



Bioaccumulation and biomagnification of hexabromocyclododecane (HBCDD) in insect-dominated food webs from a former e-waste recycling site in South China

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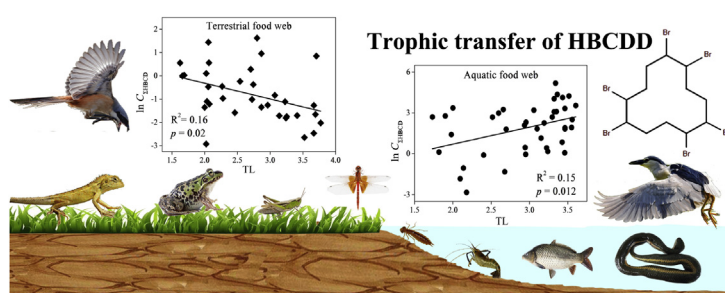
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HIGHLIGHTS

- Occurrence of HBCDD were investigated in insects and their predators.
- BMF of α -HBCDD >1 in poikilotherms while <1 in homeotherms.
- Trophic magnification of α -HBCDD was found in aquatic but not in terrestrial food web.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexabromocyclododecane (HBCDD) has frequently been detected in wildlife. However, there is limited research on its bioaccumulation and biomagnification in insect-dominated aquatic and terrestrial food webs. This study investigated the occurrence of HBCDD in insects and their predators collected from a former e-waste contaminated pond and its surrounding region. The concentrations of Σ HBCDD (sum concentrations of α -, β -, and γ -HBCDDs) ranged from nd to 179 ng g⁻¹ lipid weight. α -HBCDD was the predominant diastereoisomer in all biotic samples, and the contribution of α -HBCDD was higher in predators than in prey insects. A significantly positive linear relationship was found between Σ HBCDD concentrations (lipid weight) and trophic levels based on $\delta^{15}\text{N}$ in aquatic organisms ($p < 0.05$), while trophic dilution was observed in the terrestrial food web. This result indicates an opposite trophic transfer tendency of HBCDD in terrestrial and aquatic ecosystems. The biomagnification factor (BMF) for α -HBCDD was higher in terrestrial birds (2.03) than in frogs (0.29), toads (0.85), and lizards (0.63). This may be due to differences between poikilotherms and homeotherms in terrestrial ecosystems.

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1. Introduction

Hexabromocyclododecane (HBCDD) is an additive brominated flame retardant widely used in the building materials, upholstery

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textiles, car cushions, and electrical household equipment (Alaee et al., 2003; De Wit, 2002). The commercial product of HBCDD mainly consists of three diastereomers α -, β -, and γ -HBCDDs, of which γ -HBCDD (accounts for 75–80%) is the dominant component in the technical mixture (Janák et al., 2005). In China, the estimated domestic production of HBCDD increased by an order of magnitude from 500 tons in 2001 to 18,000 t in 2011 (Zhu et al., 2013). Due to global use, HBCDD has been widely detected in diverse wildlife, including invertebrates, fish, birds, and marine mammals around the world (Covaci et al., 2006; Fayiga and Ipinmoroti, 2017; Law et al., 2014). The Stockholm Convention listed HBCDD as a persistent organic pollutant (POP) in 2013, but HBCDD is still produced in a few countries under a “specific exemption” granted by the convention (Li and Wania, 2018). The bioaccumulation and biomagnification potential of HBCDDs for wildlife and humans still warrants attention.

Insects are an important link between primary producers (plants) and secondary consumers, and occupy multiple ecological niches in both aquatic and terrestrial food webs. Insects also play an important role in accumulating and transferring pollutants to insectivores, especially in terrestrial ecosystems (Rosenberg et al., 1986). For example, aquatic adult insects (e.g., chironomids and dragonflies) can export traditional POPs to terrestrial predators such as birds, lizards, and frogs (Kraus et al., 2014; Liu et al., 2018a). However, there are few studies focused on the bioaccumulation and transportation of HBCDD in aquatic and terrestrial insects. Only one study reported that the levels of HBCDD in three species (grasshopper, butterfly, and dragonfly) and HBCDD transfer by insects in the terrestrial food web from an electronic waste (e-waste) region in Taizhou (Zhu et al., 2017).

Due to elevated exposure in the aquatic environment, the biomagnification of HBCDD in the aquatic food web has been investigated in many studies. The trophic magnification of HBCDD has been found in many aquatic food webs, including the freshwater and marine food webs (Haukås et al., 2010; Tomy et al., 2004; Wu et al., 2010; Zhang et al., 2018). For the terrestrial food web, only a few studies have investigated the trophic transfer of HBCDD, and most were focused on birds and mammals. Sun et al. (2012) reported that the trophic magnification of α - and γ -HBCDDs in three terrestrial birds at the rural site. He et al. (2010) found a positive correlation between $\delta^{15}\text{N}$ values and α -HBCDD concentrations in six bird species, but no significance for γ -HBCDD. However, the trophic dilution of HBCDD was found in a terrestrial food web, which consists of insects, frogs, and rats (Zhu et al., 2017). Insects, amphibians, and reptiles are important components in the terrestrial ecosystem, but are often excluded from environmental contamination studies (Smith et al., 2007). Thus, further systematic studies on trophic transfer of HBCDD in terrestrial and aquatic food webs should build on these inconsistent results.

E-waste is a critical global environmental health issue, especially in developing countries. HBCDD has been frequently detected in biota samples (e.g. fish and birds) collected from e-waste recycling regions (He et al., 2010; Sun et al., 2012; Wu et al., 2010). In the present study, a total of 18 wildlife species (including insect, fish, prawn, amphibian, reptile, and bird), as well as food and habitat samples (water, soil, and plants) were collected from a former e-waste recycling site in South China. Levels and profiles of HBCDD were determined in all samples. The stable isotopes of nitrogen for biotic samples were analyzed to identify the trophic levels of the organisms, and to establish the insect-dominated aquatic and terrestrial food webs. The objective of this study was to investigate the levels and isomer profiles of HBCDD among wildlife with different habitats, and to compare the trophic transfer of HBCDD in different ecosystems.

2. Materials and methods

2.1. Sampling

All samples were collected from a pond located in Longtang Town, Qingyuan County of Guangdong Province and the surrounding region (within a 500 m radius). The pond had been heavily polluted by chemicals associated with e-waste, which had been discarded there. Details of the sampling site and sampling method were provided in our previous study (Liu et al., 2018a, 2018b). Insects including mantis (*Tenodera sinensis*), dragonfly (*Aeshnidae*, *Libellulidae*), grasshopper (*Oxya chinensis*), cricket (*Gryllus chinensis*), mole-cricket (*Gryllotalpa orientalis*), beetle (*Anomala corpulenta*), water stinkbug (*Diplonychus esakii*) and butterfly (*Papilionoidea*, *Pieridae*) were collected between September 2015 and November 2016. Other biotic samples, including Long-tailed shrike (*Lanius schach*), Eurasian blackbird (*Turdus merula*), Oriental magpie-robin (*Copsychus saularis*), lizard (Oriental garden lizard, *Calotes versicolor*), frog (Asiatic painted frog, *Kaloula pulchra*), toad (Black-spectacled toad, *Duttaphrynus melanostictus*), fish (Common carp, *Cyprinus carpio*), prawn (Oriental river prawn, *Macrobrachium nipponense*), watersnake (Chinese watersnake, *Enhydryis chinensis*) and waterbird egg (White-breasted waterhen, *Amaurornis phoenicurus*) were collected between April and May 2016. Additionally, guava (*Psidium guajava*) leaves, grass (*Gramineae*, hosts for grasshoppers), soil from the fields, and water from the pond were collected from the same sites as the organisms for contaminant analysis. More detailed information on the number, feeding habits and habitats of each species are given in Table S1 (“S” designates the Table in the Supplementary Material). A total of 115 biotic samples (1247 individuals) and 17 abiotic samples were obtained. Individual frogs, fish, prawns, and insects were too small to perform contaminant analyses, and were therefore pooled into composite samples for each taxon per sampling campaign. All samples were transported to the laboratory in an ice box; after dissection, they were freeze-dried, homogenized in a stainless steel blender, and stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2. Chemical analysis

Details on the extraction, cleanup, and quantification of HBCDDs in biotic and abiotic samples has been provided in detail elsewhere (He et al., 2010; Sun et al., 2012). Briefly, after spiking with internal standards (20 ng of ^{13}C - α , β , γ -HBCDDs), 1 g of the lyophilized biotic samples were Soxhlet extracted for 48 h using hexane: dichloromethane (1:1, v:v). The extracts were purified using concentrated sulfuric acid and further cleaned in a multilayer Florisil silica gel column. HBCDD was eluted with dichloromethane (50 mL). The extracts were further concentrated to near dryness under a gentle nitrogen flow and finally reconstituted in methanol (100 μL) for analysis. The recovery standards (20 ng of d_{18} - α , β , γ -HBCDDs) were spiked before instrumental analysis. The specific procedures for pretreatment and cleanup of insects, water, soil, and plant samples are provided in the Supplementary Material.

HBCDD diastereoisomers were analyzed using an Agilent 1200 series liquid chromatograph (LC) and an Agilent 6410 triple quadrupole mass spectrometer (MS) with an electrospray ionization source. α -, β -, and γ -HBCDDs were separated through an XDB-C₁₈ reversed-phase column (50 mm \times 4.6 mm \times 1.8 μm , Agilent). The mass transitions of m/z 640.7 \rightarrow 79/81, 652.7 \rightarrow 79/81, and 658.7 \rightarrow 79/81 were monitored for α -, β -, γ -HBCDDs, ^{13}C -HBCDDs, and d_{18} -HBCDDs, respectively. More information on instrumental analysis was provided in our previous study (Sun et al., 2018).

2.3. Quality control

The methods for quality control (QC) were performed by analyzing procedural blanks, spiked blanks, and spiked matrices. Procedural blanks were analyzed consistently for each batch of nine samples; therefore, the mean values were used for subtraction. Trace amounts of γ -HBCDD were detected in the procedural blanks, but α -HBCDD and β -HBCDD were not detected. The levels of target chemicals in the blanks were less than 10% of those in the samples. The relative standard deviations for all analytes were <15% in triplicate samples. The recoveries of spiked chemicals and surrogate standards were 76 ± 9.6 to $88 \pm 14\%$ and 74 ± 12 to $92 \pm 17\%$, respectively. The limits of detection (LODs) were set as a signal-to-noise ratio of 3. Based on the average lipid weight (lw) of biotic samples and average dry weight (dw) of abiotic samples, the LODs of HBCDDs ranged from 0.01 to $0.18 \text{ ng g}^{-1} \text{ lw}$ and $1.5\text{--}3.1 \text{ pg g}^{-1} \text{ dw}$ for biotic and abiotic samples, respectively.

2.4. Stable isotope analysis and trophic level determination

All samples for nitrogen isotope ($\delta^{15}\text{N}$) analysis were freeze-dried and ground into powder. Approximately 0.5 mg of each sample was placed into a tin capsule and analyzed using a Flash EA 112 series elemental analyzer coupled with a Finnigan MAT ConFlo III isotope ratio mass spectrometer. Stable isotope abundances were calculated based on Eq. (1):

$$\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \quad (1)$$

where $R_{\text{sample}}/R_{\text{standard}}$ is the $^{15}\text{N}/^{14}\text{N}$ ratio of the sample and reference standard. The precision for this technique is approximately $\pm 0.5\%$ (2 SD) for $\delta^{15}\text{N}$.

Trophic level (TL) of the biota species were calculated according to the following Eq. (2):

$$\text{TL}_{\text{consumer}} = (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{baseline}}) / \Delta\delta^{15}\text{N} + 2 \quad (2)$$

where $\text{TL}_{\text{consumer}}$ and $\delta^{15}\text{N}_{\text{consumer}}$ are the TL and stable nitrogen isotope abundance of the consumer, respectively; $\delta^{15}\text{N}_{\text{baseline}}$ is the stable nitrogen isotope abundance of the reference species, which was the beetle for terrestrial species and water stinkbug for aquatic species. $\Delta\delta^{15}\text{N}$ is the isotope enrichment factor and a common value of 3.4‰ was used (Post, 2002; Starrfelt et al., 2013).

2.5. Biomagnification factor and trophic magnification factor

Biomagnification factors (BMFs) were calculated as the ratios of lipid-normalized HBCDD concentrations in predator and prey species using the following Eq. (3):

$$\text{BMF} = C_{\text{predator}} / C_{\text{prey}} \quad (3)$$

where C_{predator} and C_{prey} are HBCDD concentrations ($\text{ng g}^{-1} \text{ lw}$) in the predator and prey species, respectively.

Trophic magnification factors (TMFs) for the entire food web were estimated as linear regression analyses of logarithmically transformed lipid-normalized HBCDD concentrations versus trophic level using Eq. (4). The value of TMF was calculated as the anti-ln of slope (b) of the regression line based on Eq. (5).

$$\ln C_{\text{HBCDD}} = a + b \times \text{TL} \quad (4)$$

$$\text{TMF} = e^b \quad (5)$$

where C_{HBCDD} is the concentration of HBCDD, a is the y-intercept (constant), and b is the regression slope of $\ln C_{\text{HBCDD}}$ against TL. Statistical significance of the regression Eq. (4) was defined at $p < 0.05$. A BMF or TMF value above 1 indicates that the chemical is biomagnifying, whereas a BMF or TMF below 1 implies that a chemical is not accumulated by the organism or is metabolized (Fisk et al., 2001; Tomy et al., 2004).

2.6. Statistical analysis

Statistical analyses were performed using SPSS 19 and Origin 8.5. Student t-test and One-way ANOVA were used to evaluate the interspecific differences in HBCDD concentrations. Simple linear correlation analysis was used to investigate the relationship between HBCDD levels and TLs in the biota species from the former e-waste recycling site. Values of p below 0.05 were considered statistically significant.

3. Results and discussion

3.1. Levels and profiles of HBCDD in different species

The concentrations of HBCDD diastereoisomers and ΣHBCDD (sum of α -, β -, and γ -HBCDD) in the biotic and abiotic samples are provided in Table 1. α -HBCDD and γ -HBCDD were quantified in 75% and 38% of all samples, while β -HBCDD was detected at low levels in only 3 of the 135 samples. The low detection frequency of β -HBCDD agrees with other studies of terrestrial passerine birds, freshwater fish, marine fish, and edible fish (Shaw et al., 2009; Su et al., 2018; Sun et al., 2012; Vorkamp et al., 2012).

The total HBCDD concentrations ranged from not detected (nd) to $179 \text{ ng g}^{-1} \text{ lw}$, with the maximum concentration found in waterbird eggs. The concentrations of ΣHBCDD were one order of magnitude higher in aquatic predators than in terrestrial and amphibious predators, and HBCDD levels in the insects were within the same order of magnitude as those observed in terrestrial and amphibious predators (Table 1). Among insects, aquatic insects such as dragonfly larvae ($6.0 \text{ ng g}^{-1} \text{ lw}$) and water stinkbugs ($1.1 \text{ ng g}^{-1} \text{ lw}$) had higher HBCDD levels than terrestrial insects (median values ranged from 0.31 to $0.69 \text{ ng g}^{-1} \text{ lw}$). The relatively high HBCDD levels found in aquatic species from the pond were expected since the pond was heavily polluted by chemicals associated with e-waste (Wu et al., 2010; Zheng et al., 2012). The concentrations of ΣHBCDD in suspended particles of water from the pond ($9.6\text{--}28 \text{ ng g}^{-1} \text{ dw}$) were one to two orders of magnitude higher than those found in soil from the farmland ($0.05\text{--}0.37 \text{ ng g}^{-1} \text{ dw}$). Meanwhile, HBCDD levels in plant leaves were also low with median values of 0.02 and $0.08 \text{ ng g}^{-1} \text{ dw}$.

HBCDD concentrations in terrestrial birds and aquatic species collected prior to 2011 from the same study region ranged from 5.1 to $73 \text{ ng g}^{-1} \text{ lw}$ and from 110 to $2000 \text{ ng g}^{-1} \text{ lw}$, respectively (He et al., 2010; Sun et al., 2012; Wu et al., 2010). These concentrations were one order of magnitude higher than those in the present study. This dramatic drop in HBCDD levels could be attributed to effective regulation of e-waste recycling activities by local government since 2011. Informal, small recycling plants around the pond were closed and replaced by government-authorized centralized e-waste recycling facilities (Chi et al., 2011; Zhang et al., 2012). Huang et al. (2018) also observed decreased HBCDD levels in chicken eggs from $350 \pm 57 \text{ ng g}^{-1} \text{ lw}$ in 2010 to $99 \pm 19 \text{ ng g}^{-1} \text{ lw}$ in 2016. The chicken eggs were collected from a village within the study area. Nevertheless, the concentrations of

Table 1
Concentrations of HBCDD and TLs in biotic (ng g⁻¹ lw) and abiotic samples (ng g⁻¹ dw) from a former e-waste recycling site, South China.

Species	TL ^a	α -HBCDD	β -HBCDD	γ -HBCDD	Σ HBCDD ^d
Terrestrial predator					
Lizard	2.8 ± 0.28	0.26 (nd-1.3) ^b	nd ^c	nd	0.26 (nd-1.3)
Oriental magpie-robin	1.7 ± 0.03	1.0 (1.0–1.7)	nd	nd	1.0 (1.0–1.7)
Eurasian blackbird	2.7, 3.7	nd, 0.19	nd	nd	nd, 0.19
Long-tailed shrike	2.1, 3.7	1.8, 2.3	nd	nd	1.8, 2.3
Amphibious predator					
Frog	2.9 ± 0.52	0.29 (nd-5.1)	nd	nd	0.29 (nd-5.1)
Toad	3.6 ± 0.18	0.17 (nd-0.28)	nd	nd	0.17 (nd-0.28)
Aquatic predator					
Fish	3.4 ± 0.13	18 (1.5–56)	nd	0.29 (nd-0.30)	18 (1.5–57)
Prawn	3.1 ± 0.08	9.5 (3.1–23)	nd	0.06 (nd-1.7)	9.6 (3.1–25)
Watersnake	3.3 ± 0.34	6.7 (1.1–15)	nd	nd	6.7 (1.1–15)
Watersnake egg	4.0 ± 0.37	28 (25–62)	nd	0.09 (0.06–1.4)	28 (25–63)
Waterbird egg	3.4 ± 0.06	66 (22–179)	nd	0.02 (0.01–0.05)	66 (22–179)
Insect					
Mantis	2.9 ± 0.14	0.69 (nd-0.69)	nd	nd	0.69 (nd-0.69)
Dragonfly larva	2.6 ± 0.30	5.9 (nd-21)	nd	4.4 (nd-7.9)	6.0 (nd-26)
Dragonfly adult	3.2 ± 0.13	0.31 (nd-0.43)	nd	nd	0.31 (nd-0.43)
Grasshopper	2.0 ± 0.28	0.33 (nd-3.9)	0.14 (nd-0.14)	0.19 (nd-0.19)	0.33 (nd-4.2)
Cricket	2.2 ± 0.10	0.64 (nd-1.1)	nd	nd	0.64 (nd-1.1)
Mole-cricket	2.6 ± 0.19	0.49 (nd-0.62)	nd	0.17 (nd-0.17)	0.58 (nd-0.79)
Beetle	2.0 ± 0.08	0.63 (nd-0.63)	nd	nd	0.63 (nd-0.63)
Water stinkbug	2.0 ± 0.15	1.1 (nd-28)	nd	0.31 (nd-0.59)	1.1 (nd-29)
Butterfly	2.3	0.38	nd	nd	0.38
Abiotic sample					
Grass	1.0 ± 0.04	0.04 (0.006–0.09)	0.02 (nd-0.02)	0.02 (0.003–0.06)	0.08 (0.01–0.13)
Guava	1.4 ± 0.23	0.02 (0.002–0.09)	nd	0.006 (nd-0.01)	0.02 (0.002–0.10)
Soil in corn fields	–	0.15 (0.06–0.30)	0.003 (nd-0.003)	0.07 (0.03–0.13)	0.28 (0.09–0.37)
Soil in paddy fields	–	0.05 (0.04–0.09)	nd	0.008 (0.006–0.04)	0.09 (0.05–0.10)
Particles of water	–	9.0 (4.0–17)	nd	11 (5.6–14)	21 (9.6–28)

^a Mean ± SD.

^b Median (range).

^c Not detectable.

^d Sum of α -, β -, and γ -HBCDDs.

Σ HBCDD in aquatic species found in the present study were comparable to those in aquatic species (3.5–68 ng g⁻¹ lw) from an e-waste dismantling region in Taizhou (Zhu et al., 2017), but were obviously lower than those in aquatic species (120–3500 ng g⁻¹ lw) from another Chinese e-waste recycling area (Zhang et al., 2009). The concentrations of Σ HBCDD in fish (1.5–57 ng g⁻¹ lw) was comparable to those in fish from the Canadian freshwater lakes (0.52–73 ng g⁻¹ lw) and South Korea waters (2.5–60 ng g⁻¹ lw) (Choo et al., 2019; Su et al., 2018).

The levels of Σ HBCDD in frogs (0.29 ng g⁻¹ lw) in the present study were one or two orders of magnitude lower than those in frogs (6.28 ng g⁻¹ lw) from e-waste dismantling regions in Taizhou (Zhu et al., 2017) and pond green frogs (96 ng g⁻¹ lw) from the Haihe river in Tianjin (Zhang et al., 2013). To date, few studies have investigated the occurrence of HBCDDs in insects. In e-waste dismantling regions in Taizhou, Zhu et al. (2017) reported that levels of HBCDDs in dragonflies grasshoppers, and butterflies of 0.91, 15, and 19 ng g⁻¹ lw, respectively, which are higher than those reported in the present study (0.31, 0.33, and 0.38 ng g⁻¹ lw). Little data is currently available for HBCDDs in lizards and toads. It is therefore impossible to compare the levels of lizards and toads in the present study with other studies.

γ -HBCDD accounted for 55% of the total HBCDD in suspended particles of water, similar to the proportions for suspended particles (45–66%) and sediments (57–68%) sampled from the same pond in our previous study (Wu et al., 2010). The percentages of γ -HBCDD to the total HBCDD were 34% and 21–34% for grass and soil samples. The relative abundance of γ -HBCDD in these samples was lower than that of commercial HBCDD products (75%), This may be caused by thermal isomerization, which occurs during e-waste treatment processes as well as in the production, use and

dismantling of heat-treated HBCDD-containing products (Heeb et al., 2008; Li and Wania, 2018).

α -HBCDD was the predominant diastereoisomer in all biotic samples, accounting for 87–100% of the total HBCDDs (Fig. 1). This alternation in diastereoisomer composition was possibly due to higher assimilation efficiency and lower elimination rate of α -HBCDD compared with β - and γ -HBCDDs, or bioisomerization of β - and γ -HBCDDs to α -HBCDD (Du et al., 2012; Luo et al., 2013; Zhu et al., 2012). This HBCDD profile is consistent with those reported for most aquatic and terrestrial organisms, such as invertebrates,

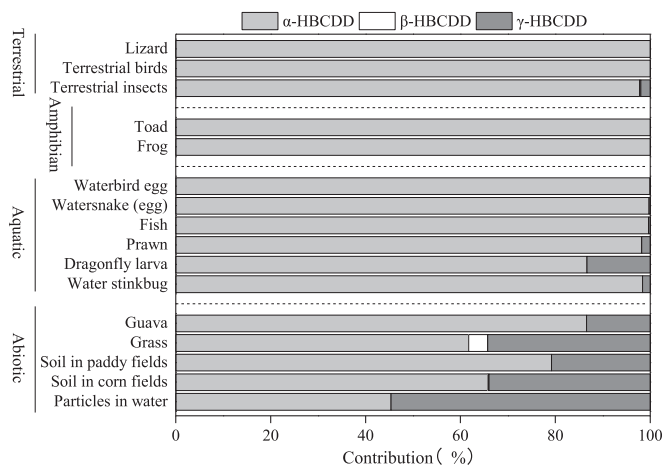


Fig. 1. Diastereomer profiles of HBCDD in biotic and abiotic samples from a former e-waste recycling site, South China.

fish, birds, and mammals (Cao et al., 2018; Covaci et al., 2006). Lower trophic level biota (such as insects and prawns) had relatively higher contributions of γ -HBCDD (2–13%) than their predators (close to zero), possibly due to the higher metabolism and biotransformation capacity for γ -HBCDD in upper TL species than in lower TL species. Some studies also found increasing contributions of α -HBCDD and decreasing γ -HBCDD against the ascending TLs in the aquatic food web (Tomy et al., 2008; Wu et al., 2010).

3.2. Biomagnification factor of HBCDD on the basis of predator/prey relations

Since γ -HBCDD was not detected in most predators, only the biomagnification factor of α -HBCDD was calculated in the present study. The lipid-normalized biomagnification factors (BMFs) for α -HBCDD in aquatic and terrestrial species was calculated using the α -HBCDD concentrations found in the predator divided by those in the corresponding prey. Amphibians included frogs and toads. The dry-weight normalized BMFs were calculated for grasshoppers to investigate the transfer of HBCDD from grass to grasshoppers. The BMFs for α -HBCDD in 14 predator-prey pairs are shown in Table 2.

The BMF values for α -HBCDD in aquatic predators ranged from 0.32 to 27. The highest BMF was found in waterbird eggs and the lowest in watersnakes. This may be due to efficient maternal transfer of α -HBCDD from mother to egg (Zheng et al., 2017). As shown in Table 1, the median concentration of α -HBCDD in watersnake eggs (28 ng g⁻¹ lw) was four times that in watersnake (6.7 ng g⁻¹ lw). The higher maternal transfer potential of halogenated organic pollutants (log K_{OW} between 5 and 8) for the watersnake was reported in our previous study (Liu et al., 2018a). Most values of BMF in the aquatic food chain were greater than 1, suggesting the biomagnification of α -HBCDD in the aquatic ecosystem, consistent with the previous studies (Kim et al., 2015; Ruan et al., 2018; Zhang et al., 2018). For example, similar biomagnification of HBCDD (BMFs ranged from 0.9 to 28 and 0.2 to 26, respectively) was found in coastal food chains in China and Norway (Haukås et al., 2010; Zhang et al., 2018). However, lower BMFs for α -HBCDD were found in Lake Winnipeg food chain (0.1–8.2) (Law et al., 2006) and Lake Ontario food chain (0.4–11) (Tomy et al., 2004). The variation of BMF values may be attributed to different compositions and structures of the food webs.

For terrestrial predators, BMF values for α -HBCDD in terrestrial birds (ranged from 1.7 to 4.1) were higher than 1, suggesting biomagnification between terrestrial birds and their prey. The biomagnification of α -HBCDD in the terrestrial food chain is in

Table 2
Biomagnification factors (BMFs) for α -HBCDD in insect-dominated food chains from a former e-waste recycling site, South China.

Predator	Prey	α -HBCDD ^a
Grasshoppers	Grass	1.52 ^b
Fish	Aquatic insects	6.25
Fish	Prawns	1.59
Waterbird eggs	Aquatic insects	26.9
Waterbird eggs	Prawns	6.84
Waterbird eggs	Fish	4.30
Watersnake	Amphibians	16.2
Watersnake	Fish	0.32
Toads	Terrestrial insects	0.29
Frogs	Terrestrial insects	0.85
Lizards	Terrestrial insects	0.63
Terrestrial birds	Terrestrial insects	2.03
Terrestrial birds	Amphibians	4.06
Terrestrial birds	Lizards	1.68

^a Lipid-weight normalized.

^b Dry-weight normalized. Amphibians included frogs and toads.

agreement with the findings of most previous studies, including grain to terrestrial phytophagous bird (7.1–51) in e-waste regions (He et al., 2010), stomach content of terrestrial insectivorous birds (1.1–30) in the Pearl River Delta (Sun et al., 2012), and the skua to penguin (11) in King George Island, Antarctica (Kim et al., 2015). But BMFs for α -HBCDD in frogs (0.85), toads (0.29), and lizards (0.63) were lower than 1, implying dilution of α -HBCDD in amphibians and lizards. This may be influenced by species specificity. The terrestrial birds were homeotherms, while the amphibians (frogs and toads) and lizards were poikilotherms. Homeotherms generally have higher energy requirements and more efficient biotransformation abilities than poikilotherms (Hop et al., 2002). This difference in BMFs for HBCDD between poikilotherms and homeotherms in a coastal food chain has previously been observed (Haukås et al., 2010).

In addition, the BMF value of α -HBCDD (1.5) in grasshoppers was more than 1, indicating biomagnification of α -HBCDD from grass to grasshoppers. In the previous study, the BMF value in grasshoppers was higher than PBDEs (0.93), but lower than PCBs (2.2) (Liu et al., 2018b). As no BMF data for insects are currently available, a comparison to other results is impossible.

3.3. Trophic transfer in terrestrial and aquatic food web

The trophic status of terrestrial and aquatic species was elucidated using stable isotopes of nitrogen ($\delta^{15}N$), and TLs for the biota are shown in Table 1 and Fig. 2. Frogs and toads are amphibians, captured from the farmland and feeding mainly on terrestrial insects. According to the stable isotopes of nitrogen ($\delta^{15}N$) in Table S2, the $\delta^{15}N$ values for amphibians (6.6–8.9‰) were lower than for aquatic predators (10–11‰). Frogs and toads were therefore considered part of the terrestrial food web for calculating the TLs and TMs.

In the terrestrial food web, a Eurasian blackbird and a Long-tailed shrike had the highest TLs (both 3.7), followed by toads (3.6), as shown in Fig. 2a. The adult dragonfly, a high-level carnivorous insect that feeds on small insects and other dragonflies, had higher TLs (3.2). Phytophagous insects had lower TLs, such as grasshoppers (2.0) and beetles (2.0). However, the lowest TL value was found in oriental magpie-robins (1.7), and the variation of TLs in terrestrial birds can be explained by feeding habits of different species (Sun et al., 2012). Waterbird and watersnake are high-level

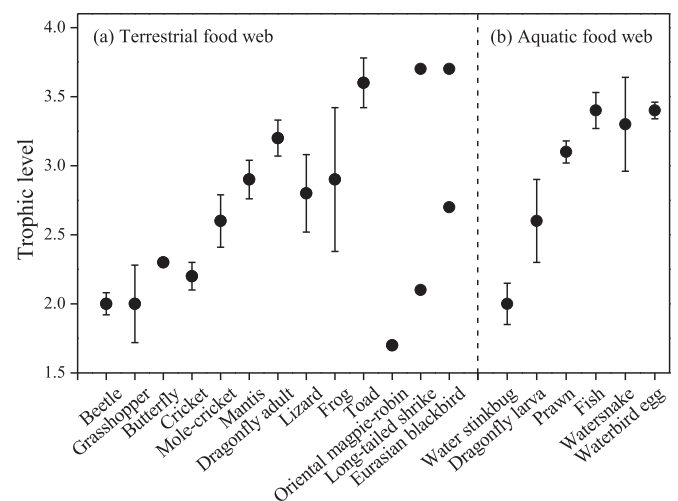


Fig. 2. Trophic level (TL) of biota (except for watersnake egg) in terrestrial and aquatic food webs. (a) Terrestrial food web; (b) Aquatic food web.

carnivorous organisms in the aquatic food web, feeding on fish and prawns. The trophic level in the aquatic food web were ordered as follows: waterbird egg \approx watersnake \approx fish > prawn > dragonfly larva > water stinkbug (Fig. 2b).

The lipid-weight based TMFs for α -HBCDD and total HBCDD in the aquatic food web were 3.7 and 3.5, respectively (Table 3). The concentrations of α -HBCDD and Σ HBCDD increased as trophic level increased ($p < 0.05$, Fig. 3 and S1), indicating significant trophic magnification in the aquatic ecosystem. These values were slightly higher than those in the freshwater food web from the same e-waste site (2.2 and 1.8 for α -HBCDD and Σ HBCDD) (Wu et al., 2010), but lower than those in the freshwater food web from another e-waste region in Taizhou (14 and 6.4, respectively) (Zhu et al., 2017). Zhang et al. (2013) reported that TMFs for α -HBCDD and the total HBCDDs in the limnic web of 2.6 and 2.4, higher than TMFs found in the marine web (1.7). However, the TMF for γ -HBCDD in the aquatic food web was 0.11, and there was a significant negative correlation between TLs and concentrations of γ -HBCDD ($p < 0.01$, Table 3 and Fig. 3). The TMF values for α - and γ -HBCDD in the aquatic food web were comparable to the respective TMFs of 2.6 and 0.3, found in a Norwegian coastal food web from an HBCDD point source (Haukås et al., 2010) and an eastern Canadian Arctic marine food web (2.1 and 0.5 for α - and γ -HBCDD, respectively) (Tomy et al., 2008). Furthermore, some studies have reported that no significant correlation between γ -HBCDD concentrations and trophic levels in aquatic ecosystems ($p > 0.05$) (Wu et al., 2010; Zhang et al., 2018; Zhu et al., 2017).

In contrast to the trophic magnification of α -HBCDD and the total HBCDD in the aquatic food web, a significant negative correlation was observed in the terrestrial food web (Fig. 3 and S1). The TMFs of α -HBCDD and the total HBCDD in the terrestrial food web were 0.51 ($p < 0.05$), suggesting trophic dilution in the terrestrial ecosystem, that may be explained by the specific food web. The present study was concerned mainly with insects, lizards, and amphibians, which had similarities to a terrestrial food web (including insects and frogs) from an e-waste region in Taizhou reported by Zhu et al. (2017). They found the TMFs for α -HBCDD, γ -HBCDD, and Σ HBCDD in the terrestrial food web were 0.08, 0.47, and 0.10, respectively, but the limited species in the food web lead to the regression equations of TMF were not statistically significant ($p > 0.05$).

The different trophic transfer tendencies of HBCDD between terrestrial and aquatic ecosystems could be attributed to two aspects: First, the levels and profiles of HBCDD in environmental matrices may influence TMF values. As stated above, the concentrations and relative abundance of γ -HBCDD in environmental samples and insects from the aquatic ecosystem were higher than those from the terrestrial ecosystem. Therefore, aquatic predators may accumulate more γ -HBCDD, and transform to α -HBCDD in vivo, causing overestimation of the TMF value for α -HBCDD in the aquatic food web. Second, species-dependent biomagnification of HBCDD in the food webs may be an important factor. In the terrestrial food web, lizards and amphibians are both poikilotherms, which generally have lower energy requirements and biotransformation abilities. A negative correlation between the α -

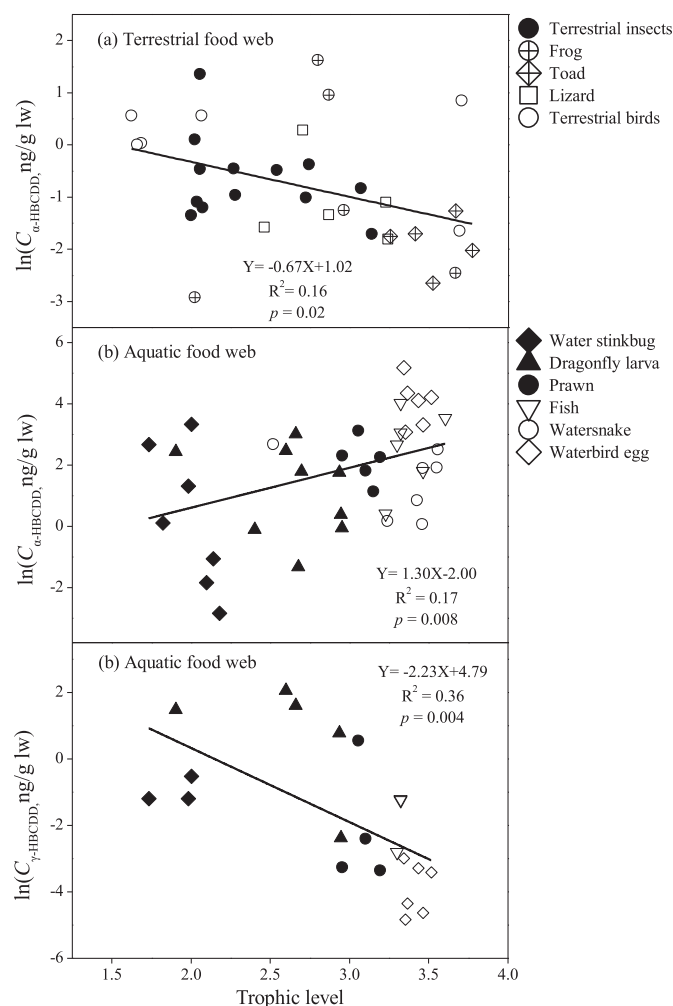


Fig. 3. Relationship between trophic level (TL) and concentrations of α -HBCDD and γ -HBCDD in terrestrial and aquatic food webs. (a) Terrestrial food web; (b) Aquatic food web.

HBCDD and trophic levels has been reported for poikilotherms, while a positive correlation has been reported for homeotherms (Haukås et al., 2010). The TMF values of POPs (mainly OCPs and PCBs) that mainly included poikilotherms were lower than those that included homeotherms (Hop et al., 2002).

4. Conclusions

This study showed the occurrence of HBCDD diastereoisomers was determined in insect-dominated terrestrial and aquatic food webs from a former e-waste region in South China. The concentration of Σ HBCDD in aquatic predators was one order of magnitude higher than in terrestrial and amphibious predators. α -HBCDD was the predominant diastereoisomer in all biotic samples, and lower

Table 3

Trophic magnification factors (TMFs) and regression parameters for α -HBCDD, γ -HBCDD, and Σ HBCDD in terrestrial and aquatic food webs.

analyte	Aquatic food web					Terrestrial food web				
	TMF	p-value	Pearson's r	R ²	regression equation	TMF	p-value	Pearson's r	R ²	regression equation
α -HBCDD	3.68	0.008	0.41	0.17	Y = 1.30X - 2.00	0.51	0.02	-0.40	0.16	Y = - 0.67X + 1.02
γ -HBCDD	0.11	0.004	-0.60	0.36	Y = - 2.23X + 4.79	na ^a	na	na	na	na
Σ HBCDD	3.50	0.012	0.39	0.15	Y = 1.25X - 1.80	0.51	0.02	-0.40	0.16	Y = - 0.68X + 1.04

^a Not available.

trophic level organisms had relatively higher contributions of γ -HBCDD. Comparing HBCDD concentrations in insects with their predators, biomagnification of α -HBCDD was found for terrestrial birds, while biodilution of α -HBCDD was found for amphibians and lizards. This may be explained by the different bioaccumulation and biotransformation abilities between poikilotherms and homeotherms. Based on lipid-weight concentrations, significant trophic magnification of α -HBCDD and Σ HBCDD was shown in the aquatic food web, whereas the terrestrial food web showed trophic dilution. Both the trophic dilution of γ -HBCDD in the aquatic food web as well as the low contribution ratio of γ -HBCDD in the predators, which may be related to a higher elimination rate and lower assimilation efficiency of γ -HBCDD in predators, and/or the bioisomerization by predators from γ -HBCDD to α -HBCDD (Du et al., 2012; Zegers et al., 2005). More studies of the role played by insects and species-specificity in terrestrial and aquatic ecosystems are therefore needed to elucidate the bioaccumulation and biomagnification behavior of HBCDD.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124813>.

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