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HUMAN DIETARY INTAKE OF ORGANOHALOGEN CONTAMINANTS AT E-WASTE RECYCLING SITES IN EASTERN CHINA

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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.

Keywords

Novel brominated flame retardants (NBFRs); hexabromocyclododecanes (HBCDs), polychlorinated biphenyls (PCBs); organochlorine pesticides; e-waste recycling in China; human dietary intake.

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 (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 (e.g. 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. 2014), 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. S1). 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^{o}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 sub-sampled into pre-cleaned extraction vials and stored at -20^{o}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.

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). Pentane (Rathburn Chemicals, UK) was HPLC grade; acetone and concentrated sulfuric acid (Fisher Scientific, UK) were AR grade.

An accurately weighed aliquot (~0.5 g) of each dried pooled sample was mixed with 5 g of anhydrous Na_2SO_4, transferred into a 33 mL stainless steel extraction cell half-filled with diatomaceous earth, spiked with 20 ng of each of ^{13}C-labelled α-, β-, and γ- HBCD as internal (surrogate) standards, topped with diatomaceous earth, and extracted using the ASE 350 (temperature 90°C, pressure 1500 psi, heating time 5 min, static time 4 min, purge time 90 s, flush volume 50%, 3 static cycles, solvent pentane/acetone 3:1). A 2 mL aliquot of the resultant extract was used for gravimetric determination of lipid content. The remainder of the extract was evaporated to incipient dryness using a Turbovap system and reconstituted with 2 mL pentane.

Extracts were cleaned with 3 mL of concentrated sulfuric acid. After separation of phases, each extract was transferred to a glass column containing 2 g of Florisil topped with 0.5 g of anhydrous Na_2SO_4 and eluted with 25 mL of pentane/acetone (3:1 v/v). Cleaned extracts were evaporated to complete dryness using a gentle stream of nitrogen and reconstituted in 100 µL of α-HBCD-d_{18} (25 pg/µL in methanol) used as recovery determination (or syringe) standard for

QA/QC purposes. Sample analysis was carried out using an LC-MS/MS system composed of a dual pump Shimadzu LC-20AB Prominence liquid chromatograph equipped with a SIL-20A autosampler and a DGU-20A3 vacuum degasser, coupled to a Sciex API 2000 triple quadrupole mass spectrometer. Details of the methodology, LC columns and mass spectrometric conditions for both chiral and achiral separation and quantification of HBCDs can be found elsewhere (Abdallah and Harrad 2011). Regular analysis of method blanks (1 blank for every 5 samples) revealed no detectable interferences from target compounds. Method limits of detection (LOD) and quantification (LOQ) were estimated based on 3:1 and 10:1 signal:noise (S:N) ratios respectively (Table S2). Good recoveries (60 - 109 %) of the ^{13}C-labelled internal standards were obtained for α-, β-, and γ-HBCDs. The accuracy and precision of the analytical method for HBCDs was assessed via replicate analysis (n=4) of NIST SRM 2794A (Organics in Freeze-Dried Muscle Tissue). The results obtained compared favourably with the reference values.

2.2.2 NBFRs

An accurately weighed aliquot (~0.5 g) of pooled sample was loaded into an ASE cell (half-filled with pre-extracted Hydromatrix), spiked with internal standards (15 ng of each of BDE 77, BDE 128, $^{13}C_{12}$-BTBPE and 30 ng of $^{13}C_{12}$-BDE 209), and extracted with hexane:acetone (3:1 v/v) using an ASE 350. After concentration to ~1 mL using the Turbovap system, extracts were eluted through activated Florisil (2 g) using 18 mL hexane (fraction 1) and 12 mL of DCM (fraction 2). Following evaporation to ~1 mL, fraction 1 was eluted through 44% acidified silica (3 g) with 20 mL hexane:DCM (1:1). Fraction 2 was reduced to 0.5 mL and solvent exchanged to hexane, prior to loading onto an isolute NH_2 cartridge and elution with hexane:DCM (1:1 v/v, 15 mL). The eluate from this cartridge was combined with that obtained by passing fraction 1

through Florisil. This combined eluate was concentrated under a gentle stream of nitrogen and solvent exchanged to iso-octane (200 µL) containing PCB 129 as recovery determination (or syringe) standard. Target analytes were quantified using a TRACE™ 1310 Gas Chromatograph coupled to ISQ™ single quadrupole mass spectrometer (ThermoScientific, Austin, TX, USA) operated in negative ion chemical ionisation mode. Chromatographic resolution of NBFRs was achieved on a HP5-MS capillary column (15 m x 0.25 mm x 0.1 µm; Agilent, CA, USA) according to a previously described method (Van den Eede et al. 2012). Recoveries of the internal standards ranged from 74 to 102 % in all samples. LOQs for the method are presented in Table S2.

2.2.3 PCBs and OCPs

Pooled samples (typically 0.5 g) were weighed accurately, homogenised, mixed with anhydrous Na_2SO_4, and spiked with PCB-143 as internal standard, prior to automated hot Soxhlet extraction for 2 h with hexane:acetone (3:1, v:v). Sample lipid content was determined gravimetrically by drying 10% of the crude extract for 1 h at 100 °C. The remaining extract was purified by elution through acidified silica (8 g; 44% H_2SO_4) with 20 mL of hexane followed by 15 mL of dichloromethane. Eluates were concentrated to incipient dryness under a gentle nitrogen flow and reconstituted in 150 µL iso-octane. Analytes were quantified using a mass spectrometer (Agilent MS 5973, Palo Alto, CA, USA) coupled to a gas chromatograph (Agilent GC 6890, Palo Alto, CA, USA) equipped with a HT-8 capillary column (30 m x 0.22 mm x 0.25 µm; SGE Analytical Science, Zulte, Belgium) operated in electron ionisation mode. Recoveries of the internal standard ranged from 81 to 106% (RSD =10%) in all samples. For every tenth sample, a procedural blank and certified reference material (SRM 1945 whale blubber) were analysed. The

LOQ (see Table S2) was defined either as three times the standard deviation of the procedural blanks, or for analytes not detectable in blanks, as S:N = 10:1.

2.3 Statistical analysis & daily intake calculations

Statistical analysis was performed using Microsoft Office Excel 2013. Exposure estimates were calculated using daily consumption rates for various food products derived from a number of publications, as described previously (Labunska et al. 2014). Adult body weights (BWs; kg) employed in our calculations were the average Chinese male body weight of 63 kg (Zhou et al. 2012), with that for children equal to that for a standard Chinese 3 year old boy living in a rural area of 14.65 kg (MHC 2012). The total dietary intake (TDI; ng/kg bw/day) was calculated according to:

$$TDI = \sum_{i=1}^{10} \left(\frac{C_i \ x \ CR_i}{BW} \right)$$

Where C_i is the concentration (ng/g ww) of OHC in a food sample and CR_i is the daily consumption rate of the foodstuff concerned (g/day) (see Table S5 for consumption rates of individual foodstuffs).

3 Results and discussion

3.1 Concentrations and patterns of contaminants in food

3.1.1 NBFRs

Concentrations of NBFRs in e-waste related samples in this study generally exceeded concentrations in the corresponding control samples by substantial margins (Table 1), indicating

a discernible influence of e-waste treatment on concentrations of these contaminants in locally produced foods. EH-TBB and BEH-TBP were detected in all e-waste related samples, with BTBPE detected in 86% of samples. Less frequently detected were PBEB and HBB (>LOQ in 36% of e-waste related samples) while DBDPE was detected only in shrimps. The highest concentration among NBFRs was found for EH-TBB (fish: 62.2 ng/g lw) followed by DBDPE (shrimps: 45.3 ng/g lw). Consistent with previous findings for waterbirds from e-waste recycling sites in South China (Zhang et al. 2011), concentrations of EH-TBB, BEH-TBP, BTBPE and PBEB in avian livers in this study (chicken: 35.0, 10.6, 15.0, and 2.3 ng/g lw; duck: 38.4, 13.7, 11.7, and 3.4 ng/g lw, respectively) exceeded those in corresponding muscle samples (chicken: 24.7, 9.0, 1.5, and <0.17 ng/g lw; duck: 24.2,7.2, 4.6, and 0.9 ng/g lw, respectively). In contrast, in both chickens and ducks, HBB was detected in muscle but not liver. Finally, while concentrations of PBEB, HBB, and DBDPE were all <LOQ in chicken and duck eggs, EH-TBB and BEH-TBP were detected in all e-waste related egg samples (average: 4.3 and 1.1 ng/g lw, respectively). No information related to the concentrations of BEH-TEBP, EH-TBB, BTBPE, DBDPE, PBEB and HBB in food samples has been identified in a meta-analysis conducted by the European Food Safety Authority (EFSA 2012). However, we are aware of one study of chicken eggs from e-waste recycling sites in South China which reported concentrations of NBFRs exceeding those in our study (Zheng et al. 2012). Specifically, this earlier study reported BTBPE, DBDPE, HBB and PBEB to be present at mean concentrations of 37.2–264, 5.97–37.9, 7.32–25.7, and 0.63–0.78, ng/g lw, respectively, compared to those in eggs in our study (range: <0.35 – 3.84 ng/g lw) (see Table 1). Another study (Fernandes et al. 2009) reported concentrations of three of our target NBFRs (HBB, BTBPE and DBDPE) in a wide range of foodstuffs in the UK, with BTBPE being the only NBFR detected above LODs and ranging from

Table 1. Concentrations of OHCs in composite food samples from e-waste recycling (Taizhou) and control sites in Eastern China.

Sample type		Site Category (Control/E-waste)	Lipid%	Concentration, ng/g lipid weight									
				∑HBCDs	∑PCBs	∑DDTs	HCB	PBEB	HBB	EH-TBB	BEH-TBP	BTBPE	DBDPE
Vegetable oil		Control	100	0.1	<1	<2	<1	<0.17	<0.15	<0.20	<0.25	<0.35	<0.45
Muscle	Fish	Control	23.4	5.9	79	100	8.3	<0.17	<0.15	4.00	1.90	2.10	<0.45
		E-waste	5.7	310	75400	820	89.2	<0.17	6.49	62.2	15.5	6.83	<0.45
	Shrimp	Control	4.5	5.7	240	54	5.4	<0.17	0.97	11.7	9.32	<0.35	9.19
		E-waste	4.5	<0.06	1170	170	11.5	6.81	<0.15	36.8	16.3	9.07	45.3
	Chicken	Control	19.0	0.09	<1	<2	6.3	<0.17	<0.15	2.66	1.78	<0.35	<0.45
		E-waste	38.6	78.7	500	51	54	<0.17	0.41	24.7	8.97	1.46	<0.45
	Duck	Control	18.2	2.4	33	<2	9.6	1.16	<0.15	2.74	<0.25	1.87	<0.45
		E-waste	48.1	26.4	1320	70	18	0.87	0.56	24.2	7.23	4.57	<0.45
	Pork	Control	24.6	3.1	<1	<2	2.4	<0.17	<0.15	2.14	1.37	2.69	<0.45
		E-waste	18.4	<0.06	<1	<2	<1	<0.17	0.41	38.2	12.4	5.40	<0.45
Liver	Chicken	Control	38.6	78.7	500	51	54	<0.17	0.41	24.7	8.97	1.46	<0.45
		E-waste	20.9	42.5	410	200	49.9	2.30	<0.15	35.0	10.6	15.0	<0.45
	Duck	Control	21.5	29.9	3	6	11.2	<0.17	<0.15	8.20	1.69	3.27	<0.45
		E-waste	14.5	5.7	570	43	15.5	3.37	<0.15	38.4	13.7	11.7	<0.45
Egg	Chicken	Control	29.6	1.7	<1	3	4.8	<0.17	<0.15	1.73	<0.25	<0.35	<0.45
		E-waste	28.5	47.5	740	61	200	<0.17	<0.15	4.86	0.94	2.02	<0.45
		E-waste	26.5	37.7	1180	32	37.4	<0.17	<0.15	4.73	1.37	3.84	<0.45
	Duck	Control	32.7	0.5	<1	6	5.2	<0.17	<0.15	1.21	<0.25	<0.35	<0.45
		E-waste	32.0	9.3	740	560	68.6	<0.17	<0.15	3.09	0.97	1.11	<0.45
		E-waste	27.0	3.0	62	75.9	40.3	<0.17	<0.15	5.42	1.65	3.07	<0.45
		E-waste	31.0	17.5	140	14	5.9	<0.17	<0.15	3.67	1.24	2.15	<0.45
		E-waste	28.8	2.2	59	140	15.6	<0.17	<0.15	4.40	0.81	<0.35	<0.45
		E-waste	29.6	14.7	2860	110	21.9	<0.17	<0.15	3.56	0.88	<0.35	<0.45

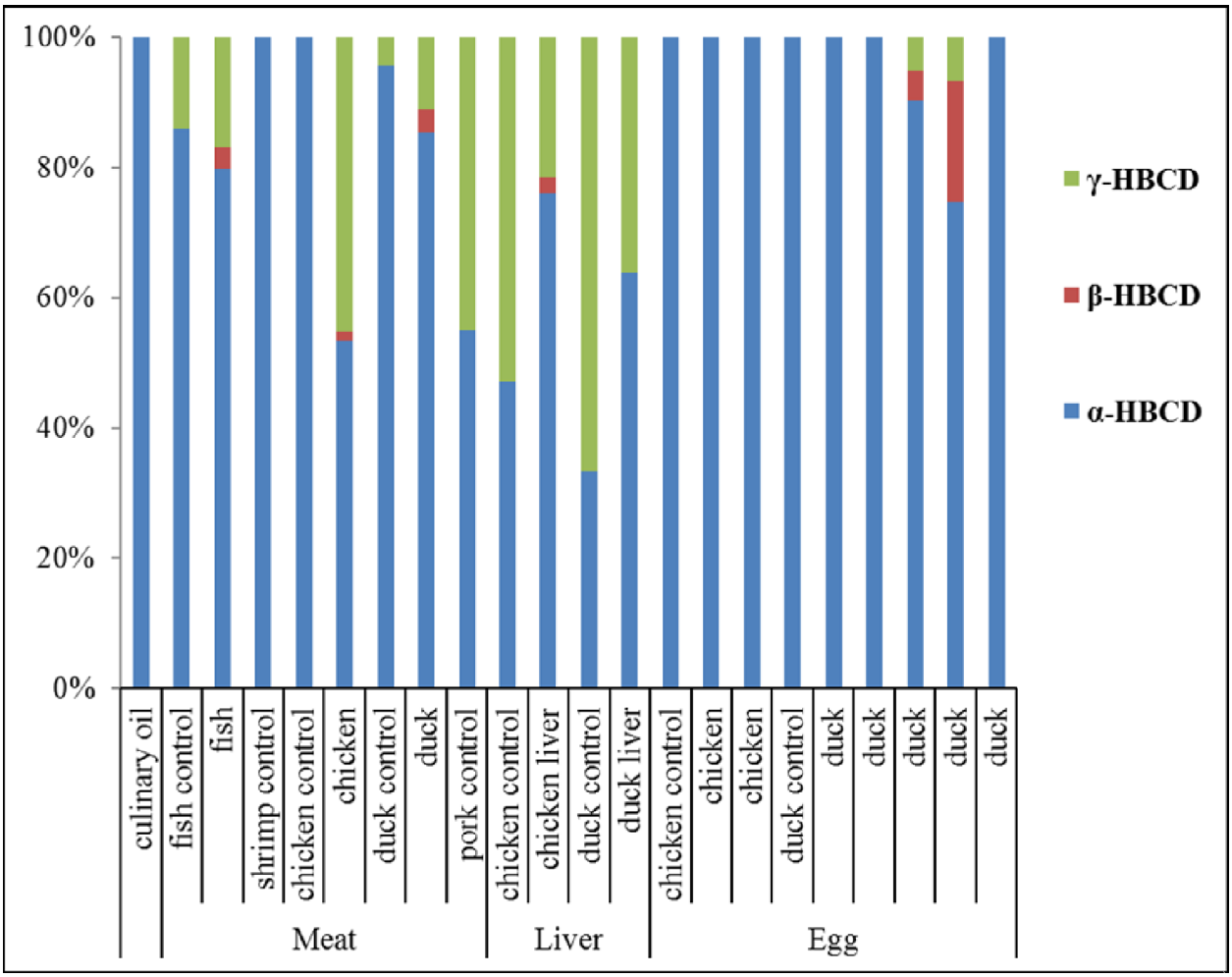
0.1 ng/g lw (in beef burger) to 3.33 ng/g lw (in lemon sole). As well as the presence of a much wider range of NBFRs; concentrations of BTBPE in our study exceeded those in UK foods. For example, BTBPE was detected in our pooled chicken liver sample at 15.0 ng/g lw, compared to 0.75 ng/g lw in the UK study, while it was present at 6.83 and 9.07 ng/g lw in our fish and shrimp samples respectively, exceeding the concentrations reported in UK fish (range: 0.26 – 3.33 ng/g lw).

3.1.2 HBCD

Amongst pooled samples, the highest concentration of ∑HBCD was detected in fish muscle (310 ng/g lw) followed by chicken muscle, chicken egg, and chicken liver (79, 47 and 43 ng/g lw, respectively) (Table 1). Concentrations of HBCD in all analysed samples are provided in Table S4. Those in most of the e-waste related samples exceeded those in corresponding controls by 1-3 orders of magnitude. However, HBCDs were <0.06 ng/g lw in e-waste related pork and shrimp samples, while the corresponding control samples contained 3.1 and 5.7 ng/g lw ∑HBCDs, respectively. Moreover, concentrations of ΣHBCDs in the duck liver control sample, exceeded five-fold that detected in duck livers from e-waste-impacted locations. A previous study from the Pearl River Delta in South China (Sun et al. 2012) reported higher concentrations of HBCDs in the muscle and stomach of three species of passerine birds collected from urban sites than in those from e-waste recycling sites. That difference was attributed to higher releases of HBCD from textile and construction applications in urban areas. This may also help explain the higher concentrations of ∑HBCDs in our control samples, which were all obtained from urban areas which were not in the vicinity of e-waste recycling operations. Furthermore, as the main application of HBCDs is in thermal insulation boards and construction materials (Covaci et al.

2006), a more widespread presence of this compound may be expected in urban areas, with no particular association expected with proximity to e-waste recycling sites. Nevertheless, e-waste-impacted samples of duck muscle, as well as of chicken muscle and liver displayed significantly higher concentrations of ∑HBCDs than corresponding controls. We hypothesise this occurs because chicken and duck housing at the Taizhou e-waste sites are often constructed from potentially HBCD-containing recycled construction materials, as well as containing old furniture and textiles that may also be treated with HBCD. This might also explain the higher concentration of ∑HBCDs in chickens than in ducks from e-waste sites in our study as chickens spend more time in their housing, though a significant contribution to the patterns from differences in feeding habits between ducks and chickens cannot be ruled out. A similar combination of factors may account for our observation that e-waste-impacted chicken eggs contained higher concentrations of ∑HBCDs (47.4 and 37.7 ng/g lw for Wenling and Luqiao e-waste sites respectively) than duck eggs from the same locations (range: 3.0 – 17.5 ng/g lw; average: 9.35 ng/g lw). To the authors' knowledge, there are no previously reported data on HBCD concentrations in domestic duck eggs. Interestingly, while the lowest ∑HBCD concentration was detected in a pooled duck egg sample from a site in the Wenling district at which e-waste activity has decreased substantially recently, the highest concentration was found in a sample from a site in the same district where e-waste recycling had only recently ceased. The farm on this former e-waste recycling area was the largest in our study with 2200 ducks onsite, and which contained several large duck shelters thickly covered with recycled textile and construction materials that potentially may contain substantial amounts of HBCDs (Alaee et al. 2003). This highlights the importance of sources of HBCDs other than e-waste treatment to our samples.

Fig. 1. α-, β- and γ-HBCD diastereomer profiles in composite food samples containing concentrations above LOQ.



Diastereomer profiles of HBCDs in pooled samples are presented in Fig. 1. In general, α-HBCD was the predominant HBCD congener contributing on average 77±31% ∑HBCDs in all our samples (from e-waste areas and controls). This accords with previous reports of the predominance of α-HBCD in biota as opposed to the higher contribution of γ-HBCD found in commercial formulations and abiotic matrices (Marvin et al. 2011). This has been attributed to several factors, including preferential biotransformation of the *β*- and *γ*-isomers (Abdallah and

Uchea 2014) in addition to higher bioavailability and higher bioaccumulation potential of α-HBCD (Szabo et al. 2011a; Abdallah et al. 2012; Fournier et al. 2012). Interestingly, while γ-HBCD comprised only 22% and 36% ΣHBCDs respectively in chicken and duck livers from e-waste related sites, in control samples of the same matrices, γ-HBCD contributed 53% and 67% of ΣHBCDs respectively. This suggests exposure of the control birds to a comparatively "fresh" HBCD source.

Table 2. Concentrations of HBCDs (ng/g lw) in individual samples of fish, and paired samples (muscle and liver) of chickens and ducks.

Sample Type		Location[a]	α-HBCD	β-HBCD	γ-HBCD	ΣHBCDs
Fish	carp	Wenling, Taizhou, Site 4	1530	56.0	350	1940
	loach	Luqiao, Taizhou, Site 5	490	30.0	190	710
	snakehead	Luqiao, Taizhou, Site 7	620	14.6	39.4	670
	bream	Shanghai supermarket, control sample	1.2	2.2	7.4	10.8
	perch	Nanjing supermarket, control sample	20.1	3.3	11.9	35.3
Duck	meat	Wenling, Taizhou, Site 1	19.2	0.5	5.6	25.3
	liver		3.1	3.5	11.9	18.5
	meat	Wenling, Taizhou, Site 2	1.6	0.1	0.9	2.6
	liver		0.2	0.4	2.5	3.1
	meat	Wenling, Taizhou, Site 2	1.7	0.2	0.9	2.8
	liver		0.7	0.2	2.7	3.7
Chicken	meat	Wenling, Taizhou, Site 2	7.6	1.2	5.1	14.0
	liver		1.9	3.5	12.8	18.3
	meat	Wenling, Taizhou, Site 1	490	9.0	150	640
	liver		190	4.4	190	390
	meat	Wenling, Taizhou, Site 2	14.4	1.4	5.4	21.1
	liver		5.4	1.8	5.7	12.9

[a] full description of sampling sites including assignment of sample codes is reported in Labunska et al. (2014)

Analyses also revealed different HBCD diastereomer profiles in liver and muscle tissues taken from individual birds (Table 2), similar to those reported recently for predatory birds in Belgium (Eulaers et al. 2014). Moreover, such intra-bird variation was exceeded still further by the variation in profiles between duck and chicken tissues.

Notably, γ-HBCD was the dominant diastereomer in some avian liver samples compared to the predominance of α-HBCD in muscle tissue from the same birds. We hypothesise this predominance of γ-HBCD in some avian liver samples reflects the profile to which the bird is exposed, as the liver is the first organ exposed after the gastrointestinal tract.

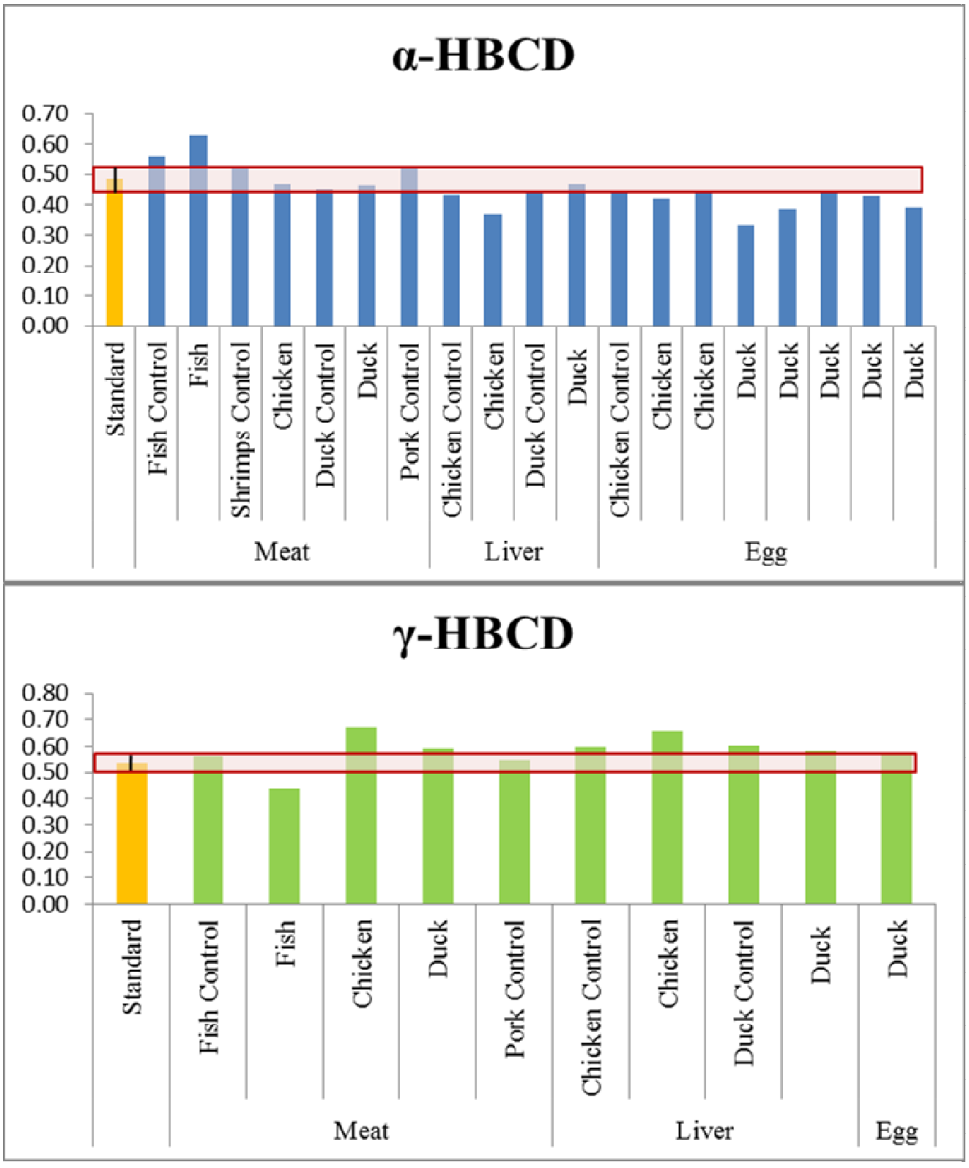
In contrast, the diastereomer profile in muscle tissue reflects more the chronic exposure after metabolism and is thereby skewed towards α-HBCD, due to the latter's enhanced bioaccumulation potential and resistance to enzymatic metabolism (Szabo et al. 2011b; Fournier et al. 2012).

HBCD enantiomer fractions (EFs) are presented in Fig. 2. Generally, muscle and eggs from ducks and chickens displayed significant enrichment of the (-)-α-HBCD and (+)-γ-HBCD enantiomers. This is in agreement with previous reports for terrestrial bird samples from e-waste, urban and rural locations in South China (He et al. 2010; Sun et al. 2012) and eggs of predatory birds from Northern Europe (Janak et al. 2008).

Fish samples showed variable EF values with enrichment of (+)-α-HBCD in loach, carp and bream, (-)-γ-HBCD in loach, and (+)-γ-HBCD in bream. Our results are consistent with previous studies reporting species-specific variation in EFs in fish (Janak et al. 2005; Köppen et al. 2010; He et al. 2013). These findings indicate potential enantioselective processes associated with

absorption, biotransformation and/or excretion of HBCDs in the fish and bird species studied, and that such processes are species-specific.

Fig 2. Enantiomer fractions (EF) of α-HBCD and γ-HBCD in pooled food samples containing concentrations above LOQ. Error bar – SD for a racemic standard.



100 3.1.3 PCBs

101 With the exception of pork and chicken liver, concentrations of ∑PCB concentrations in our e-
102 waste related food samples were all higher than in corresponding control samples (see Table 1).
103 Results for individual PCB congeners in all samples are presented in Table S3. PCBs can arise in
104 environmental samples from both primary and secondary sources and, because of their
105 persistence and long-range transport, are widely distributed environmental contaminants.

106 The relatively high levels in many of the pooled food samples from e-waste areas are, however,
107 suggestive of primary contributions from local point sources, such as recycling and disposal of
108 obsolete transformers, an activity widely practised in Luqiao (Xing et al. 2011; Zhanz et al.
109 2012) as well as handling of other electrical and electronic waste.

110 In view of the history of transformer treatment at Luqiao, it is thus unsurprising that
111 concentrations of ∑PCB from samples obtained from this site were the highest in this study. Of
112 the species considered, concentrations were highest in fish (75416 ng/g lw or 1168 ng/g ww),
113 followed by those in duck eggs (site 5, 2857 and 846 ng/g ww), duck muscle (1322 and 276 ng/g
114 ww) and chicken eggs (1179 and 312 ng/g ww). Consistent with previous studies (Rajaei et al.
115 2010; Xing et al. 2010) and possibly attributable to higher metabolic activity in liver than
116 muscle, concentrations of ∑PCB in livers of both ducks and chickens were lower than in the
117 corresponding muscle samples. It is also interesting to note that, while the concentration of
118 ∑PCB in duck muscle exceeded approximately three-fold that in chicken muscle (276 and 88
119 ng/g ww, respectively), concentrations were similar in both duck and chicken livers at ~30 ng
120 ΣPCB/g ww. This may reflect species-specific differences in metabolism.
121 Concentrations of ∑PCB in duck meat (276 ng/g ww), duck liver (32 ng/g ww) and eggs
122 (average in chicken and duck eggs was 109 and 91.2 ng/g ww respectively) substantially

exceeded those reported previously for e-waste-related sites in Taizhou (13.8, 2.1 and 7.9 ng/g ww, respectively) (Xing et al. 2010).

Table 3. Concentrations of indicator PCBs, ∑NDL-PCBs and ∑DL-PCBs in food originating from Taizhou, China; and maximum levels (ML) for these contaminants in foodstuffs (EU 2011).

	∑PCBs, indicator[c]	∑NDL-PCBs[d]	ML, ∑NDL-PCBs[e]	∑DL-PCBs-TEQ[f]	ML,∑DL-PCBs-TEQ[g]
	ng/g			pg/g TEQ	
Fish	34456 [a]	441 [b]	125 [b]	4.32 [b]	3.0 [b]
Shrimps	569 [a]	5.82 [b]		0.09 [b]	
Chicken muscle	270 [a]	206 [a]	40 [a]	3.07 [a]	1.25 [a]
Duck muscle	698 [a]	530 [a]		7.74 [a]	
Chicken liver	180 [a]	137 [a]	40 [a]	2.09 [a]	5.5 [a]
Duck liver	288 [a]	225 [a]		3.15 [a]	
Chicken egg	518 [a]	388 [a]	40 [a]	6.41 [a]	2.5 [a]
Duck egg	428 [a]	336 [a]		5.38 [a]	

[a] expressed on a lipid weight basis;
[b] expressed on a wet weight basis;
[c] sum of PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180;
[d] sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180;
[e] maximum levels for sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180;
[f] sum of PCB105, PCB118, PCB156 and PCB167;
[g] maximum levels for sum of twelve dioxin-like PCBs derived by subtraction of value for the sum of dioxins (WHO-PCDD/F-TEQ) from the sum of dioxins and DL-PCBs (WHO-PCDD/F-PCB-TEQ).

The homologue pattern of PCBs in avian-related samples originating from our e-waste sites (see Fig. S4) were dominated by hexa-PCBs (from 28% ΣPCBs in duck meat to 41% ΣPCBs in duck eggs), followed closely by penta-PCBs. In contrast, tetra- and penta-PCBs were more prominent

142 in aquatic species. Penta-PCBs comprised 36% ΣPCBs in fish and 26% ΣPCBs in shrimps, with
143 tetra-PCBs contributing 27% ΣPCBs in fish and 29% ΣPCBs in shrimps. While these homologue
144 patterns are consistent with previous observations for Taizhou (Xing et al. 2010); those in our e-
145 waste impacted fish samples differed from patterns observed in Europe, in which hexa-PCBs
146 (mostly PCB-153 and PCB-138) are dominant in fish (Roosens et al. 2008; Malarvannan et al.
147 2014). The different patterns seen in our e-waste-associated samples may reflect influences from
148 multiple local sources at e-waste recycling sites. These include releases from PCB-containing
149 transformers and/or capacitors as well as unintentional formation of some PCBs during poorly-
150 controlled combustion processes (Shen et al. 2009).
151 Concentrations of non-dioxin-like (NDL-) and dioxin-like (DL-) PCBs in comparison to
152 maximum levels (ML) promulgated by the European Commission for certain contaminants in
153 foodstuffs (EU 2011) are presented in Table 3.The sum of seven indicator PCBs (PCB-28, 52,
154 101, 118, 138, 153 and 180) in fish (534 ng/g ww) in our study exceeded the Chinese maximum
155 residue limit of 500 ng/g ww for aquatic organisms and aquatic products (MOH 2012).
156 Additionally, with the exception of chicken liver, all samples of avian origin from e-waste sites
157 in our study (Table 3) exceeded the maximum level of 200 ng/g lw set by the European
158 Commission (EC 1999), for the sum of these seven indicator PCBs in products including eggs
159 and poultry.

160 Another EC Regulation No. 1881/2006 (EC 2006) established maximum levels (ML) for dioxins
161 and DL-PCBs in a range of foodstuffs. This was amended recently (EU 2011) to include limits
162 for the sum of six marker NDL-PCBs (see Table 3). This ML for ∑NDL-PCBs was exceeded by
163 at least an order of magnitude for foodstuffs of avian origin in our study and 3.5 times in case of
164 fish. Moreover, while only four DL-PCBs were measured in this study (PCB-105, 118, 156, and

167), Table 3 shows that based on the contribution of these four congeners alone, the corresponding EU ML was exceeded for all foodstuffs studied except for livers.

3.1.4 Organochlorine pesticides

Table 1 shows that concentrations of ∑DDTs in our e-waste related food samples were all higher than in the corresponding control samples, with the exception of pork. Concentrations of DDT and its metabolites are presented in Table S3. DDT is a significant contaminant group in food samples from Taizhou, despite the ban on most uses of this pesticide in China in 1983 (Fu et al. 2003). However, an exemption was made for the use of DDT as an intermediate for dicofol production, which has been shown to be a major source of DDT to the Chinese environment over recent decades (Qiu et al. 2005). Concentrations of ∑DDT in our study were highest in fish (823 ng/g lw), followed by duck eggs from Wenling site 1 (558 ng/g lw) and chicken liver (201 ng/g lw). On a fresh weight basis, duck eggs contained the highest ∑DDT concentrations (range 1.7 - 70.2 ng/g), followed by chicken liver (15.0 ng/g ww) and duck muscle (14.6 ng/g ww). Interestingly, while duck muscle contained a higher fresh weight concentration of ∑DDTs than duck liver, the concentration in chicken liver was almost twice that in chicken muscle. Neither control nor e-waste related pork samples contained any DDT above detection limits. This is consistent with earlier findings that pork accumulates relatively low loadings of DDT (range: 0.09 – 0.89 ng/g ww) in comparison to other animal-based food products (Yu et al. 2012). Most of the duck eggs in our study contained higher ∑DDT concentrations than reported previously for chicken eggs (5.62 and 5.09 ng/g ww for Taizhou and Guiyu respectively) (Man et al. 2013). This was particularly evident for duck eggs from Wenling, site 1, which, at 70.2 ng/g (ww) ∑DDT was close to the Chinese maximum residue limit in eggs of 100 ng/g ww (MOH 2012).

188 To the authors' knowledge, there are no previously published data on concentrations of DDT and
189 its metabolites in Chinese duck eggs, with exception of one study which included duck eggs as
190 part of a pooled sample of eggs that also comprised chicken eggs and egg products (Zhou et al.
191 2012). Our data suggest that these so-called "legacy" contaminants remain prevalent in our
192 study area.
193 The differences in the relative abundance of DDT and its metabolites between bird tissues, livers
194 and eggs in our study compared to studies of other avian species, may be attributed to a variety
195 of factors. Among other influences, these include: the composition of the birds' diet, their age
196 and weight, and the levels and pattern of ΣDDT contamination in the areas they inhabit (Covaci
197 et al. 2004).
198 The principal contributor to concentrations of ∑DDT in all samples in our study, was *p,p'*-DDE
199 (see Fig. S5). Concentrations of *p,p'*-DDE ranged from <2 ng/g lw in pork to 546 ng/g lw in fish.
200 In contrast, *o,p'*-DDT was not present above detection limits in any of our samples, while *p,p'*-
201 DDT was present in 42% of samples. This predominance of *p,p'*-DDT over its *o,p'*-isomer is
202 consistent with historical contamination of the investigated area by technical DDT which mostly
203 comprises *p,p'*-DDT (up to 77% ΣDDTs). In addition, the ratio of DDT/DDE+DDD (where it
204 was possible to calculate), was always < 1 in our study, with *o,p'*-DDT undetected. This is also
205 consistent with historical contamination by technical DDT, as *o,p'*-DDT is the primary
206 contaminant in dicofol formulations accounting for 46% of the four DDTs (*o,p'*-DDT, *o,p'*-DDE,
207 *p,p'*-DDT, and *p,p'*-Cl-DDT), while *p,p'*- DDT contributes only 7% to this sum (Qiu et al. 2005).
208 In agreement with an earlier study on lake fish in China (Guo et al. 2012), *p,p'*-DDD contributed
209 significantly to ∑DDTs in both control and e-waste related fish samples in our study (25 % and
210 19% respectively). Similar DDT isomer patterns were observed for chicken and duck livers,

though they displayed slightly lower contributions of *p,p'*-DDD to ∑DDT than observed in fish (at 5% and 16% in avian liver and fish muscle respectively), while in chicken muscle and shrimps, only *p,p'*-DDE was detected.

Control chicken and duck eggs similarly contained only *p,p'*-DDE, and then at relatively low concentrations, while those from e-waste related areas contained also *p,p'*-DDT (in chicken eggs) or both *p,p'*-DDT and *p,p'*-DDD (in duck eggs). Reassuringly, none of the muscle samples in our study exceeded either the Chinese maximum residue limit for DDTs of 2000 ng/g lw (MOH 2012) or the 1000 ng/g lw ML set by the EC (EEC 1986).

Including controls, HCB was detected in 92% of the samples considered in this study, with the exception of vegetable oils and pork (see Table 1). All control samples showed lower concentrations of HCB than the corresponding e-waste related samples, with the exception of duck liver and pork. Concentrations of HCB (based on lipid weight) were also relatively high in fish (89.2 ng/g), chicken muscle and liver (54.0 ng/g and 49.9 ng/g respectively) and in duck eggs (up to 68.6 ng/g). Overall, food products of avian origin yielded the highest concentrations of HCB in our study, exceeding values reported in a previous total diet study conducted in China in 2007 (Zhou et al. 2012) for both muscle (mean:1.58 ng/g ww) and chicken eggs (mean: 0.59 ng/g ww).

3.2 Estimation of daily intakes

Our estimated exposures of both adults and children to halogenated organic contaminants via the consumption of a range of frequently-consumed local foodstuffs in e-waste recycling sites of Taizhou are presented in Table 4. The contributions to total dietary exposures for organic contaminants from different types of food are presented in Fig. 3. Comparison of total dietary

234 exposures to HBCD, PCBs, DDT and metabolites, HCB, NBFRs, and our previously reported
235 data for PBDEs (Labunska et al. 2014) are presented in Fig. 4.

236

237 3.2.1 NBFRs

238 Estimated total dietary exposure to NBFRs considered in our study decreased in the following
239 order: EH-TBB > BEH-TBP > BTBPE > DBDPE > PBEB > HBB (Table 3).

240 EH-TBB had the highest estimated exposures for both adults and children (8.03 and 18.9 ng/kg
241 bw/day respectively) followed by BEH-TBP (2.6 and 6 ng/kg bw/day respectively). The main
242 source of both EH-TBB and BEH-TBP to dietary exposure was via pork consumption (54 and
243 34% for adults and children respectively). Consumption of pork was also the principal
244 contributor to dietary exposure to BTBPE (44 and 23% for adults and children respectively). For
245 HBB, fish was the main contributor for children (44%), while for adults, both pork and fish each
246 contributed 36% of dietary exposure. Duck muscle and duck liver combined contributed over
247 50% of PBEB dietary exposure for both adults and children, while shrimps were the only food
248 type in our study found to result in exposure to DBDPE. To our knowledge, this study is the first
249 report of dietary exposures to NBFRs in Eastern China. One study has reported daily intakes of
250 several NBFRs via chicken eggs from e-waste sites in South China (Zheng et al. 2012), but
251 reported their dietary estimates as the sum of all monitored NBFRs, in contrast to our compound-
252 specific approach. Moreover, the main contributor to exposure to NBFRs in the Zheng et al study
253 was Dechlorane Plus (DP), which was not investigated in our study. Hence, it was not possible to
254 make a direct comparison between the two studies. Moreover, to our knowledge - with the
255 exception of HBB - no health based limit values (HBLVs) with legislative standing exist for the

Table 4. Estimated adult and child exposure to selected organohalogen contaminants (ng/kg bw/day) via different types of food at e-waste recycling sites in Taizhou, China. n/e – not estimated.

		Meat					Liver		Egg		TDI
		Fish	Shrimps	Chicken	Duck	Pork	Chicken	Duck	Chicken	Duck	
∑HBCDs	Adult	2.18	n/e	3.67	1.1	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	2.7	2.76	51.9	53.5	**650**
	Child	1590	22.0	60	190	n/e	10.54	10.8	220	230	**2340**
∑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	2.4	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	0.3	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	0.3	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	0.1	0.06	0.16	0.1	**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**

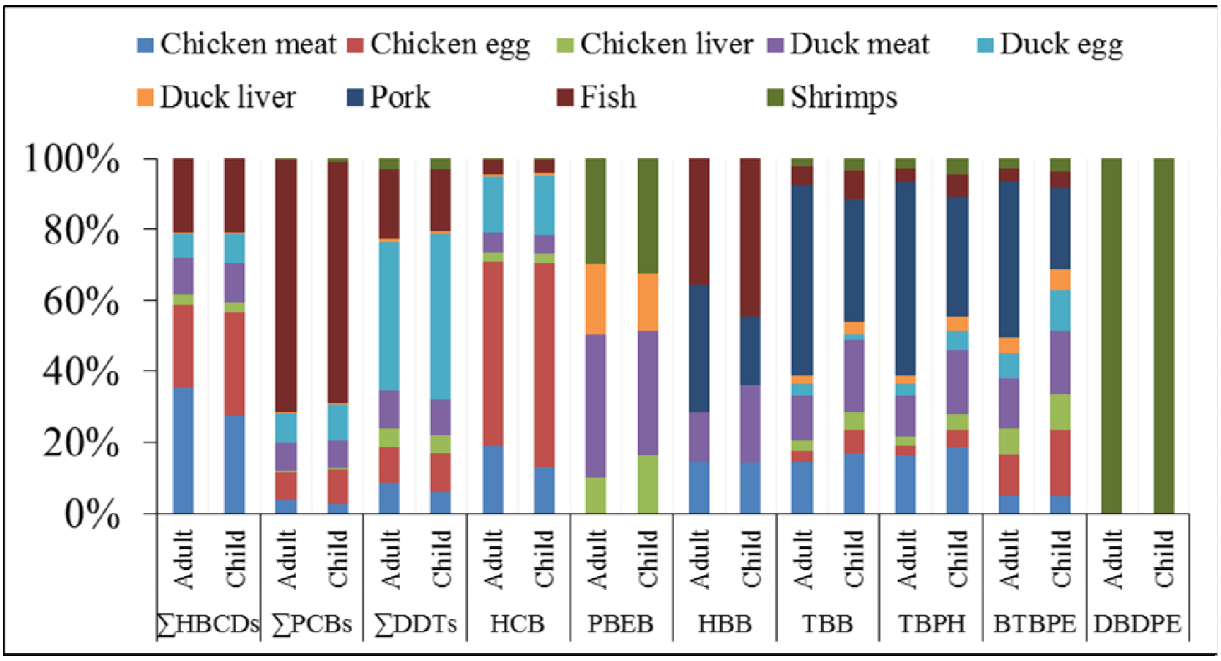
NBFRs considered in our study. For HBB, our exposure estimates are reassuringly well below the U.S. Environmental Protection Agency's (US EPA 1988) reference dose (RfD) of 2000 ng/kg bw/day.

3.2.2 HBCD

As with the NBFRs, we are unaware of any HBLV of legislative standing for HBCD. However, we were able to compare our dietary exposure estimate with those reported in other studies. Estimated dietary exposure of both adults and children to ∑HBCD in our study (10.4 and 36.1 ng/kg bw/day) was significantly higher than reported previously for a Swedish market basket study (0.14 ng/kg bw/day) (Törnkvist et al. 2011), as well as for the Belgian population (0.37 ng/kg bw/day) (Goscinny et al. 2011). Chicken muscle and eggs were the main contributors to ∑HBCDs exposure for both adults and children at e-waste sites in Taizhou accounting for over 50% of the dietary exposure combined (Fig. 3). This contrasted with two studies from Sweden (Remberger et al. 2004; Törnkvist et al. 2011) in which fish was the main contributor to dietary intake of HBCD. Such differences likely reflect both differences in local dietary preferences and variations in environmental contamination of the study areas. Our estimate of daily ∑HBCD intake from chicken egg consumption (154 ng/day) was similar to that reported for chicken eggs at e-waste sites in South China (range: 80 – 490 ng/day) (Zheng et al. 2012), but exceeded significantly that reported in Romania (0.02 ng/day) (Dirtu and Covaci 2010).

Our exposure estimates for adults and children to ∑HBCD *via* consumption of chicken eggs (2.44 and 10.5 ng/kg bw/day respectively), exceeded significantly those reported for the Belgian population (0.004 ng/kg bw/day) (Goscinny et al. 2011).

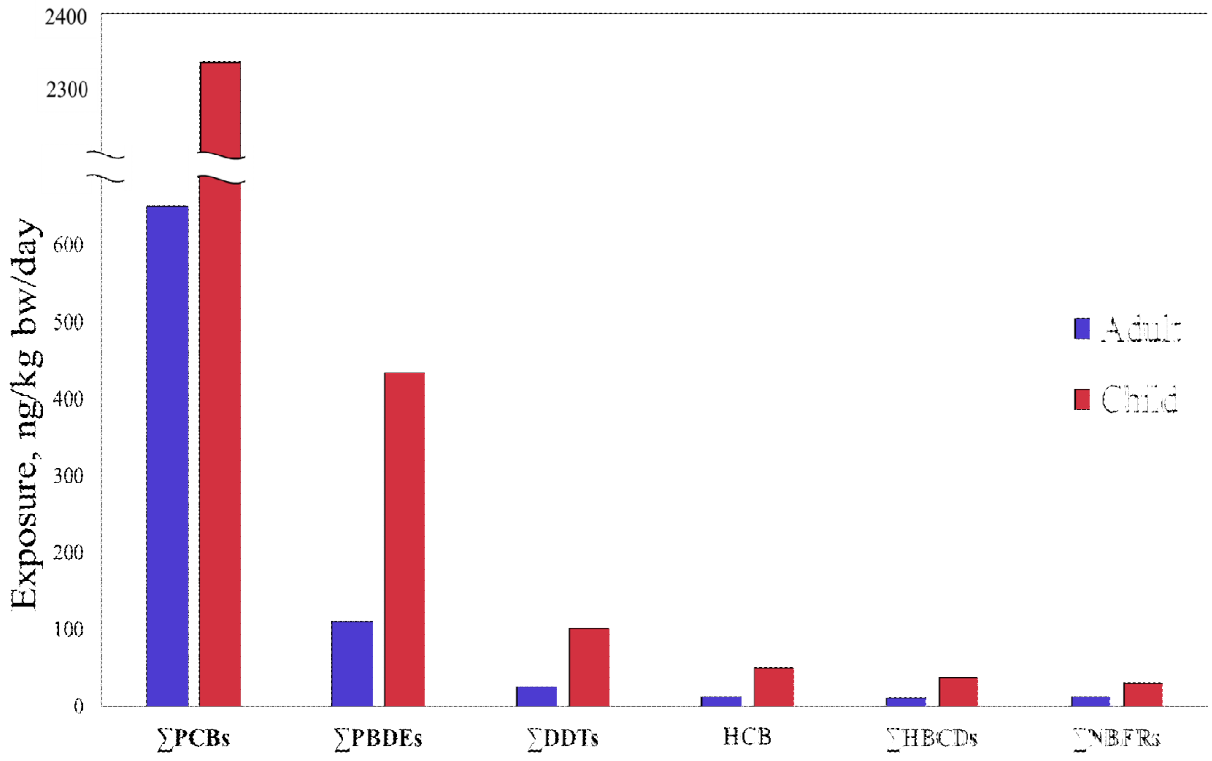
Fig. 3. Contributions to total dietary exposures for organic contaminants from different types of food originating from Taizhou, China.



Fish contributed a further 21% to our estimate of dietary exposure to ∑HBCD for both adults and children, at 2.18 and 7.49 ng/g bw/day, respectively; values that exceeded those reported for the populations of nine Chinese coastal cities (range: 0.004 – 1.00 ng/kg bw/day) (Xia et al. 2011). Interestingly, while chicken muscle and eggs were the main contributors to ∑HBCD exposure (adults: 35 and 23 % respectively), duck muscle and eggs contributed greatly to ∑PBDE exposure (adults: 56 and 3 % respectively) as was previously reported (Labunska et al. 2014). Our estimate also exceeded that of rural residents of Tianjin, China (1.64 ng/kg bw/day) but was similar to that reported for urban residents (6.16 ng/kg bw/day) (Zhang et al. 2013). In comparison to other countries, our estimate of exposure to ∑HBCDs *via* fish consumption was in line with the average estimate for Japanese adults (range: 1.3 – 3.7 ng/g bw/day) (Nakagawa et

al. 2010). The contribution of duck muscle and eggs to ΣHBCDs exposure was lower than that from chicken muscle and eggs. Consistent with other studies (e.g. Goscinny et al. 2011), of the avian tissues studied, liver made the lowest contribution to our estimated dietary intake of ΣHBCD.

Fig. 4. Estimated total dietary exposures to PCBs, DDTs, HCB, HBCDs, NBFRs, and previously reported data on PBDEs (Labunska et al. 2014).



3.2.3 PCBs

Dietary exposure to PCBs (650 and 2340 ng/kg ΣPCBs bw/day for adults and children respectively) was the highest of all of the contaminants considered in this study and exceeded

307 that for PBDEs in our previous study of the individual samples from which the pooled samples
308 analysed here were taken (see Fig.4). Moreover, it exceeded substantially the Minimal Risk
309 Levels (MRL) for ΣPCBs of 20 ng/kg bw/day derived by the Agency for Toxic Substances &
310 Disease Registry (ATSDR 2000). Fish was the major contributor to total dietary exposure to
311 PCBs (Fig. 3) followed by eggs (both duck and chicken) and duck muscle. Additionally, we
312 estimated dietary intake of the four DL-PCBs measured in our study (i.e. PCB-105, 118, 156 and
313 167) based on their dioxin-like toxicity equivalence (TEQ) (Van den Berg et al. 2006; EU 2011)
314 (see Table 5). While adult intake (2.83 pg TEQ/kg bw/day) was within the range of tolerable
315 daily intake (TDI) for dioxin-like chemicals of 1 – 4 pg TEQ/kg bw/day established by the
316 World Health Organisation (WHO) (van Leeuwen et al. 2000); estimated intake for children at
317 10.22 pg TEQ/kg bw/day was 2.5 times the WHO TDI upper limit for all 12 DL-PCBs
318 combined. Moreover, DL-PCBs-TEQ monthly intakes in our study (84.9 and 307 pg TEQ/kg
319 bw/month for adults and children respectively) exceeded the provisional tolerable monthly intake
320 (PTMI) of 70 pg TEQ/kg bw, which was established by Joint FAO / WHO Expert Committee on
321 Food Additives (JECFA 2002).

322 We compared our estimates with those reported elsewhere. Specifically, a study at an e-waste
323 recycling site in Luqiao, Eastern China (Song et al. 2011) reported the estimated dietary intake of
324 adults to PCDD/Fs and DL-PCBs combined to be 402 pg TEQ/kg bw/month, *via* consumption of
325 six types of local food (rice, vegetable, chicken, chicken eggs, duck, and crucian carp). Although
326 this exceeded our exposure estimate, it is important to emphasise that our DL-PCB-TEQ
327 exposure estimates are based on exposure to only 4 out of the 12 PCB congeners deemed to
328 display dioxin-like toxicity. Moreover, the exposure estimates of Song et al (2011) are calculated
329 using WHO-1988 TEFs (Van den Berg et al. 1998), compared to the current re-evaluated WHO-

2005 TEFs (Van den Berg et al. 2006) used in our study. The use of the WHO-1998 TEFs to our data raises our estimated monthly dietary intake of DL-PCBs to 332 and 1197 pg TEQ/kg bw/month for adults and children respectively. Our data thus suggest dietary exposure to PCBs and, potentially, other related contaminants in the study area, is of substantial health concern, particularly for children.

Table 5. Concentrations of four DL-PCBs (pg TEQ/g ww) and dietary intake (pg TEQ/kg bw/day) by adults and children from e-waste recycling sites in Eastern China.

	Concentrations (pg TEQ/g ww)					Intake, pg TEQ/kg bw/day	
	PCB 105	PCB 118	PCB 156	PCB 167	∑PCBs	Child	Adult
Fish	1.16	2.79	0.24	0.13	4.32	5.89	1.71
Shrimps	0.02	0.06	0.00	0.00	0.09	0.12	0.03
Chicken meat	0.14	0.34	0.03	0.03	0.54	0.37	0.14
Duck meat	0.41	1.05	0.10	0.05	1.62	1.10	0.31
Chicken Liver	0.04	0.10	0.01	0.00	0.16	0.05	0.01
Duck Liver	0.06	0.11	0.01	0.00	0.18	0.06	0.02
Chicken Egg	0.45	0.20	0.03	0.06	0.74	1.51	0.35
Duck Egg	0.34	0.14	0.02	0.03	0.54	1.11	0.26
Total						**10.22**	**2.83**

3.2.4 Organochlorine pesticides

The highest exposure to ∑DDTs in our study was via consumption of duck eggs (11.0 and 47.2 ng/kg bw/day for adults and children respectively) followed by fish (5.1 and 17.4 ng/kg bw/day for adults and children respectively) (Table 3). Consumption of these two products accounted for over 60% of dietary exposure to ∑DDTs for both adults and children (Fig. 3). Exposure to ∑DDTs *via* fish in our study was similar to that reported for adults in South China (range: 5.74 – 5.84 ng/kg bw/day) (Guo et al. 2010), higher than that reported in another recent study (Man et

al. 2013) around e-waste sites in Taizhou (3.39 ng/kg bw/day), but lower than that in Guiyu (6.88 ng/kg bw/day).

Exposure to ∑DDTs *via* consumption of chicken and duck muscle as well as chicken eggs in our study was between 2.27 and 2.78 ng/kg bw/day and 6.11 and 11.04 ng/kg bw/day for adults and children, respectively. Exposure of adults to ∑DDTs via eating chicken eggs in our study (2.57 ng/kg bw/day) was similar to the 2.35 ng/kg bw/day reported for Taizhou previously (Man et al. 2013). However, exposure to ∑DDTs via consumption of duck eggs in our study was over four-fold that received via eating chicken eggs. Total dietary exposure to ∑DDTs in our study (11.0 and 47.2 ng/kg bw/day for adults and children respectively) exceeded substantially that reported for 12 provinces in China (range: 0.008 – 0.13 ng/kg bw/day) (Zhou et al. 2012). In contrast, our exposure estimates 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 (FAO/WHO 2001), and the WHO's proposed acceptable daily intake of 20000 ng ΣDDTs/kg bw/day. While we did not expect e-waste treatment to represent an important source of DDTs to the local environment, our study nevertheless reveals exposures well above those reported elsewhere in China, and moreover demonstrates that duck eggs are an important pathway of human exposure to DDT and its metabolites. This is important as a recent study attributed elevated levels of DDTs in milk, placenta and hair of mothers from Taizhou to high seafood intake, but did not mention consumption of duck eggs (Man et al. 2014).

Total dietary exposure to HCB (12.6 and 49.2 ng/kg bw/day for adults and children respectively) (Table 3) was well within the corresponding US EPA RfD of 800 ng/kg bw/day (IRIS 1991). However, as with DDTs, dietary exposures in our study exceeded substantially those reported elsewhere. For example, human adult exposures to HCB were: in Catalonia, Spain, 1.0 ng/kg

bw/day (Martí-Cid et al. 2008), in Northwest Russia, 3.1 ng/kg bw/day (Polder et al. 2010), and in 12 provinces in China, 9 ng/kg bw/day on average (Zhou et al. 2012). Consumption of chicken eggs (6.57 and 28.3 ng/kg bw/day for adults and children) and chicken muscle (2.4 and 6.46 ng/kg bw/day for adults and children) combined contributed around 70% of our estimates of total dietary exposure to both adults and children (Fig. 3) followed by duck eggs and muscle (about 20% total exposure). Chicken eggs from Wenling showed the highest HCB concentration on both a lipid (197.4 ng/g) and wet weight basis (23.5 ng/g), with the concentration detected falling just below the 200 ng/g lw maximum residue level promulgated by the EC (EEC 1986).

This study reveals substantially elevated concentrations of a wide range of OHCs in foods originating from an area where unregulated e-waste treatment is practised. Even though only 4 of the 12 designated dioxin-like PCB congeners were measured in this study; concentrations of dioxin-like PCBs expressed as TEQ, exceeded the EU limit value in 6 out of the 8 food groups studied. Combined with our earlier report based on the same samples, of substantially elevated exposure of young children to PBDEs 47 and 99; the data reported here add to growing concerns about the adverse health impacts of unregulated e-waste treatment. Efforts to discontinue such activities should be prioritised in order to minimise further release of toxic chemicals into the environment. Meanwhile, educational programs are recommended in areas where rudimentary e-waste treatment is conducted, in order to help the local population to minimise their exposure to chemical contaminants – for example, by restricting access of their livestock to e-waste contaminated land.

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5 Supplementary Materials

The following materials are available as supplementary information: a description of pooled samples (Table S1); locations of sampling sites (Fig. S1); limits of quantification (LOQs) of target compounds (Table S2); comparison of reference values for α- and β-HBCD from NIST SRM 2794A (Organics in Freeze-Dried Mussel Tissue) and values obtained in our study (Fig. S2); concentrations of HBCD isomers in pooled food samples from e-waste and control sites (Table S3); HBCD diastereomer profiles in selected individual food samples (Fig S3); concentrations of PCBs and DDTs in pooled food samples (Table S4); PCB and DDT congener/isomer profiles in pooled food samples (Fig. S4 and Fig S5); and a Table summarising published data and data used in this study on daily consumption rates for food products (Table S5).

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