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Human dietary intake of organohalogen contaminants at e-waste recycling sites in Eastern China

Iryna Labunska [a,b,*], Mohamed Abou-Elwafa Abdallah [b,c], Igor Eulaers [d,e], Adrian Covaci [d], Fang Tao [b], Mengjiao Wang [a], David Santillo [a], Paul Johnston [a], Stuart Harrad [b]

[a] Greenpeace Research Laboratories, Innovation Centre Phase 2, Rennes Drive, University of Exeter, Exeter EX4 4RN, United Kingdom
[b] School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, United Kingdom
[c] Department of Analytical Chemistry, Faculty of Pharmacy, Assiut University, 71526 Assiut, Egypt
[d] Toxicological Center, University of Antwerp, 2610 Wilrijk, Belgium
[e] Ethology group, Department of Biology, University of Antwerp, 2610 Wilrijk, Belgium

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ABSTRACT

This study reports concentrations and human dietary intake of hexabromocyclododecanes (HBCDs), polychlorinated biphenyls (PCBs) as well as selected "novel" brominated flame retardants (NBFRs) and organochlorine pesticides, in ten staple food categories. Samples were sourced from areas in Taizhou City, eastern China, where rudimentary recycling and disposal of e-waste is commonplace, as well as from nearby non-e-waste impacted control areas. In most instances, concentrations in foods from e-waste recycling areas exceeded those from control locations. Concentrations of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis-(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TBP) in samples from e-waste sites were 3.09–62.2 ng/g and 0.81–16.3 ng/g lipid weight (lw), respectively; exceeding consistently those in foods acquired from control sites by an order of magnitude in many cases. In contrast, while concentrations of HBCD in some foods from e-waste impacted areas exceed those from control locations; concentrations in pork, shrimp, and duck liver are higher in control samples. This highlights the potential significance of non-e-waste sources of HBCD (e.g. building insulation foam) in our study areas. While concentrations of DDT in all foods examined except pork were higher in e-waste impacted samples than controls; our exposure estimates were well below the provisional tolerable daily intake of 0.01 mg/kg bw/day derived by the Joint FAO/WHO Meeting on Pesticide Residues. Concentrations of ΣPCBs resulted in exposures (650 and 2340 ng/kg bw/day for adults and children respectively) that exceed substantially the Minimal Risk Levels (MRLs) for ΣPCBs of 20 ng/kg bw/day derived by the Agency for Toxic Substances & Disease Registry. Moreover, when expressed in terms of dioxin-like toxicity equivalency based on the four dioxin-like PCBs monitored in this study (DL-PCBs) (PCB-105, 118, 156, and 167); concentrations in e-waste impacted foods exceed limits set by the European Union in 6 of the 8 food groups studied and result in dietary exposures for children (10.2 pg TEQ/kg bw/day) that exceed the WHO tolerable daily intake of 1–4 pg TEQ/kg bw/day.

1. Introduction

Electrical and electronic waste (e-waste) can contain a wide range of hazardous chemicals, including brominated flame retardants (BFRs), and polychlorinated biphenyls (PCBs) (Robinson, 2009). Moreover, improper e-waste treatment techniques, such as open burning of plastics to recover metals, introduce additional chemicals as by-products, including an additional source of dioxin-like PCBs (DL PCBs) (Frazzoli et al., 2010), over and above their presence in commercial PCB formulations. Such rudimentary recycling and disposal practices can result in high occupational and incidental exposure to a range of hazardous substances, and generate locally severe environmental contamination. Once released to the environment surrounding e-waste treatment facilities, BFRs and PCBs may accumulate in soils and sediments (Tang et al., 2010; Zhang et al., 2012; Labunska et al., 2013a; Liu et al., 2013) and become available for uptake by both terrestrial and aquatic organisms (Fu et al., 2010; Shang et al., 2013). Consequently, contaminants may enter the food chain with resultant pervasive and prolonged exposure to people residing in the vicinity of e-waste recycling areas.

A range of health effects has been reported in association with e-waste recycling activities in China, including decreased child height (Zheng et al., 2008), increases in adverse birth outcomes (Xu et al., 2012) and increased cancer risk in e-waste dismantling workers. Exposure to high concentrations of polychlorinated dibenzodioxins/furans

* Corresponding author at: Greenpeace Research Laboratories, Innovation Centre Phase 2, Rennes Drive, University of Exeter, Exeter EX4 4RN, United Kingdom.
E-mail address: iryna.labunska@greenpeace.org (I. Labunska).

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(PCDDs/Fs), polybrominated diphenyl ethers (PBDEs) and PCBs may well play a contributing role in the incidence of these conditions (Wen et al., 2008). It has also been suggested that PBDE exposure through e-waste recycling operations may interfere with the thyroid hormonal system and cause genotoxic damage (Yuan et al., 2008).

Food has been reported as one of the main routes of human exposure to organohalogen chemicals (OHCs), including exposure to PCBs (Xing et al., 2009; Song et al., 2011), PBDEs (Ni et al., 2012, 2013; Chan et al., 2013), hexabromocyclododecane (HBCD) (Zheng et al., 2012; He et al., 2013) and "novel" BFRs (NBFRs) (Zheng et al., 2012). Despite this, data on human dietary exposure to BFRs and PCBs associated with e-waste recycling are still limited or – in the case of HBCD and NBFRs – are non-existent.

Relatively few studies exist that report human dietary exposure to multiple classes of OHCs, with even fewer addressing such exposures arising as a consequence of e-waste treatment. Some of those studies focus on exposure via a single type of food for multiple contaminants, e.g. monitoring a range of BFRs via consumption of domestic eggs originating from e-waste sites in South China (Zheng et al., 2012), while others assess exposure to a single class of contaminant (e.g. PBDEs), via consumption of a number of different food items, for example, chicken muscle and eggs from e-waste sites in Southeast China (Qin et al., 2011). Our study estimates cumulative dietary exposures to selected OHCs via consumption of a range of animal-derived foodstuffs produced in an area in which rudimentary e-waste treatment is commonplace.

We have reported previously on human dietary exposure to PBDEs via consumption of duck eggs (Labunska et al., 2013b), and nine other staple foodstuff categories (Labunska et al., 2014) originating from e-waste recycling areas in Taizhou, eastern China. The current study was designed to investigate human dietary exposure to NBFRs and PCBs arising through consumption of the same foodstuffs, as well as to selected organochlorine pesticides (OCPs). While we did not expect e-waste treatment to be a source of OCPs, information on dietary exposure to these legacy contaminants permits better understanding of overall cumulative exposure to OHCs — many of which can exert toxicological effects. Moreover, the presence of NBFRs in food samples is of interest. Firstly, no regulations on the production or use of these alternative BFRs exist, so it is likely that their use as replacements for regulated BFRs will be increasing. Secondly, some NBFRs appear to be bioaccumulative, with bioaccumulation factors (Log BAFs) for 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and hexabromobenzene (HBB) reported to range from 3.32 to 6.08 and from 3.31 to 5.04 respectively in aquatic species from a natural pond in an electronic waste recycling site in South China (Wu et al., 2011). Combined, these factors suggest that concentrations of NBFRs in food will likely rise substantially in the future. This is concerning, because although relatively little is known about their toxicity (Covaci et al., 2011; Stieger et al., in press), a recent study has reported *in vitro* endocrine disruptive properties for both 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis-(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TBP) (Saunders et al., 2013).

The specific OHCs investigated in the current study were: α-, β- and γ-HBCD, tri- to deca-chlorinated PCBs (33 congeners), dichlorodiphenyltrichloroethane (DDT) and its metabolites, hexachlorobenzene (HCB), and a range of NBFRs, comprising: pentabromoethylbenzene (PBEB), HBB, EH-TBB, BEH-TBP, BTBPE, and decabromodiphenyl ethane (DBDPE).

2. Methodology

2.1. Sample collection and preparation

A full description of the study area and sampling sites is provided in our earlier publications (Labunska et al., 2013b, 2014). Briefly, 127 samples of foodstuffs, comprising: fish, shrimps, meat, liver and eggs from chickens and ducks, and pork were purchased in Wenling and Luqiao districts located within Taizhou City, one of the largest e-waste recycling areas in Eastern China (Fig. 1). Control samples (n = 62) were also procured, along with culinary vegetable oils (n = 10) which were not directly impacted by e-waste treatment. While most control samples were purchased from supermarkets and local markets in Shanghai City and Nanjing City; chicken and duck liver control samples were obtained from a local market in Taizhou City, but were reported by vendors to originate from locations around the city that were not involved in any e-waste recycling.

Our earlier estimates of exposure to PBDEs were based on analysis of 189 individual food samples from e-waste and non-e-waste impacted areas. The wider range of contaminants measured in this study, necessitated the preparation of composite or 'pooled' samples in order to reduce the number of samples requiring analysis. To achieve this, portions of homogenised individual samples were combined according to food category (e.g. chicken eggs, duck meat etc.) and whether they originated from e-waste or non-e-waste impacted areas.

Treatment of the individual food samples used here for preparation of pooled samples, has been described previously (Labunska et al., 2014). In short, samples of meat, fish, shrimps and liver were cooked to reflect the condition of the foodstuffs as the point of consumption, then freeze dried, homogenised and stored at −20 °C. Fat and liquids formed during cooking were discarded.

Chicken eggs were heat treated as has been described previously for duck eggs (Labunska et al., 2013b), and only yolks were subject to analysis. Pooled samples were then prepared by mixing equal amounts of each sample from each product type (2 g per sample for shrimps, 3 mL per sample for vegetable oils and 1 g per sample for all others). Pooled samples were then homogenised thoroughly using a Waring 32BL80 commercial blender, followed by further homogenisation using a mortar and pestle. Each homogenised pooled sample was subsampled into pre-cleaned extraction vials and stored at −20 °C until analysis. Descriptions of the origins of these pooled samples are presented in Table S1. Pooled samples of meat, fish, shrimps and liver were prepared using individual samples from both Wenling and Luqiao districts combined. For chickens' eggs, separate pooled samples were prepared for Wenling and Luqiao district respectively using individual yolks from each site. In the case of duck egg yolk, one pooled sample was prepared per location for each of the five e-waste locations monitored in Wenling and Luqiao (Labunska et al., 2013b). One pooled control sample was prepared for each food category examined.

In addition to obtaining information on human exposure to a wide range of OHCs, we also took the opportunity to enhance understanding of how diastereomer and enantiomeric profiles of HBCDs vary between fish species, as well as how such profiles vary between muscle and liver in chickens and ducks. To do so, we analysed individual samples of 5 fish species – common carp (*Cyprinus carpio*), loach (*Misgurnus angullicaudatus*), snakehead (*Channa argus*), Chinese bream (*Megalobrama amblycephala*) and Chinese perch (*Siniperca chuatsi*) – as well as three paired samples (i.e. muscle and liver from the same three animals) for both chickens and ducks. Note that paired muscle and liver samples were only analysed for these e-waste related samples from individual animals but not for the pooled control samples.

2.2. Sample extraction, clean up and analysis

2.2.1. HBCDs

Extraction was carried out using a pressurised liquid extraction technique utilising an Accelerated Solvent Extractor ASE 350 (Dionex). Diatomaceous earth (30/40 mesh) and Florisil (60/100 mesh) were purchased from Thames Restek (UK); anhydrous Na_2SO_4 — from Fisher Scientific (UK). Native α-, β-, and γ-HBCD standards (50 μg/mL in toluene) were obtained from Cambridge Isotope Laboratories (Andover, MA, USA), while isotope-labelled ^{13}C α-, β-, γ-HBCDs and α-HBCD-d_{18} were purchased from Wellington Laboratories (Guelph, ON, Canada).