FOOD AS A MAJOR SOURCE OF HUMAN EXPOSURE TO PBDEs AROUND E-WASTE RECYCLING SITES IN EASTERN CHINA

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of chemicals used widely as flame retardants in a variety of commercial products, including electrical and electronic equipment. Due to growing recognition of their toxicity, high environmental persistence, and potential to bioaccumulate, PBDE formulations have come under increasing regulatory control[1]. Despite these restrictions, PBDEs are still released into the environment during poorly controlled recycling and disposal of electrical and electronic wastes (e-wastes), in some cases resulting in severe pollution problems and contamination of locally produced food[2]. Taizhou City in Zhejiang Province (Eastern China) has reportedly been involved in e-waste operations for about 30 years and is one of the largest centres for such activities in China[3]. However, despite documentation of environmental contamination by PBDEs in China as a result of e-waste recycling, studies on human dietary exposure to PBDEs around such sites are limited[4,5]. We have recently estimated human exposure to PBDEs via consumption of eggs from ducks foraging in contaminated areas around Taizhou City[6]. This study aims to provide a comprehensive estimation of dietary exposure to PBDEs through foodstuffs produced from locally reared animals and aquatic organisms at e-waste recycling areas in Taizhou.

Materials and methods

1. **Description of sampling sites**

Over 120 samples (including controls) of foods, including pork, fish, shrimps, chicken eggs, chickens, and ducks, were purchased between November 2012 and February 2013 from local farm owners, fishermen and families. The samples from e-waste sites were procured from seven locations situated within 1 to 300 metres of present or former e-waste and scrap metal recycling facilities around Taizhou City, Eastern China. “Control” samples of all foods except duck and chicken livers, but including culinary oils, were purchased in Shanghai City and Nanjing City. Duck and chicken liver controls were purchased from a local market in Taizhou City, and were reported by vendors to be mixed livers from ducks or chickens from nearby locations not involved in e-waste recycling.

2. **Sample preparation and GC/MS analysis**

All samples except culinary oils and chicken eggs were cooked, freeze dried and then homogenised. Excess fat and liquids exuded during cooking were excluded from analysis. Chicken eggs were prepared as described previously[6]. In summary, homogenised chicken yolks (0.2 g) were spiked with internal (or surrogate) standards F-BDE-69, F-BDE-160, and ^{13}C-BDE-209, mixed with Hydromatrix and anhydrous sodium sulphate, and extracted with pentane using ASE 350 (Dionex) system. Following extraction, 20 µL toluene was added as a “keeper” solvent, before extracts were evaporated to incipient dryness under nitrogen and reconstituted immediately with 50 µL toluene containing 2.5 ng of PCB-209 as a recovery determination (or syringe) standard (RDS). Freeze dried samples (0.5 g) were prepared in a similar way to eggs but with a corresponding increase of acidified silica for in-cell clean up to effect lipid removal. Purified extracts were analysed by GC/MS using electron capture negative ionisation (ECNI) in the selected ion monitoring (SIM) mode with methane as reagent gas as described previously[6].

3. **Statistical analysis**

Principal component analysis (PCA) was performed using IBM SPSS Statistics version 21.0.0 for Windows XP and Microsoft Excel 2010. Results were considered significant at $p < 0.05$.

4. **Estimation of PBDE intake (DI)**

PBDE concentrations measured in freeze dried samples were converted to wet weight to permit calculation of daily intakes, based on daily consumption rates for various food products drawn from the most appropriate information. Dietary intakes were calculated assuming that the inhabitants of the e-waste areas studied derived all their intake of the food categories analysed from local sources. Normalisation to body weight for adults was based on an average Chinese male body weight of 63 kg and on a standard Chinese 3 year old boy living in a rural area of 14.65 kg. Low, median, and high-end estimates of daily ∑PBDE intakes were calculated by multiplying average food consumption rates by 5th, 50th, and 95th percentile concentrations respectively. We also calculated daily PBDE intake via ingestion of dust, based on previously reported data on PBDE concentrations in dust from the Taizhou area and dust consumption rates of 0.03 and 0.06 g/day for adults and children respectively[7].

Results and discussion

1. Concentrations of PBDEs in food samples

All samples collected from locations close to e-waste activities contained concentrations of PBDEs significantly higher than those detected in corresponding control samples (see Table 1). This "e-waste treatment increment" was most marked for fish, for which samples from e-waste areas contained, on average, lipid weight (lw)-normalised ∑PBDE concentrations around three orders of magnitude higher than in fish from control sites.

Table 1. Average, median and range of ∑PBDE concentrations (in ng/g lw and, in parentheses, ng/g ww) detected in food samples originating from e-waste recycling sites in Taizhou and control sites in Eastern China

∑PBDE	E-waste sites	Control sites	∑PBDE	E-waste sites	Control sites
Chicken meat			**Chicken liver**		
average	1160 (349)	2.3 (0.19)	**average**	459 (48.7)	3.3 (0.12)
median	354 (38.7)	0.07 (0.005)	**median**	230 (16.8)	4.1 (0.11)
range	18.2 – 3970	<0.018 - 10.7	**range**	24.5 - 1473	0.9 – 4.6
Duck meat			**Duck liver**		
average	150 (40.9)	10.0 (0.74)	**average**	256 (11.4)	18.2 (1.52)
median	66.7 (16.1)	11 (0.84)	**median**	110 (4.5)	19.6 (1.65)
range	11.2 - 593	4.1 – 15.5	**range**	16.6 - 1150	13.3 – 20.8
Chicken egg			**Pork**		
average	656 (77.8)	7.0 (2.1)	**average**	53.8 (7.9)	<0.036 (<0.02)
median	307 (42.2)	4.8 (1.4)	**median**	16.0 (1.4)	<0.036 (<0.02)
range	<0.024 - 3620	2.8 – 23.6	**range**	4.2 – 205	<0.036 (<0.02)
Fish			**Shrimp**		
average	4180 (44.2)	2.5 (0.29)	**average**	28.0 (0.3)	<0.194
median	2130 (37.9)	1.0 (0.29)	**median**	25.8 (0.4)	<0.194
range	702 - 12600	0.4 – 7.8	**range**	<0.194 – 58.1	<0.194

Average ∑PBDE concentrations (lw based) were highest in samples of fish (4180 ng/g), followed by samples of chicken meat (1160 ng/g), chicken eggs (656 ng/g) and chicken liver (459 ng/g). On a wet weight basis (ww), however, chicken meat showed the highest average concentrations (349 ng/g), followed by chicken eggs (77.8 ng/g), chicken liver (48.7 ng/g) and fish (44.4 ng/g). The maximum ∑PBDE lipid weight concentration (12600 ng/g lw) was recorded for a sample of fish, while the maximum wet weight concentration (1223 ng/g ww) was in a chicken meat sample. While BDE-209 was the biggest contributor to ∑PBDE in chicken meat, liver and egg samples, BDE-47 predominated in fish, followed by BDE-100.

Average ∑PBDE concentrations for chicken meat, chicken liver, and chicken eggs were among the highest reported for these foodstuffs to date. In our samples, both average and median ∑PBDE concentrations in chicken meat samples exceeded those in chicken liver, consistent with previous observations that attributed this finding to greater metabolic activity in liver than in muscle. ∑PBDE concentrations in duck and duck liver samples in our study were lower than in chicken meat and chicken liver samples respectively, most probably due to a combination of species-specific differences in habitat preferences and differences in soil and sediment contamination. Average and median ∑PBDE concentrations in fish were 4180 ng/g lw (44.2 ng/g ww) and 2130 ng/g lw (37.9 ng/g ww) respectively. Shrimp samples had much lower concentrations of PBDEs (average 28 ng/g lw, 0.3 ng/g ww) than fish samples. The EU recently proposed an Environmental Quality Standard (EQS) of 8.5 ng/kg ww for PBDEs in fish (sum of six congeners: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154)[8]. Average concentrations in our study for these six PBDEs in shrimps and fish (0.32 ng/g and 42.8 ng/g ww respectively) far exceeded this EQS. The culinary oils analysed here contained only low concentrations of PBDEs compared to other foods studied. The average and median ∑PBDE concentration in these oils was 1.1 ng/g for both parameters. The following PBDEs were present in culinary oils above detection limits: BDE-47 and BDE-99 in six samples, BDE-183, BDE-197 and BDE-209 in three samples, and BDE-154 in one sample out of the 10 samples analysed.

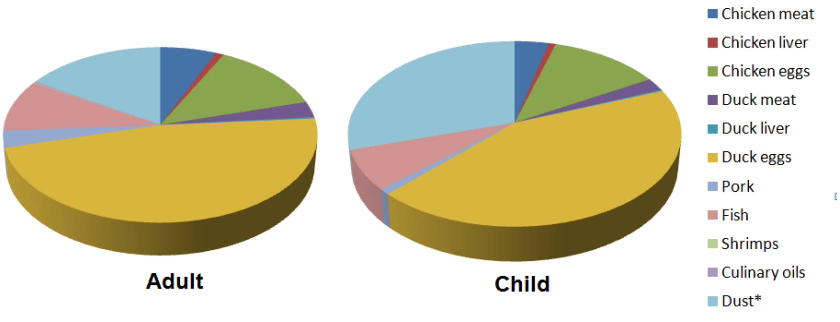
2. PCA analysis of PBDE patterns

Principal component analysis (PCA) was conducted to evaluate differences in PBDE congener profiles in food samples collected from e-waste recycling sites as well as to compare those profiles with corresponding patterns in control samples. Overall, PCA indicated that food samples collected from Taizhou e-waste recycling areas display PBDE congener patterns that differ substantially from those in corresponding control samples, indicative of a heavy influence from contamination from waste recycling and disposal activities. In addition, the various food matrices sampled in this study show marked differences in PBDE patterns.

3. Estimation of PBDEs daily intake

Estimated adult daily median ∑PBDE intakes from foodstuffs in our studies decreased in the following order: duck eggs>chicken eggs>fish>chicken meat>pork>duck meat>chicken liver>duck liver>culinary oils>shrimps. A similar order, with only slight variations, was estimated for children: duck eggs>chicken eggs>fish>chicken meat >duck meat>pork >chicken liver>duck liver>shrimps >culinary oils.

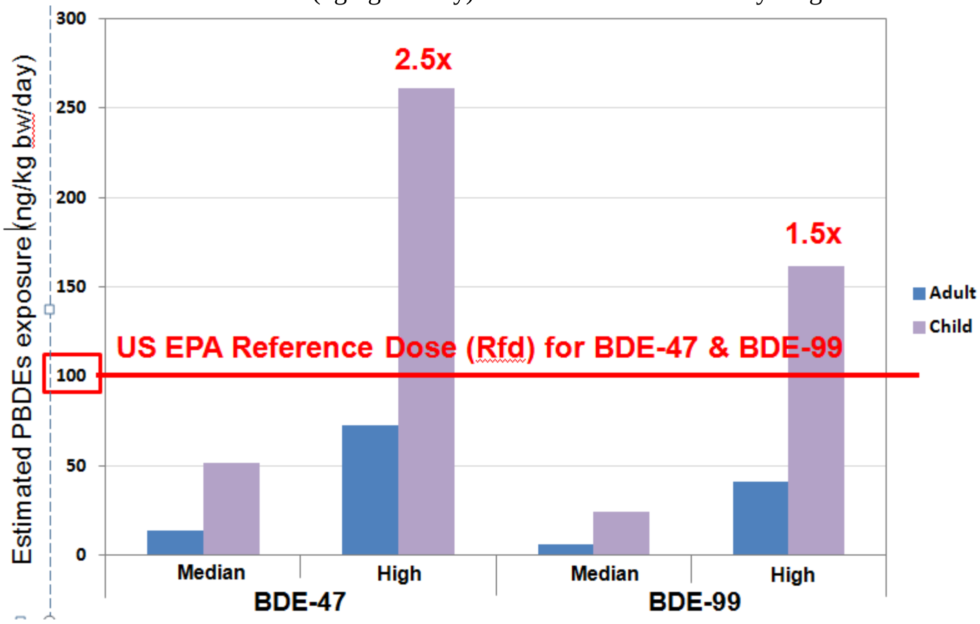
Fig 1. Contribution of each food type and dust to estimated daily ∑PBDE median exposure in e-waste recycling sites in Taizhou, China



Estimated high-end daily ∑PBDE intakes for adults via chicken meat and duck eggs were the highest recorded contributions in our study (20070 ng/day and 27300 ng/day respectively), underlining the importance of these foodstuffs for human dietary exposure to PBDEs. Including exposure via ingestion of contaminated dust at e-waste recycling sites (see Fig 1) increases our median ∑PBDE daily intakes by approximately 19% for adults and 42% for children. While this highlights the potential importance of dust ingestion at the most contaminated locations, dietary exposure remains the principal exposure pathway in most circumstances. Normalised to body weight, our median estimates of exposure to individual key PBDE congeners (BDE-47, BDE-99 and BDE-209) for adults and children did not exceed the reference dose (RfD) values promulgated by the US EPA (see Fig 2).

However, high-end exposure estimates for BDE-47 and BDE-99 in children were approximately 2.5 and 1.5 times the RfDs respectively, while for adults, high-end exposure estimates approached the RfD for BDE-47. Moreover, our estimates of median exposure to BDE-99 (6.2 ng/kg bw/day and 25.3 ng/kg bw/day for adults and children respectively), exceeded substantially (by around 20 times for adults and over 80 times for children) the no adverse effect level (NAEL) for impaired spermatogenesis of 0.23 – 0.30 ng/kg bw/day[9]. Furthermore, for children, estimates were close to the NAEL for impaired neurodevelopmental toxicity (18.8 – 41.4 ng/kg bw/day), while the high end exposure estimates (41.4 ng/kg bw/day and 163.7 ng/kg bw/day for adults and children respectively), exceeded both NAELs. This highlights the potential for adverse human health impacts arising from exposure to PBDEs at e-waste recycling sites in Taizhou.

Fig 2. Exposure to BDE-47 & BDE-99 (ng/kg bw/day) via food from e-waste recycling sites in Taizhou, China



Acknowledgments

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References

1. EU Directive 2003/11/EC. (2003); *OJ* L42: 45– 46
2. Leung AOW, Chan JKY, Xing GH, Xu Y,Wu SC, Wong CKC, Leung CKM, Wong MH. (2006) *Environ. Sci. Pollut.Res*. 17(7): 1300-1313
3. Han W, Feng J, Gu Z, Chen D, Wu M, Fu J. (2009); *Bull. Environ. Contam. Toxicol.* 83: 783–788
4. Chan JKY, Man YB, Wu SC, Wong MH. (2013); *Sci. Tot. Environ.* 463-464: 1138-1146
5. Zhao G, Wang L, Zhou H, Wang D, Zha J, Xu Y, Rao K, Ma M, Huang S, Wang Z. (2009); *Sci. Tot. Environ.* 407: 2565-2575
6. Labunska L, Harrad S, Santillo D, Johnston P. (2013a); *Environ. Sci. Technol.* 47(16): 9258-9266
7. Ma J, Addink R, Yun SH, Cheng J, Wang W, Kannan K. (2009); *Environ. Sci. Technol.* 43:7350–7356
8. EC Proposal for a Directive of the European Parliament and of the Council Amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the Field of Water Policy COM(2011) 876 final (2012)
9. Bakker MI, de Winter-Sorkina R, de Mul A, Boon PE, van Donkersgoed G, van Klaveren JD, Baumann BA, Hijman WC, van Leeuwen SPJ, de Boer J, Zeilmaker MJ. (2008); *Mol. Nutr. Food Res.* 52:204 – 216