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Level changes and human dietary exposure assessment of halogenated flame retardant levels in free-range chicken eggs: A case study of a former e-waste recycling site, South China

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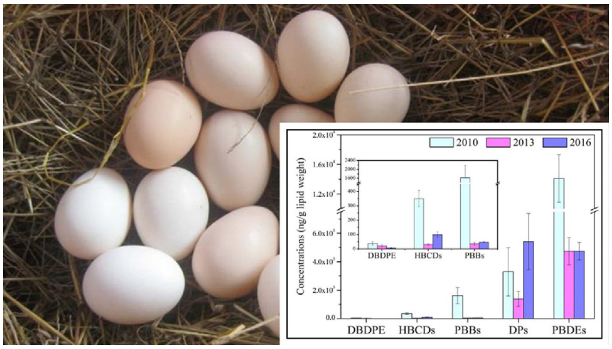
HIGHLIGHTS

- HFR levels and composition in free-range chicken eggs over six years were reported.
- PBDE, PBB, HBCD and DBDPE levels were significantly decreased from a study in 2010.
- Different HFR congener/stereoisomer profile changes were observed over time.
- Dietary intake of HFRs via home-produced eggs was high, especially for PBDEs.

GRAPHICAL ABSTRACT



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ABSTRACT

To assess the impacts of e-waste regulations on environmental pollution, we built on a previous study from 2010 to investigate the levels and human dietary exposure of halogenated flame retardants (HFRs) in free-range chicken eggs from Baihe village in 2013 and 2016. The concentrations of PBDEs, PBBs, HBCDs, and DBDPE showed a significant decrease ($p < 0.05$) from 2010 to 2013/2016, suggesting the efficacy of regulatory policies. The relative contribution of BDE209 were higher in 2013 and 2016 than in 2010, accounting for 67.8%, 61.4%, and 27.7%, respectively. The concentration ratios of PBB209:PBB153 were much lower in 2013 (1.51) and 2016 (1.32) than in 2010 (29.5). These observed different profiles likely due to the different environmental behaviors of HFRs (e.g. the different atmospheric migration abilities of PBDE congeners and degradation of PBB209). Our exposure estimates suggested high dietary intake of HFRs via home-produced eggs. As for PBDEs, considering the worst situation (highly polluted eggs were consumed), the margin of exposure (MOE) of BDE99 for both adults and children were 1.5 and 0.3 in 2013, and 1.1 and 0.2 in 2016, respectively, which were below 2.5. According to the CONTAM panel, an MOE larger than 2.5 indicates no health concern. Therefore, these MOE values represent a significant potential health concern due to the adverse impacts of PBDEs on human neurodevelopment and fertility.

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1. Introduction

Halogenated flame retardants (HFRs) are a potentially highly hazardous class of e-waste-associated contaminants. In recent years, due to growing recognition of their toxicity, potential bioaccumulation, and high environmental persistence, stricter policies have been placed on some HFRs, such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCDs), which were recently included in the Stockholm Convention on persistent organic pollutants (Stockholm convention, 2009, 2013). However, other HFRs are extensively used and remain unregulated. This is the case for dechlorane plus (DP), which was first synthesized in the late 1960s and is now used as a flame retardant in cable coatings, electronic connectors, and plastic roofing materials (Ma et al., 2014; Wu et al., 2017), with annual production rate estimated to be as high as 5000 tons (Wang et al., 2010). Decabromodiphenyl ethane (DBDPE) was introduced as a replacement for deca-BDEs, and has been on the market for >20 years, with annual production volume range of 10–50 million pounds for 2006 (Wei et al., 2012). It has been suggested that PBDEs and HBCDs may affect neurodevelopment and fertility by disrupting thyroid hormone (Fromme et al., 2014). However, available data on non-regulated HFRs indicates that these chemicals might also be persistent, bioaccumulative, and toxic (Covaci et al., 2011).

Longtang, known as “the renewable copper city of China”, was once one of the largest e-waste recycling centers in Qingyuan, Guangdong Province (Zhang et al., 2012). However, primitive e-waste recycling activities, including peeling and melting plastic, combusting or roasting circuit boards, and extracting metals with strong acids (Wong et al., 2007), have resulted in the extensive release of HFRs to the local environment (Gao et al., 2011; Nie et al., 2015), as well as high dietary intake of HFRs through the food chain. Eggs are considered as a good indicator of ambient persistent organic contaminant levels due to their high fat content (Windal et al., 2009). Therefore, in a previous study, we analyzed HFR levels in home-produced eggs from the heavily polluted e-waste site in Baihe village (N 23°36′ E 113°04′), Longtang (Zheng et al., 2012). A total of 11 chicken eggs were sampled in Baihe village in July 2010, and revealed extremely high HFR levels (mean values of 14,100, 3290, 350, 1620, and 37.9 ng/g lipid for PBDEs, DP, HBCDs, PBBs, and DBDPE, respectively). Levels of dominant HFRs (PBDEs) in eggs were approximately 30 times higher than those in eggs from e-waste recycling areas in Taizhou, Eastern China (mean: 459 ng/g lipid) (Labunska et al., 2014), and approximately three orders of magnitude greater than those (7.8 ng/g lipid weight) detected in home-produced chicken eggs from Belgium (Covaci et al., 2009).

In order to mitigate e-waste contamination, laws and regulations have been passed to ban and control e-waste importation and disposal in China (Ni and Zeng, 2009). In Longtang, the renewable metal industry is suffering due to regulations for e-waste imposed by the Qingyuan city government. In 2010, these included: cancellation of the discount on value-added tax in the e-waste industry (South Reviews, 2018), regulations that banned family-run e-waste workshops; encouraging the transfer of e-waste workshops to an established industry park since 2011 (The People's Government of Qingyuan, 2011). Since Qingyuan county's Twelfth Five Year Plan on environmental protection and ecological construction in 2011 (The People's Government of Qingyuan, 2011), many regulations for hazardous waste and its disposal have been created. These have included a specific project on environmental renovation of Qingyuan on April 26, 2012 (The People's Government of Qingyuan, 2012); an implementation plan to accelerate the transformation and upgrading of renewable metal industries in Qingyuan on April 3, 2013 (The People's Government of Qingyuan, 2013); and an implementation plan to develop Qingyuan into a national environmental protection model city on July 22, 2015 (The People's Government of Qingyuan, 2015). These measures indicated that the Qingyuan government must prohibit illegal e-waste recycling activities and renovate illegal small e-waste recycling plants. Furthermore, operators of e-waste dismantling, utilization, and disposal factories must register with Qingyuan government agencies.

Currently, the implementation of legislation and regulations governing e-waste in Longtang is crucial for assessing the potential for adverse human health impacts arising from exposure to HFRs at e-waste recycling sites. Therefore, the aim of the present study was to analyze HFR concentrations in home-produced chicken eggs from Baihe village in Longtang three and six years after our previous study in 2010 (Zheng et al., 2012), and to assess the local residents' potential human dietary exposure to HFRs via consumption of chicken eggs.

2. Materials and methods

2.1. Sampling

Baihe is a small village, with dozens of homes, and it is belongs to an administrative village called Sihe village (Qingyuan county, Guangdong province, South China) (Fig. 1). Baihe village was once a typical e-waste recycling region with many small-scale and family-run workshops. Before the legislations, due to the farmer's weak awareness of environmental protection, the e-waste was usually dismantled in the family backyard and the remnant was stacked casually inside or outside of the farmhouse. However, since 2011, rules that banned family-run e-waste workshops had been created by the Qingyuan government, and all the family-run workshops were moved to the local e-waste disposal centers. Therefore, to evaluate the implementation of e-waste legislation and regulations in the study area, we analyzed HFR concentrations in free-range chicken eggs from Baihe village three and six years after our previous study in 2010. A total of 62 home-produced eggs laid by free-range chickens were collected from Baihe village in July 2013 (*n* = 38) and September 2016 (*n* = 24). The free-range hens at Baihe village were generally feed by local produced grain and hunting food around the farmhouse. The collected egg samples were cleaned with deionized water and carefully transported to the laboratory. The egg contents were transferred to clean glass jars, which were stored at −20 °C until chemical analysis.

2.2. Sample preparation

Egg samples were extracted and cleaned according to the previously published method (Gao et al., 2009), with minor modification. First, all samples were freeze-dried in the freezing dryer and homogenized into powder with a mortar and pestle. Then, approximately 2 g of the lyophilized samples were weighed and spiked with surrogate standards (BDE77, BDE181, BDE205, $^{13}C_{12}$-BDE209, and $^{13}C_{12}$-labeled α-, β-, γ-HBCD) prior to Soxhlet extraction with 200 mL hexane/acetone (1:1, v/v) for 48 h. An aliquot of the extracts (10% of the extracts) was used to determine lipid content (gravimetrical method). The rest of the extracts was treated with concentrated H_2SO_4 (Analytical Reagent, AR) to remove the lipids, then equally divided into two subsamples for further purification. The two parts were concentrated until almost dry under gentle nitrogen and solvent exchanged to hexane (1–2 mL).

The first part used for determination of PBDEs, DBDPE, DP, and PBBs was cleaned through a multilayer florisil/silica gel column (i.d. = 1.0 cm) consisting of 20 cm of florisil (3% H_2O deactivated, w/w), 2 cm of neutral silica (3% H_2O deactivated, w/w), and 8 cm sulfuric acid silica (44% sulfuric acid, w/w), topped with a 2-cm layer of anhydrous sodium sulfate (Na_2SO_4). The column was eluted with 55 mL hexane, and all eluent was collected. The second part used for determination of HBCDs was purified with a simple silica gel column (i.d. = 1.0 cm) packed with 12 cm neutral silica (3% H_2O deactivated, w/w), and topped with a 2-cm layer of anhydrous Na_2SO_4. The column was eluted with 13 mL of hexane followed by 5 mL of dichloromethane: hexane (1:1, v/v) and 45 mL of dichloromethane: hexane (1:1, v/v). The first and the second fractions were discarded, and the last fraction was collected. The collected extracts were concentrated until almost dry under a gentle