HUMAN DIETARY EXPOSURE TO ORGANOHALOGEN POLLUTANTS ARISING FROM RUDIMENTARY E-WASTE RECYCLING

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Introduction

Rudimentary electrical and electronic waste (e-waste) recycling activities introduce a wide range of hazardous chemicals into the environment. Amongst these contaminants are brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs)[1], as well as additional by-products, such as dioxins, that are formed during open burning of plastics to recover metals[2]. Such rudimentary recycling and disposal practices can result in high occupational and incidental exposure to a range of hazardous substances, and cause severe local environmental contamination. Once released to the environment surrounding e-waste treatment facilities, contaminants may enter the food chain with resultant pervasive and prolonged exposure to people residing in the vicinity of e-waste recycling areas. Food has been reported as one of the main routes of human exposure to the organohalogen chemicals (OHCs) PCBs[3] and BFRs, such as polybrominated diphenyl ethers (PBDEs)[4], hexabromocyclododecane (HBCD)[5, 6] and “novel” BFRs (NBFRs)[5]. However, human dietary exposure to OHCs associated with e-waste recycling is still poorly or – in the case of HBCD and NBFRs – not investigated.

We have reported previously on human dietary exposure to PBDEs via consumption of duck eggs[7] and nine other staple foodstuff categories[8] originating from e-waste recycling areas in Taizhou, Eastern China. The current study was designed to investigate whether consumption of the same foodstuff results in human dietary exposure to an expanded range of OHCs, i.e. HBCD, PCBs, selected NBFRs, and organochlorine pesticides (OCPs). To date, no regulations on the production or use of NBFRs exist, so it is likely that their use as replacements for regulated BFRs is increasing and, as a result, their concentrations in food will rise substantially in the near future. Some NBFRs have already been reported to be bioaccumulative and potentially endocrine disruptive[9]. The 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), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis-(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TBP), 1,2 bis(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenyl ethane (DBDPE).

Materials and methods

For the current study, we analyzed the 24 composite samples, prepared from 189 individual diet samples (including controls), that were earlier investigated for PBDEs[8]. To achieve composite samples, portions of homogenised individual samples were combined according to food category (e.g. chicken eggs, duck meat etc.) and according to area (i.e. e-waste or non-e-waste impacted). A full description of the study areas and sampling sites is provided in our earlier publications[7, 8]. Upon preparation, composite samples were divided into 4 aliquots which were analysed separately for HBCDs, NBFRs, PCBs and OCPs, respectively. A full description of sample treatment and analysis is reported elsewhere[10]. Briefly, aliquots for HBCD and NBFRs analysis were extracted using accelerated solvent extraction (ASE), and those for PCBs and OCPs analysis were Soxhlet extracted. HBCD quantification was carried out *via* LC-MS/MS[11], while quantification of NBFRs, PCBs and OCPs *via* GC/MS[10, 12].

Results and discussion

1. Concentrations of OHCs in foodstuffs

E-waste recycling operations in Taizhou appear to be a significant source of the majority of targeted compounds to locally procured foodstuff. Amongst the targeted NBFRs, EH-TBB, BEH-TBP, DBDPE and BTBPE were prominently present in e-waste regions compared to control regions. EH-TBB and BEH-TBP were detected in all e-waste related samples, and BTBPE in 86% of samples, with maximum concentrations of 62.2 ng/g lw (fish), 16.3 ng/g lw (shrimp) and 15.0 ng/g lw (chicken) respectively. For HBCDs, the influence of e-waste recycling was less clear, especially for avian samples, suggesting a diversity of e-waste and non-e-waste related sources for this contaminant. The highest concentration of ∑HBCD was detected in fish (310 ng/g lw) followed by chicken meat, chicken egg, and chicken liver (78.7, 47.5 and 42.5 ng/g lw, respectively). PCBs were particularly dominant contaminants in foodstuffs from e-waste sites, especially in fish (75 400 ng/g lw), possibly related to transformer recycling activities in Luqiao. Moreover, based upon concentrations of the four DL-PCBs measured in the current study (CB 105, 118, 156, and 167), the corresponding maximum levels in food established in the European Union[13] were exceeded for all foodstuffs, except for livers. DDT (and its derivatives) and HCB were widely detectable, reaching maximum concentrations in fish (820 ng/g lw) and chicken eggs (200 ng/g lw) for ∑DDT and HCB respectively.

2. *Estimation of dietary exposure*

Table 1 presents estimated adult and child exposures *via* each type of food along with estimated total dietary intakes (∑DI). Of the targeted NBFRs, EH-TBB yielded the highest estimated exposure for both adults and children (8.02 and 18.1 ng/kg bw/day, respectively) followed by BEH-TBP (2.59 and 6.00 ng/kg bw/day, respectively). The main contributor to estimated EH-TBB, BEH-TBP and BTBPE dietary exposure was pork consumption (Fig. 1). Estimated total dietary exposure to NBFRs decreased in the following order: EH-TBB > BEH-TBP > BTBPE > DBDPE > PBEB > HBB. To our knowledge, this study is the first to estimate dietary human exposure to NBFRs in Eastern China.

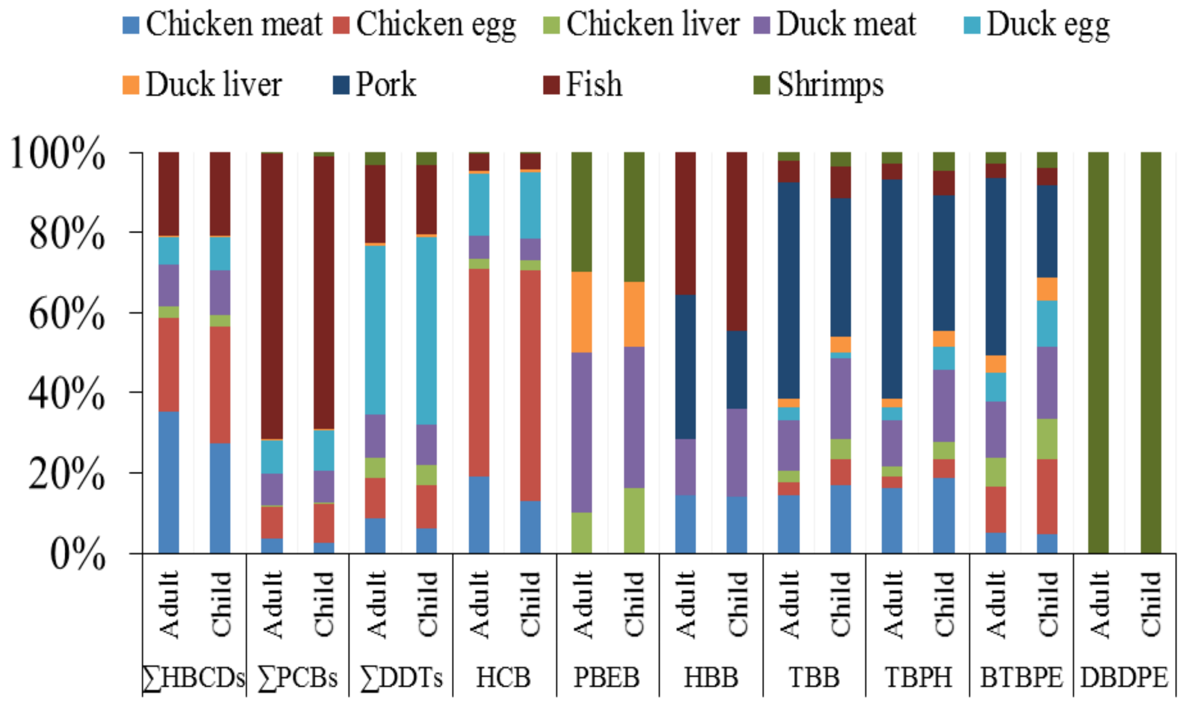
Table 1. Estimated adult and child exposure to selected organohalogen contaminants (ng/kg bw/day) *via* different foodstuffs at e-waste recycling sites in Taizhou, China. n/e – not estimated[a].

		Meat					Liver		Egg		∑DI
		Fish	Shrimp	Chicken	Duck	Pork	Chicken	Duck	Chicken	Duck	
∑HBCDs	Adult	2.18	n/e	3.67	1.10	n/e	0.28	0.03	2.44	0.71	10.4
	Child	7.49	n/e	9.86	3.95	n/e	1.08	0.11	10.5	3.06	36.1
∑PCBs	Adult	460	1.23	22.3	52.6	n/e	2.70	2.76	51.9	53.5	650
	Child	1590	22.0	60.0	190	n/e	10.5	10.8	220	230	2340
∑DL-PCBs[b]	Adult	5.89	0.12	0.37	1.1	n/e	0.05	0.06	1.51	1.11	10.22
	Child	1.71	0.03	0.14	0.31	n/e	0.01	0.02	0.35	0.26	2.83
∑DDTs	Adult	5.06	0.81	2.27	2.78	n/e	1.31	0.21	2.57	11.0	26.0
	Child	17.4	3.16	6.11	9.95	n/e	5.13	0.83	11.0	47.2	100
HCB	Adult	0.55	0.06	2.40	0.72	n/e	0.33	0.08	6.57	1.93	12.6
	Child	1.88	0.22	6.46	2.57	n/e	1.27	0.30	28.3	8.29	49.2
PBEB	Adult	n/e	0.03	n/e	0.04	n/e	0.01	0.02	n/e	n/e	0.10
	Child	n/e	0.12	n/e	0.13	n/e	0.06	0.06	n/e	n/e	0.37
HBB	Adult	0.05	n/e	0.02	0.02	0.05	n/e	n/e	n/e	n/e	0.14
	Child	0.16	n/e	0.05	0.08	0.07	n/e	n/e	n/e	n/e	0.36
EH-TBB	Adult	0.43	0.16	1.15	1.01	4.34	0.23	0.18	0.27	0.25	8.02
	Child	1.49	0.62	3.09	3.62	6.22	0.89	0.71	1.18	0.32	18.1
BEH-TBP	Adult	0.11	0.07	0.42	0.30	1.41	0.07	0.06	0.07	0.08	2.59
	Child	0.37	0.28	1.12	1.08	2.02	0.27	0.25	0.28	0.33	6.00
BTBPE	Adult	0.05	0.04	0.07	0.19	0.61	0.10	0.06	0.16	0.10	1.38
	Child	0.16	0.15	0.18	0.68	0.88	0.38	0.22	0.71	0.44	3.80
DBDPE	Adult	n/e	0.2	n/e	n/e	n/e	n/e	n/e	n/e	n/e	0.20
	Child	n/e	0.77	n/e	n/e	n/e	n/e	n/e	n/e	n/e	0.77

a - DI was not estimated for contaminant present in sample at concentration below corresponding detection limit;
b – intake calculated for sum of four DL-PCBs (CB-105, 118, 156, and 167), pg TEQ/kg bw/day.

To the best of our knowledge, no health based limit values (HBLVs) with legislative standing exist for the targeted NBFRs with the exception of HBB for which our exposure estimates were well below the U.S. Environmental Protection Agency's[14] reference dose (RfD) of 2 000 ng/kg bw/day. Similarly, there are no HBLVs of legislative standing for HBCD. However, our estimates of dietary exposure of both adults and children to ∑HBCD (10.4 and 36.1 ng/kg bw/day, respectively) were significantly higher than those reported previously for a Swedish market basket study (0.14 ng/kg bw/day)[7], and for the Belgian population (0.37 ng/kg bw/day)[8]. Our estimate of daily ∑HBCD intake from chicken egg consumption (154 ng/day) was, however, similar to that reported for chicken eggs collected in the vicinity of e-waste sites in South China (range: 80 – 490 ng/day)[5]. Major contributors of HBCD exposure in the current study, for both adults and children at e-waste sites in Taizhou, were consumption of chicken meat and eggs (together accounting for over 50% of the dietary exposure combined), followed by fish (Fig. 1).

Fig. 1 Contributions to □DI for organic contaminants from different types of foodstuffs originating from Taizhou, China.



Estimated dietary intakes of ∑PCBs (predominantly from fish, eggs and duck muscle) were extremely high, i.e. 650 and 2 340 ng/kg ∑PCBs bw/day for adults and children, respectively, and exceeded substantially the Minimal Risk Levels (MRL) for ∑PCBs of 20 ng/kg bw/day derived by the Agency for Toxic Substances & Disease Registry[15]. Moreover, the estimated intakes of DL-PCB (CB 105, 118, 156, and 167) for children, at 10.22 pg TEQ/kg bw/day, is more than 2.5 times higher than the WHO upper bound tolerable daily intake (TDI) of 4 pg TEQ/kg bw/day[16] (established for all 12 DL-PCBs). Additionally, estimated monthly intakes of DL-PCBs on a TEQ basis (84.9 and 307 pg TEQ/kg bw/month for adults and children, respectively) exceeded the provisional tolerable monthly intake (PTMI) of 70 pg TEQ/kg bw, which was established by the Joint FAO/WHO Expert Committee on Food Additives[17]. Although intakes of DDT in our study (26 and 100 ng/kg bw/day for adults and children, respectively) fell well below both the provisional tolerable daily intake (PTDI) for DDT of 0.01 mg/kg bw/day, derived by the Joint FAO/WHO Meeting on Pesticide Residues[18], and the WHO's proposed acceptable daily intake of 20 000 ng ∑DDTs/kg bw/day, our results show the underestimated significance of egg consumption (especially of duck) as an under-studied source.

Similarly, while the total dietary exposure to HCB (12.6 and 49.2 ng/kg bw/day for adults and children, respectively) fell well within the corresponding US EPA RfD of 800 ng/kg bw/day[19], the current study highlighted the significance of contribution of foods of avian origin to ∑DI for HCB. Consumption of chicken eggs (6.57 and 28.3 ng/kg bw/day for adults and children, respectively) and chicken muscle (2.4 and 6.46 ng/kg bw/day for adults and children, respectively) combined contributed around 70% of our estimates of the $\sum$DI for both adults and children.

In conclusion, the results of the current study highlight the urgency of addressing and, as far as possible, discontinuing current rudimentary and poorly controlled e-waste recycling practices in order to prevent further unnecessary human exposure to hazardous chemicals.

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