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EMERGING HALOGENATED FLAME RETARDANTS AND HEXABROMOCYCLODODECANES IN FOOD SAMPLES FROM AN E-WASTE PROCESSING AREA IN VIETNAM

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Abstract

This study reports concentrations of selected emerging halogenated flame retardants (HFRs) and hexabromocyclododecanes (HBCDs) in foodstuffs sourced from an e-waste processing area in Vietnam and two reference sites in Vietnam and Japan. Concentrations of all target HFRs in e-waste-impacted samples in this study exceed significantly ($p<0.05$) those detected in the controls, suggesting e-waste processing activities exert a substantial impact on local environmental contamination and human dietary exposure. Significant linear positive correlations in concentrations of *syn*-Dechlorane Plus (DP) and *anti*-DP were found between soils and those in co-located chicken samples ($p<0.05$). This implies soil is an important exposure source of DPs in chickens at our sampling sites. The estimated dietary intakes of emerging HFRs in this study were 170 and 420 ng/kg bw/day, for adults and children respectively; while daily ingestions of HBCDs were an estimated 480, 1500 ng/kg bw/day for adults and children, respectively. Exposure at the site monitored in this study exceeds substantially estimates of dietary exposure to HBCDs in e-waste processing sites and non e-waste processing areas elsewhere.

Keywords: Emerging HFRs; HBCDs; Food; Soil; E-Waste; Dietary exposure

1. Introduction

HFRs have been used widely to ensure manufactured goods such as plastics, textiles, building materials, vehicle components and electronic equipment meet fire safety regulations.[1,2] Some HFRs like polybrominated diphenyl ethers (PBDEs) are subject to bans and restrictions within the EU as well as elsewhere.[3] As a result, there is likely increasing demand for emerging HFRs, such as DP, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP), pentabromobenzene (PBBz), hexabromobenzene (HBB), and decabromodiphenyl ethane (DBDPE). Recently, such emerging HFRs have been detected in various environmental matrices, including indoor dust, air, sediment, soil, and sewage sludge.[4–10] Studies of the environmental behaviour of emerging HFRs are scarce, with the limited information available suggesting that, similar to regulated HFRs like PBDEs, they may be toxic, persistent, bioaccumulative, and subject to long-range transport. This information includes: the detection of DP, EH-TBB, BEH-TEBP, HBB and BTBPE in the Arctic,[11,12] the long half-life and biomagnification potential of BTBPE in juvenile rainbow trout,[13] a recent report that oral exposure to DP can induce hepatic oxidative damage and perturbations of metabolism and signal transduction in male mice,[14] and studies showing accumulation of some emerging HFRs in fish, birds and dolphins.[15–17]

Moreover, increasing attention is being paid to environmental contamination with HFRs arising from emissions occurring during end-of-life treatment of treated goods. Particular concern exists about situations where electrical and electronic waste (e-waste) is dismantled under rudimentary conditions. Numerous studies have shown elevated contamination of air, dust, soil, and sediments with PBDEs in such locations, [18–20] with a smaller number of recent studies reporting elevated human dietary exposure to local populations in such areas. In contrast, relatively few data exist about environmental contamination with emerging HFRs in areas where such informal e-waste processing is conducted, although a recent study reported concentrations of EH-TBB and BEH-TEBP in foodstuffs from a Chinese e-waste impacted location to exceed those from control locations.[21] In addition to PBDEs, hexabromocyclododecanes (HBCDs) have also been frequently detected in the environment and human milk sampled in the vicinity of rudimentary e-waste processing sites.[22–24] However, studies of human exposure via consumption of food sourced from locations where rudimentary processing of e-waste is conducted are scarce. Zheng et al.[25] reported the estimated human exposure to HBCDs via ingestion of eggs sourced from an e-waste recycling site in South China, while Labunska et al.[21] reported human dietary exposure to HBCDs via consumption of a variety of foodstuffs including fish and pork as well as chicken eggs, liver, and muscle from e-waste recycling sites in Taizhou, China.

The available data for PBDEs and HBCDs suggest that fish, pigs, and free-range chickens reared in e-waste impacted locations accumulate these compounds – likely through uptake from their environment (e.g. soil and sediment) and food. Consequently, elevated dietary exposure to such HFRs is likely for people consuming food derived from such animals reared in the vicinity of e-waste processing areas. To date however, evidence of similar exposure to emerging HFRs via consumption of fish, pork, and chicken liver, eggs, skin and muscle derived from e-waste impacted areas is very limited. Bui Dau is a small village where e-waste processing started at the beginning of the 21st century in Vietnam. Concentrations of polychlorinated biphenyls, and organophosphorus flame retardants, tetrabromobisphenol A, emerging HFRs, PBDEs and HBCDs in human and environment samples have already been reported in this area.[23,24,26] Against this backdrop, and also as part of the study above to investigate site-specific contamination levels in Bui Dau, this study's objective is to determine concentrations of emerging HFRs and HBCDs in such foodstuffs collected from a location impacted by rudimentary e-waste processing in Bui Dau, Vietnam. These data are compared with concentrations detected in samples of the same matrices sourced from non-e-waste impacted control locations in Vietnam and Japan, and are combined with information on their consumption by local inhabitants to estimate human exposure to these contaminants. Concentrations of emerging HFRs and HBCDs are also measured in soil samples from the same e-waste impacted locations, to investigate the impact of soil contamination on chicken tissues and eggs.

2. Methods

2.1 Sampling and pretreatment

Samples were collected in January 2014 from an e-waste processing area in Bui Dau (Cam Xa, Hung Yen province) in Vietnam. The locations of the sampling sites are presented in Fig. 1. The sampling area is a rural village of approximately 200 households. The main supplies of livestock products and fish for the local people in Bui Dau are from neighbouring communities,[24] and the livestock and fish raised in farm yards in Bui Dau are intended mainly for consumption by the families themselves with any small surpluses sold commercially. E-waste processing activities such as dismantling of electrical wires and metals, shredding of plastics into pellets, manual recycling of TVs, printers, printed circuit boards and other computer components are mainly family-based, with e-waste handled in the backyards of domestic buildings, in which livestock are raised. Fresh chicken eggs (n=3 from each site) were collected from chicken farm owners at six sampling sites (site 1-site 6) shown in Fig. 1. In addition, five chickens (one from each site) were also purchased from chicken owners at five locations (site 1-site 5), from which samples of chicken muscle (n=5), chicken liver (n=5), and chicken skin (n=5) were derived. Soil samples (one from each site) were collected at the same time from the backyards where the chickens were raised. Each soil sample analysed consisted of five sub-samples from the same backyard homogenised before analysis.

In addition to chicken, egg, and soil samples; five tilapia (*Oreochromis mossambicus*) samples were collected from the river (site 7), with a further five fish samples (3 rohu (*Labeo rohita*) and 2 tilapia) collected from the fish pond located in Bui Dau. Moreover, two samples of pork muscle were purchased from a market stall in Bui Dau village.

Control samples One control chicken egg sample and one control chicken muscle sample were purchased from Thanh Hoa province, situated approximately 175 km distant from the e-waste processing location. Additional control samples of chicken egg, muscle, liver, and skin were purchased in Tsukuba, Japan, with control samples (n=1 in each case except for chicken egg (n=3)) of pork and fish purchased in Hanoi City.

Sample treatment prior to analysis Following collection, egg samples were boiled on location in a large pan for 8 minutes at 100 °C and then cooled to room temperature. Egg yolks were then separated from the egg white and wrapped in pre-cleaned aluminum foil, prior to storage at -20 °C until shipping to the laboratory with ice bags.

2.2 Sample Preparation for GC/MS Analysis

Seven emerging HFRs (PBBz, HBB, BEH-TEBP, BTBPE, DBDPE, *syn*- and *anti*-DP) as well as α-, β- and γ-HBCDs were measured in all samples (CAS numbers and full names of emerging HFRs are provided as supporting material).

Following homogenization and freeze-drying, approximately 5 g of each sample was extracted firstly using a rapid solvent extractor (SE-100; Mitsubishi Chemical Analytec Co., Ltd.) at 35 °C for 40 min with 50% acetone in n-hexane at a flow rate of 2 mL/min, followed by secondary extraction at 80 °C for 40 min with toluene at a flow rate of 2 mL/min. Resultant extracts were evaporated and solvent exchanged to 10 mL toluene. An aliquot (1 mL) of the extract was used to determine lipids by evaporation to dryness and gravimetry. A further 2 mL aliquot of the crude solvent extract was taken before being spiked with a known amount of $^{13}C_{12}$-labelled internal (or surrogate) standards ($^{13}C_{12}$-HBB, $^{13}C_{12}$-BTBPE, $^{13}C_{12}$-BDE209, $^{13}C_{12}$-α-, β-, γ-HBCDs). These 2 mL aliquots were eluted through a gel permeation chromatography column packed with SX-3 Bio-Beads (Bio-Rad Laboratories, Inc.); the eluate from which was separated into two further aliquots. The first of these aliquots was subjected to further purification by passing through a 2 g deactivated silica gel column (eluted with 10 mL 50% diethyl ether in hexane) followed by a 8 g florisil column (eluted with 50 mL hexane and 50 mL dichloromethane). The final eluate was concentrated and solvent exchanged to 50 μL nonane containing $^{13}C_{12}$-BDE 138 as a recovery determination standard. The second aliquot was evaporated to nearly dryness and transferred to 2 mL hexane, which was then partitioned against 3-4 mL

concentrated sulfuric acid, prior to evaporation to incipient dryness and resolubilisation in 100 μL methanol. Instrumental analysis of target emerging HFRs was performed using an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electron impact (EI) mode. 2 μL of cleaned extract was injected on a DB-1HT capillary column (15 m × 0.25 mm i.d., 0.1 μm film thickness; Agilent Technologies, Inc.) via cool on-column injection. The injection temperature was set at 100 ˚C, hold 0.1 min, ramp 100 ˚C/min to 300 ˚C, hold 15 min. The GC temperature program was set at 100 ˚C, hold 1 min, ramp 8 ˚C/min to 310 ˚C, hold 10 min.

Determination of α-, β- and γ-HBCDs was achieved 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. (Applied Biosystems, Foster City, CA, USA) operated in electrospray negative ionization (ESI) mode equipped with a Varian Pursuit XRS3 C18 analytical column (150 mm × 2 mm I.D., 3 μm particle size). Details of this instrumental method are provided elsewhere.[21,27]

2.3 Quality assurance/quality control

Quality assurance (QA) and control (QC) was achieved via regular analysis of procedural blanks and matrix spike samples – the latter comprising food samples purchased in Japan and spiked with known amounts of the target emerging HFRs and HBCDs. A 9-point calibration curve spanning the concentration range 1.25–1,000 pg/μL including the $^{13}C_{12}$-labelled HFRs was employed.

Initial evaluation of analyte recoveries was assessed via the following matrix spiking experiment. Samples of chicken liver, egg, skin, muscle, and fish were purchased in Japan as low-contamination controls. Aliquots (5 g) of these were spiked with known amounts of both native and isotopically-labelled analytes included in the present study, and the samples were extracted and cleaned-up using the standard procedure. After deducting levels in the unspiked control samples, the recoveries of native compounds were from 56-98% and the recoveries of internal standards ranged from 90-117%.

2.4 Statistical Analysis and daily intake calculations

Pearson's correlation analysis was conducted to investigate relationships in concentrations of BTBPE, *syn*-DP, *anti*-DP, and HBCDs between chicken and soil samples. Statistical analysis was performed using IBM SPSS Statistics 21.0 and a p value <0.05 was regarded as indicating statistical significance.

Dietary intakes (DI) (ng/kg bw/day) were calculated thus:

$$DI = \sum_{i=1}^{n} \frac{Ci \times CRi}{BW}$$

Where Ci is the concentration (ng/g ww) of HFR in a food item i and CRi is the daily consumption rate of the foodstuff i (g/day; values given in supporting material). Body weight (BW; kg) values employed in this study were assumed to be 51 kg for adults according to our sampling questionnaire and 14.65 kg for children based on WHO-

growth chart data for Vietnamese children under 3 years old. No previous information exists about consumption rates of the foodstuffs (fish, chicken liver, poultry, and meat) in Vietnam, so we used information provided in a previous study of an e-waste processing area in Eastern China.[21]

As we measured HFRs concentrations in egg yolk only, concentrations on a whole egg basis were calculated and the weight of eggs was corrected for the eggshell weight for calculating daily intakes of HFRs via chicken egg consumption according to a previous study.[19]

3. Results and discussion

3.1 Detection of HFRs in food samples

Table 1 shows concentrations of HFRs in food, co-located soil and co-located sediment samples.[28] Of our target emerging HFRs: PBBz, HBB, BEH-TEBP, BTBPE, DBDPE, *syn*-DP, *anti*-DP were detectable in chicken samples, with the same HFRs (except PBBz) found in soil samples. In contrast, only BTBPE was detected in river fish, only DBDPE was detectable in pork and no emerging HFRs were detected in pond fish.

Most strikingly, concentrations of all target emerging HFRs in e-waste-impacted samples in this study exceed substantially those detected in the corresponding controls. This demonstrates substantial impact of the e-waste processing activities on

the environment in Bui Dau. These findings are consistent with previous studies of PBDEs, PBEB, HBB, EH-TBB, BEH-TEBP, BTBPE, and DBDPE in Taizhou, eastern China.[21,29]

DPs were the most frequently detected emerging HFR (100% detection) in chicken samples (muscle, liver, egg, skin), followed by BTBPE and HBB with a detection frequency of 70% and 50%, respectively. PBBz was less frequently detected in chicken samples while BEH-TEBP was only detected in chicken egg samples. In contrast, the most frequently detected compounds in foods from e-waste processing sites in Taizhou, eastern China were EH-TBB and BEH-TEBP.[21] This likely reflects different waste compositions at the two locations. Interestingly, in this study, despite the theoretical predictions that organic contaminants for which Log K_{OW}>7 become increasingly less prone to uptake by biota;[30] we detected DBDPE (for which Log K_{OW} is a reported to be 11.1[3] in chicken muscle, egg and pork samples in this study. The most abundant emerging HFR detected in chicken was DP, with average concentrations of ΣDP in chicken ranged between 520 and 5,100 ng/g lipid weight (lw), comprising around 90% of the sum of emerging HFRs measured in this study. This is consistent with previous findings for chicken egg samples from e-waste recycling sites in South China.[25] DP was not measured in samples taken from Taizhou in the study of Labunska et al.,[21] so comparison is not possible in this instance. The predominance of DP is likely attributable to its classification as a high production volume (HPV) compound[31], a term used to describe a chemical produced in the United States in quantities exceeding 450 t per year, and the significant

biomagnification potentials of both *syn*- and *anti*-DP in food samples.[32,33] Furthermore, DP is used in electrical cable coatings[34] and dismantling of electrical wires was one of the main e-waste processing activities in Bui Dau. Consequently, DP may be discharged to the environment during the handling of electrical cables. With respect to our other targeted emerging HFRs, average concentrations in chicken samples of PBBz, HBB, BEH-TEBP, BTBPE, and DBDPE were <1.5-2.0, 1.5-6.8, <1.3-2.0, 54-70, and <2.8-280 ng/g lipid weight (lw) respectively. The highest concentration of ΣDP (25,000 ng/g lw) was found in chicken liver, at the high end of values(nd-9630 ng/g lw) previously reported for ΣDP in food samples.[25,33,35,36] Only limited studies of the presence of emerging HFRs in food samples from e-waste processing sites, especially in different chicken tissues, are available. One previous study reported concentrations of ΣDP, DBDPE, BTBPE and HBB in chicken eggs from e-waste recycling sites in South China, to fall within the ranges 665-3,290, 5.97-37.9, 37.2-264 and 7.32-25.7 ng/g lw, respectively.[25] These concentrations exceed those found for ΣDP (4.0-2,300 ng/g lw) and HBB (<1.3-2.0 ng/g lw) in this study, but are similar to those we report here for DBDPE (<2.8-620 ng/g lw) and BTBPE (<2.8-160 ng/g lw) in eggs. Average concentrations of HBB and BTBPE in chicken livers (<0.15 and 15.0 ng/g lw, respectively), chicken muscle samples (0.41 and 1.46 ng/g lw) and chicken eggs (<0.15 and 2.93 ng/g lw) from e-waste processing areas in Taizhou,[21] are much lower than those in this study (results shown in Table 1). Moreover, the concentrations of ΣDP in chicken samples in this study were comparable to those in chicken liver (4.4 ng/g ww) and muscle samples (0.92 ng/g

ww) from e-waste processing sites in China.[37] Our analyses of DP concentrations in liver, muscle and skin tissues taken from individual chickens, revealed DP concentrations were highest in chicken liver, followed by chicken muscle, similar to data reported recently for chicken in China.[37] Additionally, concentrations of BTBPE in avian (watercock) and fish samples taken from an e-waste processing area in southern China ranged between 0.07-2.41 and <0.012-0.15 ng/g lw, respectively.[16] These values are exceeded substantially in our chicken and fish samples. In contrast, concentrations of DBDPE in avian muscle and fish samples in our study are similar to those reported previously.[16]

In samples originating from areas not impacted by e-waste processing activities, concentrations of HBB, BTBPE, and DBDPE were determined in a selection of UK and Irish food samples.[38] Only BTBPE was detectable in this earlier study, at concentrations of 0.96, 0.75, 0.29, and 0.55 ng/g lw in fish, chicken liver, and chicken eggs, respectively;[38] substantially lower than those detected in our study. Compared to the presence of BTBPE in UK food samples, BTBPE was not detected in control samples collected in Vietnam and Japan.

Concentrations in soil In co-located soil samples, concentrations of HBB, BEH-TEBP, BTBPE, DBDPE, *syn*-DP, and *anti*-DP were in the range 0.15-21, <0.050-0.4, 0.19-34, 0.42-64, 0.20-13, and 0.83-31 ng/g dry wt (dw) respectively. The detection frequency was 100% except for BEH-TEBP which was detected in only 20% of

samples. PBBz was not detected in any soil samples in this study. DBDPE was the most dominant compound in soil, accounting for around 50% of the total emerging HFRs in our study.

Concentrations of emerging HFRs in soil in our study exceed (DBDPE and BTBPE) or are comparable with (ΣDP) those detected in soils taken from locations in China surrounding but not directly impacted (e.g. close to workshops) by e-waste processing.[16,39] Moreover, concentrations of ΣDP in soil in this study exceeded by 3 orders of magnitude those found in soils from residential, business and industrial areas in northern China.[40] In contrast, the concentration of ΣDP in a single surface soil directly impacted (i.e. close to a workshop) by e-waste recycling in South China was 3,327 ng/g dw[39] - 2 orders of magnitude higher than the average concentration detected in our study. Similarly elevated concentrations of DP (5,900-10,000 ng/g dw) have also been reported in soil samples directly impacted by e-waste activities in Qingyuan county.[37]

3.2 Concentrations and diastereomer patterns of HBCDs in food samples and co-located soil samples

Concentrations of HBCDs in food samples in this study are shown in Table 1. HBCDs were detected in all chicken tissues, river fish, pork, and soil samples. In chicken and fish samples, the levels of HBCDs tend to be higher than those of emerging HFRs except DP while in pork samples the levels of HBCDs were comparable to those of

emerging HFRs in line with reports by Labunska et al.[21] and Zheng et al..[25] While HBCDs are known to be mainly used in polystyrene foam and fabrics, they were used to a minor extent in electrical equipment housing.[41] This latter minor application, could explain the elevated levels of HBCDs in this study, as TVs, DVDs, computers and printer housings were processed on a large scale in Bui Dau. Coupled with their environmental stability, persistence and past high production volume[42], these factors may account for the levels of HBCDs in this study exceeding those for most of the emerging HFRs monitored. In contrast, HBCDs were not detected in pond fish. This study's finding that HBCD concentrations in e-waste-impacted samples exceed those in corresponding controls differs to that of Labunska et al.,[21] who reported that HBCD concentrations in some control samples exceeded those in samples derived from e-waste-impacted locations. To our knowledge, very few data exist about concentrations of HBCDs in foods reared in locations where unregulated e-waste processing is conducted. Average concentrations of ΣHBCDs in chicken liver (3,200 ng/g lw) and egg (3,600 ng/g lw) samples in our study exceeded substantially those found in chicken liver (42.5 ng/g lw) and eggs (42.6 ng/g lw) from an e-waste processing area in Taizhou City[21] as well as in chicken eggs (44.2-350 ng/g lw) from another e-waste processing site in South China (Qingyuan City).[25] Moreover, HBCDs concentrations (0.59-670 ng/g wet weight (ww)) in food samples in this study exceed markedly those detected in similar foodstuffs around the world including China (<LOD to 9.2 ng/g lw),[43] the USA (12-616 ng/g lw),[44] Romania (0.04-0.25 ng/g ww),[45] Sweden (0.005-0.63 ng/g ww),[46] Belgium (<0.01-0.35 ng/g ww),[47] and the UK (0.02-0.30 ng/g ww).[48]

As shown in Table 1, HBCD concentrations in animal-related food sampled from the e-waste processing site in Vietnam varied substantially between species and different chicken tissues. The highest concentrations were found in chicken eggs, followed by chicken liver, chicken skin and chicken muscle; with concentrations in fish and pork samples much lower than those from chickens. Such interspecies differences indicate that the uptake and metabolism of HBCDs is organism-dependent.

The mean ΣHBCDs concentration in soil in this study was 120 ng/g dw, varying from 0.030 to 580 ng/g dw, comparable to HBCD concentrations in surface soils from e-waste processing areas in South China, ranging from 0.38-284 ng/g dw.[22] In contrast, concentrations of HBCDs in soil from the vicinity of HBCD production facilities in Sweden, Belgium, Germany and China (111-23,200 ng/g dw) exceed significantly those in this study; while those in soils from urban Guangzhou (1.7-5.6 ng/g dw) and from open waste dumping sites in India, Vietnam, Malaysia, Indonesia, and Cambodia (< nd to 2.4 ng/g dw) were at the low end of the range detected in our study.[22,49]

The HBCD diastereomer profiles detected in foodstuffs and co-located soils in this study are shown in Fig. 2 along with the profile reported for the HBCD commercial formulation.[50] Fig. 2 shows γ-HBCD to be the dominant isomer in soil samples in this study, similar to profiles observed in commercial technical products and related abiotic environmental matrices such as sediment, soil and sewage sludge.[42] However, in all food samples (whether sourced from e-waste impacted or control locations), α-

HBCD predominated, in line with previous data for biota.[42,51] Furthermore, α-HBCD was relatively more abundant in chicken egg, muscle, and skin than in liver, indicating tissue-specific variation in the relative abundance of different diastereomers, whereby γ-HBCD is more prevalent in liver samples than the other tissues studied. As highlighted previously,[21] we believe the diastereomer pattern in avian liver samples reflects more closely the pattern present in its diet and soil, as liver is the first organ exposed following the gastrointestinal tract. In contrast, other avian tissues display a pattern more influenced by metabolism post-exposure.

Fig. 3 shows the enantiomer fraction (EF) values for α-, β-, and γ-HBCD in chicken and co-located soil samples. Average EF values in our soil samples were 0.46, 0.53, and 0.54 for α-, β-, and γ-HBCD, respectively, compared with those in commercial HBCD (0.514, 0.510, and 0.503).[22] This slight deviation from racemic suggests some edaphic enantioselective degradation of HBCDs, consistent with an earlier study that reported enantioselective biodegradation of (+)-α-HBCD in soils.[52] In contrast, in soil samples from e-waste recycling areas and industrial areas in South China, negligible enantioselective degradation was implied by mean EF values ranging from 0.503 to 0.507, 0.494 to 0.506, and 0.502 to 0.511 for α-, β-, and γ-HBCD, respectively.[22]

With respect to biotic matrices, in this study, (+)-α-HBCD was clearly enriched in chicken skin and egg while (-)-α-HBCD dominated in chicken liver. As proposed above to explain the different diastereomer profile detected in chicken liver; the

different enantiomer profile observed in the liver may reflect the profile to which the bird is exposed; while that in skin and egg may reflect *in vivo* enantioelective processing post-exposure. To the best of our knowledge, no studies have been reported to investigate the enantioselectivity of α-HBCD enantiomers in all three of these chicken tissue types examined here. However, in an earlier study by our group of chicken liver, eggs and muscle tissue from e-waste impacted locations in Taizhou, China[21]; while (-)-α-HBCD was enriched in all three tissue types, the enrichment was markedly greater in liver than in egg or muscle tissue – an observation not in consistent with the present study.

Other studies have reported EFs of HBCDs in birds. He et al. [52] reported that spotted dove and Chinese francolin displayed EF values enriched in the (-)-α-enantiomer, while Chinese pond heron and its main prey (fish) displayed relatively more (+)-α-HBCD in an e-waste region in South China. Similarly, Janak et al. [53] found peregrine falcon eggs and common tern eggs were enriched in (-)-α-HBCD, while white-tailed sea eagle eggs were depleted in the same enantiomer. Chicken muscle, egg, and liver in our study displayed relative enrichment of (+)-γ-HBCD, consistent with previous reports for chicken eggs and muscle from e-waste recycling sites in eastern China,[21] bird samples from an e-waste area in South China[52] and predatory birds' eggs from Sweden and the Netherlands.[55] In summary, our findings confirm the complex species and tissue-specific variations that exist in the enantioselective behaviour of HBCDs in birds.

3.3 Relationships between concentrations of HFRs in chicken and co-located soil samples

Significant linear positive correlations were found between concentrations of *syn*-DP in soils and those in co-located chicken muscle, liver, and eggs ($p<0.05$, $r^2= 0.921$, 0.925, 0.928, respectively for muscle, liver, and egg). Similar correlations were found for *anti*-DP ($p<0.05$, $r^2= 0.876$, 0.879, 0.885, respectively for muscle, liver, and egg). Combined, these observations suggest that at our sampling sites, soil is an important source of DPs in chickens, consistent with the findings of Zheng et al..[37] This is further substantiated by comparison of values of the fraction of *anti*-DP (f_{anti} – the fractional contribution of *anti*-DP to ΣDP (sum of *anti*- and *syn*-DP) in soil and co-located chicken tissue samples. Observed f_{anti} values ranged from 0.67-0.81 in soil, compared to 0.67-0.82 in chicken tissues and 0.65–0.80 in technical DP products.[25,57] A slight caveat to this conclusion is the fact that significant correlation was not observed between concentrations of either DP isomer in chicken skin samples and co-located soil samples. With respect to other HFRs, the potential importance of soil as a source of BTBPE contamination in chickens at our sites is indicated by the observation of significant correlations between its concentrations in soil and in co-located samples of chicken liver ($r^2=0.985$, $p<0.01$) and muscle ($r^2=0.909$, $p<0.05$). Conversely, no such correlations were detected between BTBPE concentrations in soil and those in chicken skin and eggs. Similarly, no significant correlations were found between concentrations of any HBCD isomer in any chicken tissue and soil, which

suggests substantial metabolism and/or that food and air could be more important influences on the HBCD concentrations in chickens.

3.4 Estimated daily intake of emerging HFRs and HBCDs via consumption of foodstuffs included in this study

Very few studies have estimated human dietary exposure to emerging HFRs. Estimated dietary exposure of the sum of our target emerging HFRs for adults and children in this study were 170 and 420 ng/kg bw/day, respectively. The health effects of this exposure cannot be assessed due to the current lack of health based limit values for emerging HFRs exposure by other researchers. We have, however, compared our estimates with those reported previously. DPs account for >90% of estimated exposure for both adults and children (130 and 350 ng/kg bw/day, respectively) followed by BTBPE (31 and 61 ng/kg bw/day, respectively), while EH-TBB predominated in one study of dietary exposure of the population living in the vicinity of e-waste impacted sites in eastern China, in which DPs were not investigated.[21] Another study calculated average estimated daily intakes of emerging BFRs via eggs from one South China recycling area to range from 970 to 4,530 ng/day,[25] which is higher than our estimate of exposure via egg ingestion of 350 ng/day. Furthermore, the same study concurred with our finding that DP was the dominant contributor to emerging HFRs exposure via egg ingestion.

Daily dietary exposure to HBCDs of individuals living in an e-waste impacted area in this study was estimated at 480 and 1500 ng/kg bw/day for adults and children, respectively. This exceeds estimated dietary exposure to HBCDs in e-waste impacted locations in China (10.4 and 36.1 ng/kg bw/day for adults and children),[21] and is substantially in excess of estimated fish-related dietary exposure in the Netherlands and Sweden (0.12 and 0.14 ng/kg bw/day, respectively)[46,58] as well as estimated dietary exposure of non-e-waste impacted populations in Spain, Belgium and China (2.58, 0.99, 0.432, 39.28 ng/kg bw/day, respectively).[43,59,60] However, as stated above, the main food supplies for the community in Bui Dau are from neighbouring communities. As a consequence, our assumption that Bui Dau inhabitants source all their fish, chicken meat, liver, and eggs from e-waste impacted sites and thus our estimates of the daily intake of emerging HFRs and HBCDs via consumption of such foodstuffs represents a worst case – albeit not wholly unrealistic - scenario.

For most of our target emerging HFRs and HBCDs, the main contributors to dietary exposure of both adults and children in our study were chicken liver and chicken eggs while fish was the predominant contributor to dietary exposure to BTBPE in our study. In previous studies it has been reported that fish, seafood, meat and meat products are the principal contributors to HBCDs dietary exposure.[43,46,59,60] We are aware of only one previous study of dietary exposure to emerging HFRs in e-waste impacted areas [21]. In that study, consumption of pork was the principal contributor to dietary exposure of both adults and children to EH-TBB, BEH-TEBP, and BTBPE.[21]

4. Conclusions

A number of emerging HFRs were found in chicken, fish, and pork samples from an e-waste processing site in Vietnam, as well as high levels of HBCDs. The most abundant emerging HFR detected was DP and some enantioselective enrichment of both α- and γ-HBCD was observed in chicken samples. For most of our target compounds, the main contributors to dietary exposure of both adults and children were chicken liver and chicken eggs. Estimated daily dietary intakes of HBCDs were higher than those reported from other countries. This study provides evidence that emerging HFRs are already entering the waste stream leading to environmental contamination when such waste is treated in an unregulated fashion. The elevated concentrations of DP are of particular note. We hypothesise that over time, environmental contamination with emerging HFRs will rise as increasing numbers of products containing these chemicals reach the end of their useful life.

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collection and preparation.

Table 1. Average, median and range of concentrations of Emerging HFRs and HBCD (ng/g lw) in food and co-located soil and sediment samples (ng/g dw) from an e-waste processing (Bui Dau, Vietnam) and control sites.

		Chicken muscle (n=5)	Chicken liver (n=5)	Chicken skin (n=5)	Chicken egg (n=15)	Soil (n=5)	River fish (n=5)	Pork (n=2)	Sediment[c] (n=8)	Control chicken muscle-1 (n=1)[a]	Control chicken egg-1 (n=3)[a]	Control chicken muscle-2 (n=1)[b]	Control chicken egg-2 (n=1)[b]	Control chicken liver (n=1)[b]	Control chicken skin (n=1)[b]	Control fish (n=1)[a]	Control pork (n=1)[a]
Lipid%		6.0	15	43	42	--	4.0	18	--	21	42	2.0	44	12	46	17	30
PBBz	average	<1.5	2.0	1.3	0.92	<0.15	<0.36	<0.36	--	<1.5	<0.31	<1.5	<0.31	<0.36	<0.31	<0.36	<0.36
	median	<1.5	<0.36	0.42	0.96	<0.15	<0.36	<0.36	--	<1.5	<0.31	<1.5	<0.31	<0.36	<0.31	<0.36	<0.36
	range	--	<0.50-3.7	<0.50-2.0	0.19-1.9	--	--	--	--	--	--	--	--	--	--	--	--
HBB	average	6.4	6.8	3.0	1.5	6.9	<0.36	<0.36	0.033	<1.5	<0.30	<1.5	<0.30	<0.36	<0.30	<0.36	<0.36
	median	<1.5	<0.36	0.49	1.4	1.3	<0.36	<0.36	--	<1.5	<0.30	<1.5	<0.30	<0.36	<0.30	<0.36	<0.36
	range	<1.5-10	<0.36-11	<0.30-5.8	<1.3-2.0	0.15-21	--	--	ND[d]-0.23	--	--	--	--	--	--	--	--
BEH-TEBP	average	<6.5	<1.5	<1.3	2.0	0.13	<1.5	<1.5	<0.20	<6.5	<1.3	<6.5	<1.3	<1.5	<1.3	<1.5	<1.5
	median	<6.5	<1.5	<1.3	<1.3	<0.050	<1.5	<1.5	--	<6.5	<1.3	<6.5	<1.3	<1.5	<1.3	<1.5	<1.5
	range	--	--	--	<1.3-3.0	<0.050-0.40	--	--	ND-1.6	--	--	--	--	--	--	--	--
BTBPE	average	60	54	70	67	10	40	<0.70	0.89	<3.1	<0.62	<3.1	<0.62	<0.70	<0.62	<0.70	<0.70
	median	46	12	25	18	5.2	55	<0.70	--	<3.1	<0.62	<3.1	<0.62	<0.70	<0.62	<0.70	<0.70
	range	<3.1-100	<0.70-130	<0.62-100	<2.8-160	0.19-34	<1.0-57	--	ND-5.7	--	--	--	--	--	--	--	--
DBDPE	average	6.9	<3.0	<2.8	280	21	<3.0	2.5	3.1	<7.5	<2.5	<7.5	<2.5	<3.0	<2.5	<3.0	<3.0
	median	<7.5	<3.0	<2.8	<2.5	12	<3.0	--	--	<7.5	<2.5	<7.5	<2.5	<3.0	<2.5	<3.0	<3.0

	range	<7.5-9.9	--	--	<2.5-620	0.42-64	--	--	ND-20	--	--	--	--	--	--	--	--
***syn*-DP**	average	310	1600	170	140	3.8	<0.36	<0.36	0.17	<1.6	<0.32	<1.6	<0.32	<0.36	<0.32	<0.36	<0.36
	median	76	170	90	5.0	0.60	<0.36	<0.36	--	<1.6	<0.32	<1.6	<0.32	<0.36	<0.32	<0.36	<0.36
	range	<1.6-1400	<0.36-8000	0.13-790	3.4-560	0.20-13	--	--	ND-1.8	--	--	--	--	--	--	--	--
***anti*-DP**	average	1200	3500	350	450	10	<0.36	<0.36	0.45	<1.6	<0.32	<1.6	<0.32	<0.36	<0.32	<0.36	<0.36
	median	260	210	160	8.0	2.3	<0.36	<0.36	--	--	--	--	--	--	--	--	--
	range	<1.6-1600	7.5-17000	0.32-3000	5.1-1800	0.83-31	--	--	ND-4.8	--	--	--	--	--	--	--	--
ΣDP	average	1500	5100	520	590	14	<0.36	<0.36	0.59	<1.6	<0.32	<1.6	<0.32	<0.36	<0.32	<0.36	<0.36
	median	340	380	250	13	2.9	<0.36	<0.36	--	--	--	--	--	--	--	--	--
	range	<1.6-3000	7.5-25000	0.44-3800	4.0-2300	1.3-44	--	--	ND-6.7	--	--	--	--	--	--	--	--
α-HBCD	average	34	1700	600	2800	6.7	2.5	0.90	--	0.10	0.10	17	1.6	<0.020	1.0	<0.020	<0.020
	median	20	1000	640	2500	5.0	2.3	--	--	--	--	--	--	--	--	--	--
	range	1.2-55	180-2500	20-850	330-3500	1.0-8.9	0.10-3.3	--	--	--	--	--	--	--	--	--	--
β-HBCD	average	0.15	28	0.06	79	4.8	0.41	<0.020	--	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
	median	0.25	20	0.10	70	3.8	0.51	--	--	--	--	--	--	--	--	--	--
	range	0.10-2.0	2.5-35	0.02-0.15	15-80	0.50-8.0	0.040-0.65	--	--	--	--	--	--	--	--	--	--
γ-HBCD	average	5.3	1500	330	700	110	0.50	0.20	--	<0.020	<0.020	0.57	0.95	<0.020	<0.020	<0.020	<0.020
	median	8.9	890	450	910	100	0.60	--	--	--	--	--	--	--	--	--	--
	range	0.10-15	160-3000	3.8-580	200-2300	56-710	0.050-0.12	--	--	--	--	--	--	--	--	--	--
ΣHBCD	average	39	3200	930	3600	120	3.4	1.1	--	0.10	0.10	18	2.6	<0.050	1.0	<0.050	<0.050
	median	29	1900	1000	3500	110	3.4	--	--	--	--	--	--	--	--	--	--
	range	2.0-80	330-5500	25-1400	540-5800	0.030-580	0.20-4.1	--	--	--	--	--	--	--	--	--	--

[a] Control samples collected in Vietnam; [b] Control samples collected in Japan; [c] from Someya et al., submitted; [d] ND= not detected.

Table 2. Estimated dietary exposure (ng/kg bw/day) to emerging HFRs and HBCD of adults and children living in e-waste impacted areas of Bui Dau, Vietnam. ne = not estimated

Foodstuff	Exposed group/HFR	PBBz	HBB	BTBPE	BEH-TEBP	DBDPE	*syn*-DP	*anti*-DP	α-HBCD	β-HBCD	γ-HBCD	ΣHBCD
Chicken Muscle	Adult	ne	0.17	1.2	ne	0.16	11	32	14	0.06	2.2	16
	Children	ne	0.28	2.1	ne	0.26	19	54	23	0.10	3.6	27
Chicken Egg	Adult	0.010	0.010	0.28	0.010	0.20	1.7	5.0	73	2.1	18	93
	Children	0.020	0.030	0.97	0.040	0.71	5.8	16	250	7.1	63	320
Chicken Liver	Adult	0.030	0.10	0.75	ne	ne	29	50	180	3.0	160	350
	Children	0.090	0.31	2.4	ne	ne	93	157	580	9.6	510	1100
Chicken Skin	Adult	0.010	0.010	0.35	ne	ne	0.76	2.9	11	ne	6.2	17
	Children	0.010	0.020	0.58	ne	ne	1.3	4.8	18	ne	10	29
Fish	Adult	ne	ne	28	ne	ne	ne	ne	1.8	0.29	0.35	2.4
	Children	ne	ne	55	ne	ne	ne	ne	3.4	0.56	0.68	4.7
Pork	Adult	ne	ne	ne	ne	4.6	ne	ne	1.7	ne	0.37	2.0
	Children	ne	ne	ne	ne	1.7	ne	ne	0.61	ne	0.14	0.75
Total	Adult	0.040	0.29	31	0.010	5.0	43	90	290	5.0	190	480
	Children	0.12	0.64	61	0.040	2.7	120	230	880	17	590	1500

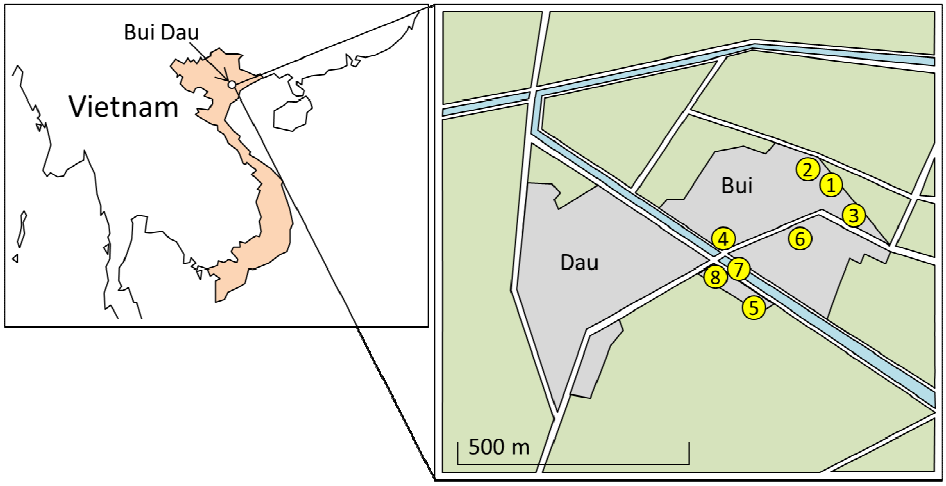

Fig. 1. Sampling sites in Bui Dau, Cam Xa, Hung Yen province, Vietnam.

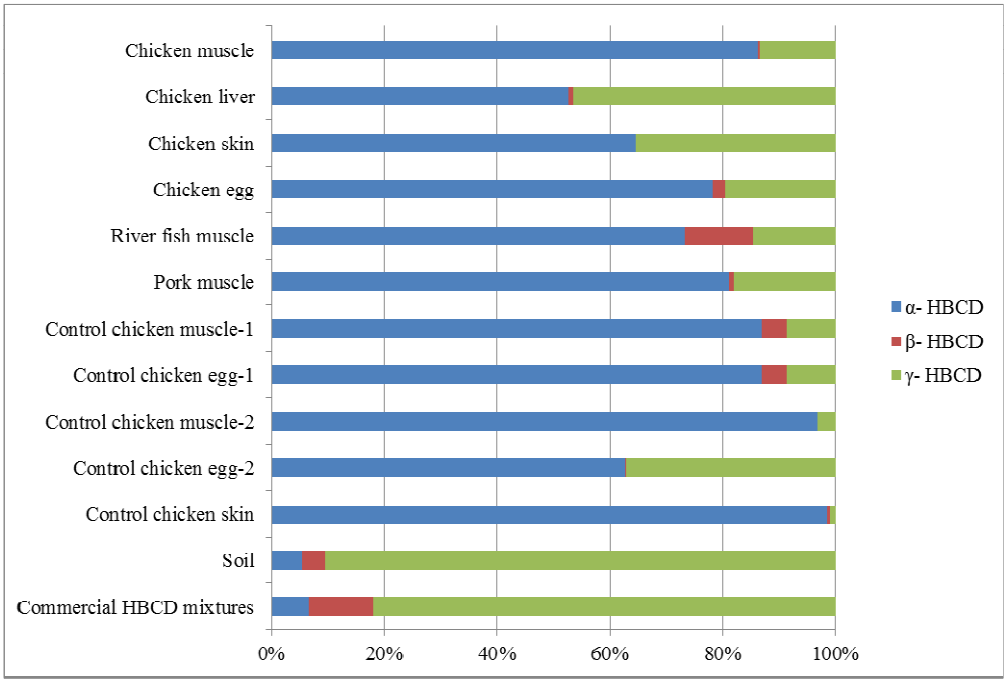

Fig. 2. Diastereomer profiles in food and co-located surface soil samples from e-waste processing areas in Vietnam this study and commercial HBCD mixtures (Covaci et al., 2006)

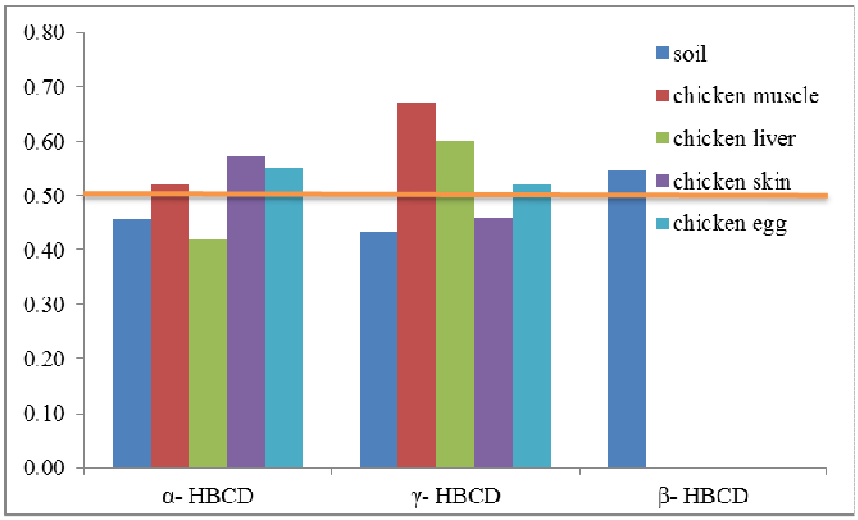

Fig. 3: Enantiomer fractions (EF) of α-HBCD, γ-HBCD and β-HBCD in chicken and co-located samples (line at EF=0.50 indicates racemic value)

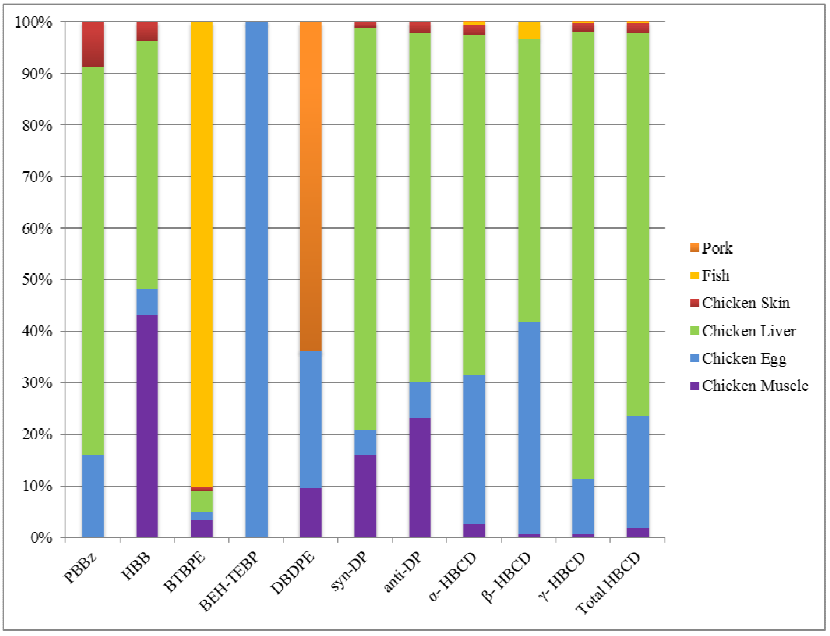

Fig. 4: Contributions of different food groups to total dietary exposures to emerging HFRs and HBCDs of children in Bui Dau, Vietnam

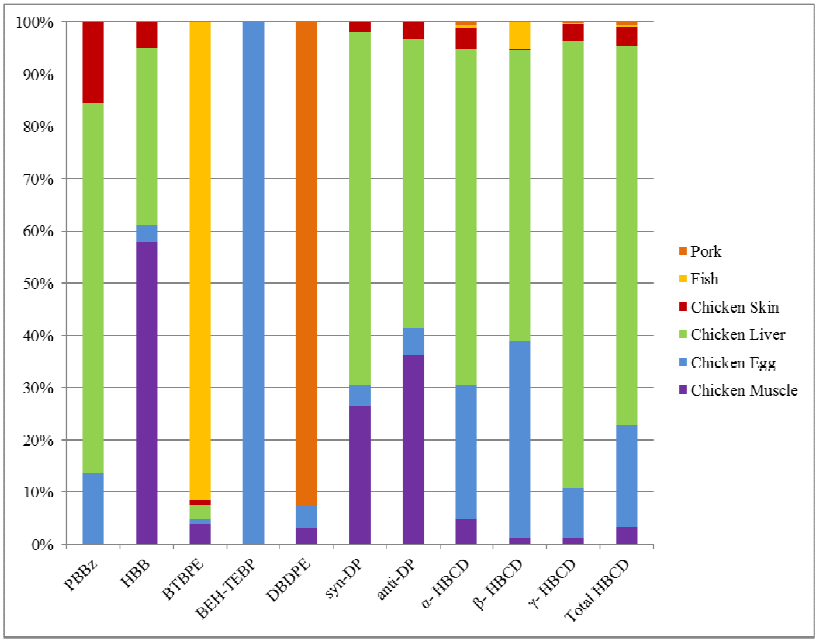

Fig. 5: Contributions of different food groups to total dietary exposures to emerging HFRs and HBCDs of adults in Bui Dau, Vietnam

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