluminum foil, sealed in zip bags and stored at −20 °C until analysis.

2.2. Chemicals and materials

Standards of EH-TBB, BEH-TEBP and their isotope labeled internal standards (IS) $^{13}C_6$-BEH-TEBP-D_{34} (MBEH-TEBP) and $^{13}C_6$-EH-TBB-D_{17} (MEH-TBB) were purchased from Wellington Laboratories (Guelph, ON, Canada). Standards of tricresyl phosphate (TMPP, mixtures of 4 isomers), TEHP, EHDPHP, tri-n-propyl phosphate (TNPP), tri-n-butyl phosphate (TNBP), TPHP, tris(2-chloroethyl) phosphate (TCEP) and TDCIPP were purchased from Chiron AS (Trondheim, Norway). TCPP mixture (2 isomers, tris (1-chloroisopropyl) phosphate (TCIPP) is the major component) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Triamyl phosphate (TAP, IS) was purchased from TCI Europe (Zwijndrecht, Belgium). Isotope labeled IS of PFRs, TCEP-D_{12}, TDCIPP-D_{15}, TPHP-D_{15}, and TBOEP-D_6 were synthesized by Dr. Vladimir Belov (Max Plank, Germany) and had a purity of >98%. TBOEP standard was purchased from Acros (Belgium) and had a purity of 94%. DSC-18 sorbent, Z-SEP sorbent and Supelclean™ ENVI™-Florisil® cartridges (500 mg, 3 mL) were purchased from Supelco (Bellefonte, PA, USA). Aminopropyl silica (APS) cartridges (500 mg, 3 mL) were purchased from Agilent (Santa Clara, CA, USA). Silica gel, anhydrous magnesium sulfate ($MgSO_4$), concentrated sulfuric acid (H_2SO_4, 98%) and all solvent in used (chromatography grade) were purchased from Merck (Darmstadt, Germany).

2.3. Sample preparation and analysis

The sample preparation and analysis method were described in details by Xu et al. (2015) and are given in the Supplementary Information (SI). Briefly, about 2 g freeze-dried yolk or whole egg sample (for albumen only 1 g was used) was spiked with IS (MEH-TBB, MBEH-TEBP, TAP, TPHP-D_{15}, TDCIPP-D_{15} and TCEP-D_{12}), then extracted with ultrasonication and vortexation in 5 mL acetonitrile:toluene (9:1, v/v). After solvent exchange to hexane, the extract was performed with multi-step clean-up to further remove lipid and pigment. First, the extract was fractionated on a Florisil cartridge: the first fraction (F1) was eluted with 8 mL hexane and the second fraction (F2) was eluted with 5 mL acetonitrile. After concentrated under a gentle nitrogen flow, the F1 was further cleaned-up on 2 g acid silica (10%, pre-cleaned with 6 mL hexane) with 10 mL hexane:dichloromethane (1:1, v/v, F3). F2 was concentrated to 2.5 mL, adding with 200 mg Z-SEP/DSC18 mixture sorbent to perform dispersive SPE for the removal of interference. After centrifugation, the supernatant of F2 was combined with F3, then, solvent-exchange to 2 mL of hexane, which was further fractionated on an APS cartridge. Elution was performed with 10 mL hexane (F4) and 12 mL hexane:dichloromethane (1:1, v/v, F5). Both fractions were evaporated to nearly dryness, and then resolubilized