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Bioconcentration and trophic transfer of polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in aquatic animals from an e-waste dismantling area in East China

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Eight aquatic biota species were collected from an e-waste dismantling area in East China to investigate bioconcentration and trophic transfer of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The mean concentrations of PCBs varied widely from 6.01×10^4 to 2.27×10^6 pg per g dry weight (dw). The $\sum_{25}$PCB concentrations in eels were significantly higher than those in other species. The levels of PCDD/Fs changed from 8.13 pg per g dw in toads to 617 pg per g dw in stone snails. World Health Organization-toxic equivalents (WHO$_{2005}$-TEQs) ranged from 2.57 to 2352 pg WHO-TEQ per g dw with a geometric mean value of 64.7 pg WHO-TEQ per g dw, which greatly exceeded the maximum levels of 4 pg per g ww set by the European Commission. The log-transferred bioconcentration factors (BCFs) of 25 PCB congeners ranged from 1.0 to 6.6, with the highest value for CB-205 in crucian carp and the lowest value for CB-11 in frog. A parabolic correlation was observed between log BCF and log K_{ow} ($R^2 = 0.53$, $p < 0.001$), where the maximum value occurred at a log K_{ow} of approximately 7. A similar correlation was also found in the plot of log BCF against the number of chlorine atoms of PCBs ($R^2 = 0.57$, $p < 0.001$), indicating that medium-halogenated congeners of PCBs are more easily accumulated by aquatic biota species. There were no significant correlations between the log-transferred concentrations and trophic levels of aquatic species, suggesting that trophic magnification for PCBs and PCDD/Fs was not observed in this study.

Environmental impact

E-waste dismantling regions have been the subject of great concern in recent years due to the serious environmental contamination associated with e-waste dismantling activities. As a notorious e-waste recycling area in East China, Taizhou has been a hot spot for persistent organic pollutant (POP) research. The present study was conducted to investigate the bioconcentration and trophic transfer tendencies of PCBs and PCDD/Fs in various aquatic biota species in this e-waste area. The high concentrations of POPs in these species reflected the lasting impact of e-waste recycling activities on the local environment over more than three decades. Bioconcentration of PCBs was ubiquitously observed in all the species, and significant parabolic relationships were found between log BCFs and the number of chlorine atoms of PCB congeners as well as their log K_{ow}s. The present results provided important information about the bioaccumulation tendency of POPs in aquatic biota species.

1 Introduction

Electrical and electronic products have become ubiquitous throughout the entire world. With the demand for new products and rapid development of electric technology, the life span of electronic products is being shortened.[1,2] Consequently, the older and outdated electronic products are discarded as electronic waste (e-waste) into the environment. It is estimated that 70% of the 40 million tons of e-waste generated worldwide every year is exported to China.[3,4] Meanwhile, China discards about 4 million computers annually, and this value is expected to increase exponentially.[4,5]

In the process of dismantling e-waste, persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are released, resulting in the contamination of the environment.[2,6–9] Once in the environment, the contaminants can accumulate in

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fatty tissues of living organisms and eventually enter human bodies *via* the food chain.[9,10]

Taizhou City located on the coastline of East China is one of the largest dismantling areas in China, which has been involved in e-waste recycling activities for nearly 30 years.[11] Most of the e-waste in Taizhou is disassembled primitively (burning, melting and acid chemical bath) and ends up in the surrounding environment.[2,10] Previous studies have documented high levels of POPs in local environmental matrices such as air, soil, sediments and biotic samples.[12,13] For biota species, more concern was focused on bioaccumulation, bioconcentration and biomagnification in the environment. Wu *et al.*[9] investigated bioaccumulation of PCBs and PBDEs in wild aquatic species with log BAF (bioaccumulation factor) of 1.2 to 8.4 for PCBs. They also demonstrated that log BAFs generally increased at log K_{ow} < 7, then decreased with further increasing log K_{ow}. Jiang *et al.*[10] reported BAFs of PCBs in three kinds of prawn muscle tissues (397) and mud crab (*Scylla serrata Forsskal*) (366) from aquaculture ponds. Shang *et al.*[14] investigated the bioaccumulation of PCDD/Fs, PCBs and PBDEs by earthworms in field soils, and found a second-order polynomial in the plot of BSAF (biota-soil accumulation factor) *versus* log K_{ow} with the maximum BSAF at a log K_{ow} of approximately 6.5. Wu *et al.*[15] evaluated the biomagnification extent of PCBs and PBDEs in a highly contaminated freshwater food web, and found trophic magnification factors (TMFs) for 53 PCB congeners and 18 PBDE congeners as 0.75–5.10 and 0.26–4.47, respectively.

Literature on the trophic transfer of these contaminants in aquatic food chains or webs is still scarce. In the present study, eight aquatic biota species were collected from a small river from a Taizhou e-waste recycling area to investigate the concentration levels, congener distributions, homologue profiles, bioconcentration and trophic transfer of PCBs and PCDD/Fs.

2 Materials and methods

2.1 Study area and sample collection

The study area is located in Baifengao village, Luqiao district, Taizhou City (N28°32′43.45″, E121°21′41.57″). This area was chosen because of its history in recycling obsolete transformers and electrical waste from China and other parts of the world over the last 30 years.[16] Household e-waste recycling factories existed around the village and dismantling activities resulted in wastewater discharge in the surrounding environment. The Chinese Government set stricter environmental regulations for the dismantling industries in 2005 to stop this kind of severe pollution.[17] In this study, biota samples were collected in July 2012 (details are listed in Table 1). Crucian carps (*Carassius auratus*), grass carps (*Ctenopharyngodon idellus*), eels (*Monopterus albus*), crabs (*Eriocheir sinensis*), stone snails (*Bellamya purificata*) and apple snails (*Ampullaria gigas spix*) were captured using fishing nets. Frogs (*Rana plancyi*) and toads (*Bufo raddei*) were caught at the paddy field along the banks of the river. Three water samples were simultaneously collected using amber glass bottles which were pre-rinsed with acetone. The biota samples were wrapped into polyethylene bags with a zip lock and transported to the analysis laboratory. In the laboratory, samples of similar species and body sizes were classified, and their muscle tissues were dissected. The tissues were pooled, homologized and kept at −20 °C.

2.2 Chemicals

Pesticide-grade solvents dichloromethane (DCM), *n*-hexane, acetone and toluene were obtained from Tedia Company Inc. (Fairfield, OH, USA). Silica gel 60 (0.063–0.100 mm) was purchased from Merck (Darmstadt, Germany). Basic alumina (150 mesh) was obtained from Sigma-Aldrich, Inc. (Ventura, CA, USA). Carbon (Carbopak C, Supelco 10258) and Celite (545 coarse, Fluka 22140) were obtained from Supelco Inc. (Bellefonte, PA, USA) to produce the carbon mixture (18% w : w). Anhydrous sodium sulfate, concentrated sulfuric acid and sodium hydroxide were purchased from domestic manufactures. Isotope standard solutions (68a-LCS and 68a-IS for PCBs, 1613B-LCS and 1613B-IS for PCDD/Fs) were bought from Wellington Laboratories (Guelph, Ontario, Canada). Preparation of acidified and basic silica gel, and activation of involved sorbents are described in our previous work.[18]

2.3 Extraction and clean-up procedure

Prior to extraction, samples were freeze-dried. The freeze-dried samples were then extracted and cleaned up as described by Liu *et al.*[19] In brief, 2 g of biota sample was spiked with ^{13}C-labeled surrogate standards (68a-LCS for PCBs, 1613B-LCS for PCDD/Fs) and extracted using an Accelerated Solvent Extractor (ASE300, Dionex, USA). The extract was evaporated to dryness for the gravimetric determination of the lipid weight. Prior to clean-up, the extract was reconstituted in *n*-hexane and the lipid was removed with acidified silica gel. The lipid free extract was purified through a multilayer silica gel column, a basic alumina column and an activated carbon column in sequence, respectively. PCBs and PCDD/Fs were separated on an activated carbon column. The final eluate was concentrated to <1 mL and transferred into vials. Contents in the vials were further reduced to 20 μL under a gentle stream of nitrogen. Injection standards (68a-IS for PCBs, 1613B-IS for PCDD/Fs) were then added to the vials prior to the instrumental analysis. For water samples, liquid–liquid extraction (LLE) was employed using dichloromethane as the extraction solvent and the extracts were purified following the same procedure as above.

2.4 Instrumental analysis

PCBs and PCDD/Fs were analyzed using a high-resolution gas chromatograph (HRGC) coupled to a high-resolution mass spectrometer (HRMS) in selective ion monitoring (SIM) mode at a resolution of ≥10 000. A 60 m DB-5MS column (J&W, Scientific, 0.25 μm film thickness, 0.25 mm i.d.) was used for GC separation. The detailed instrumental parameters are described elsewhere.[14,20] A total of seventeen 2,3,7,8-substitued PCDD/Fs and twenty five PCB congeners including twelve dioxin-like PCBs (CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, and -189), six indicator PCBs (CB-28, -52, -101, -138, -153,

Table 1 Sample details and concentrations of PCBs and PCDD/Fs in the aquatic biota species (pg per g dw)

Species	Numbers	Lipid content (%)	Trophic levels	$\sum_{25}$PCBs	$\sum_{17}$PCDD/Fs	TEQ[a]
Crucian carps (*Carassius auratus*)	5 (pooled)	6.31 ± 2.78	2.00 ± 0.11	$1.6(1–2.15) \times 10^{6}$[b]	28.3(16–55.8)	197(78.5–333)
Grass carps (*Ctenopharyngodon idellus*)	5 (pooled)	16.9 ± 3.56	3.96 ± 0.12	$1.32(0.5–1.92) \times 10^{6}$	67(33.9–105)	152(58.6–349)
Frogs (*Rana plancyi*)	8 (pooled)	7.46 ± 3.20	3.51 ± 0.13	$1.38(0.32–2.8) \times 10^{5}$	30.4(12.9–68.3)	39.5(7.29–73.9)
Toads (*Bufo raddei*)	5 (pooled)	6.13 ± 3.35	3.98 ± 0.02	$0.6(0.25–1.04) \times 10^{5}$	8.13(2–13.2)	2.57(0.3–5.9)
Stone snails (*Bellamya purificata*)	3 (pooled)	4.80 ± 2.58	3.22 ± 0.18	$1.07(0.17–1.6) \times 10^{6}$	617(174–1296)	154(14.3–347)
Apple snails (*Ampullaria gigas spix*)	4 (pooled)	3.37 ± 0.56	2.81 ± 0.43	$0.83(0.51–14.9) \times 10^{5}$	46.6(18.6–64)	4.25(2.77–5.69)
Crabs (*Eriocheir sinensis*)	1 (pooled)	6.58	3.18	1.36×10^{5}	183	65.8
Eels (*Monopterus albus*)	1	17.6	4.59	2.27×10^{6}	31.7	2352

[a] $\sum$TEQ = $\sum$TEQ(PCBs) + $\sum$TEQ(PCDD/Fs). [b] Arithmetic mean, minimum and maximum concentrations are listed.

and -180) and some other PCBs (CB-3, -11, -15, -202, -205, -208 and -209) were quantified.

2.5 Stable isotope analysis and trophic level determination

The ratio of heavier to lighter stable isotopes of nitrogen (^{15}N/^{14}N), expressed as δ^{15}N, successively enriched from prey to predator, which provides a continuous variable to the relative trophic position of an organism within a food web.[21,22] In the present study, an isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher, MA, USA) was used to investigate δ^{15}N of various biota species. Prior to stable isotope analysis, 50 mg of powdered samples were weighed in a tin cup and combusted in the analyzer. Nitrogen isotopic compositions were calculated according to the following equation:[22]

$$\delta^{15}\mathrm{N} = [(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{sample}}/(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{standard}} - 1] \times 1000 \qquad (1)$$

where $(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{standard}}$ values were based on atmospheric nitrogen (air).

The trophic level was determined as the equation below.[22]

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

where $\mathrm{TL}_{\mathrm{consumer}}$ is the trophic level of biota. $\delta^{15}\mathrm{N}_{\mathrm{baseline}}$ was the δ^{15}N of reference species and assumed to occupy trophic level 2. $\Delta\delta^{15}$N is the isotope enrichment factor with a range of 3–5‰.[23] 3.4‰ is commonly applied in ecotoxicological studies for every trophic level.[21,23]

2.6 Quality assurance/quality control (QA/QC)

Analytical blanks were processed for each batch of ten samples for quality control. The limit of detection (LOD) was defined as signal-to-noise (S/N) = 3. The LODs for PCBs and PCDD/Fs were 0.05–48.7 and 0.09–37.6 pg per g dry weight (dw) in biota; 0.001–0.02 and 0.0004–0.002 pg mL^{-1} in water, respectively. 68a-LCS and 1613B-LCS as surrogate standards were used in qualitative and quantitative analysis of PCBs and PCDD/Fs, and 68a-IS and 1613B-IS as internal standards were used to calculate recoveries. The recoveries (mean ± standard deviation) were 86.0 ± 31.6 and 77.8 ± 13.2%, respectively. Only some indicator PCBs (CB-28 and -52) and OCDF were detected at relatively low levels in laboratory blanks (<15% of the level in the samples), so the concentrations in the species were not corrected with the laboratory blanks.

3 Results and discussion

3.1 Concentrations of PCBs and PCDD/Fs

The contaminant levels, lipid contents and trophic levels of aquatic species are presented in Table 1. The mean $\sum_{25}$PCB concentrations varied widely from $0.6(0.25–1.04) \times 10^5$ pg per g dw in toads to 2.27×10^6 pg per g dw in eels. They were generally higher than those reported in Guiyu, another e-waste dismantling area,[24] some non-e-waste dismantling areas in China,[9,25] Belgian North Sea and Western Scheldt Estuary.[26] However, $\sum_{25}$PCB in crucian carps was $1.6(1–2.15) \times 10^6$ pg per g dw which was comparable to those in grass carps and silver carp (9.89×10^5 pg per g dw) in the Taizhou e-waste recycling region,[11] but one order of magnitude lower than the data in crucian carps.[16]

In stone snails the $\sum_{25}$PCB concentrations (1.07×10^6, range of $(0.17–1.6) \times 10^6$ pg per g dw) were ten times higher than the data in apple snails (8.25×10^4, range of $(5.05–14.9) \times 10^4$ pg per g dw). $\sum_{25}$PCB levels in apple snails were equivalent to those of snails (*Ampullariidae*) observed by Fu *et al.*[6] The concentrations in crabs were higher than those from aquaculture ponds in Taizhou,[10] the coasts of Brittany and Normandy in France[27] and Belgian North Sea and the Western Scheldt Estuary,[26] but were lower than those in coastal south eastern Georgia.[28] The high PCB levels generally could be attributed to their lipophilic nature and thus are prone to accumulate in fatty tissues of organisms. In the present study, a positive correlation ($R^2 = 0.44$, $p = 0.07$) was observed between $\sum_{25}$PCB concentrations and lipid contents of aquatic species.

$\sum_{25}$PCB concentrations in water were 13.4(10.5–15.3) pg mL^{-1}, which were lower than those reported by Wu *et al.*[9] (204, range of 196–206 pg mL^{-1}) and Yang *et al.*[29] (52.4 pg mL^{-1}) in the same e-waste recycling area.

The mean $\sum_{17}$PCDD/F concentrations were about four orders of magnitude lower than $\sum_{25}$PCB concentrations in aquatic biota species (Table 1). It should be noted that no significant correlation was observed between PCDD/F and PCB concentrations. The $\sum_{17}$PCDD/F concentrations varied from 8.13(2–13.2) pg per g dw in toads to 617(174–1296) pg per g dw in stone snails. The mean $\sum_{17}$PCDD/F concentrations in crucian carps were slightly lower than those in grass carps, but in the range of the data in frogs and apple snails. For water samples, only 1234678-HpCDF, OCDF and OCDD were detected, with a total concentration of 0.02 pg mL^{-1}.

The TEQ values for the $\sum$(PCDD/Fs and dl-PCBs) in the aquatic species ranged from 2.57 to 2352 pg WHO-TEQ per g dw (geometric average 65 pg WHO-TEQ per g dw) (Table 1). These values greatly exceeded the maximum permissible level of 4 pg g^{-1} ww for fish and other aquatic animals as food recommended by the European Commission.[30] However, the comparison of concentrations in the present study with the literature was difficult due to different units (wet, dry or lipid weight basis), the number of congeners, and species' life cycle (diet, migratory behaviour and metabolization capacities).[10,27] The TEQ for dioxin-like (dl) PCBs in apple snails was comparable with that in an e-waste recycling area.[8] The TEQ value in eels (1.55 pg WHO-TEQ per g dw) was lower than that from River Elbe and its tributaries, Germany (0.48–22 pg WHO-TEQ per g ww).[31] The TEQs of PCDD/Fs in apple snails were lower than that reported by Liu *et al.* (75.5 pg WHO-TEQ per g dw).[8]

3.2 Homologue profiles of PCBs and PCDD/Fs

For biota species, all 25 PCB congeners were detected except CB-11 and CB-169 in some species. Six indicator PCBs were predominant, accounting for 58.3–98% of the $\sum_{25}$PCBs. The indicator PCBs were equally distributed in crucian carps and grass carps. This indicated that they have similar accumulation and absorption patterns. CB-28 accounted for approximately 47.7% of the total indicator PCBs in apple snails and 47.9% in crabs while CB-153 represented about 52.2% of those in toads. CB-138 and -153 were the most predominant congeners in frogs and eels, accounting for 73% and 70.1% of the total indicator PCBs, respectively. In recent years, CB-11 has attracted great attention due to its unique source and ubiquitous presence in the environment.[18] In this study, the concentration of CB-11 varied from 5.5 to 1178 pg per g dw (geometric average of 104 pg per g dw), occupying less than 1% of the $\sum_{25}$PCBs.

For mono- to nona-CBs, penta-CBs were the major contributors to the $\sum$PCBs (36.9%) in biota species, followed by tetra- (24.4%) and then hexa-CBs (21%) (Fig. 1). These profiles are similar to those reported in the literature.[9,32] Furthermore, the low (mono-, di-) and high (octa-, nona-) CBs were detected but in small proportions. The percentage of highly chlorinated homologues (penta- to octo-CBs) increased with trophic level, while a decreasing trend was observed for the low chlorinated homologues (mono- to tetra-CBs). A significant negative linear correlation was found between the di-CBs and trophic levels ($R^2 = 0.67$, $p = 0.008$). This finding could be attributed to the differences in the trophic position and/or biotransformation and metabolism capacity of species.[10,22] Hexa-CBs contributed 50.5% of the $\sum$PCBs in toads, in which hepta-CBs had a proportion of 18.7%. Tri-CBs accounted for 30.5% of the $\sum$PCBs in apple snails and 24.3% in crabs. Penta- and hexa-CBs represented 82.9% of the $\sum$PCBs in eels. The homologue profile for PCBs in crucian carps showed a relatively uniform composition. While for water samples, CB-28 accounted for 42–47.1% of $\sum_{25}$PCBs; tri- and tetra-CBs occupied 51.2–74.4% of the $\sum$PCBs.

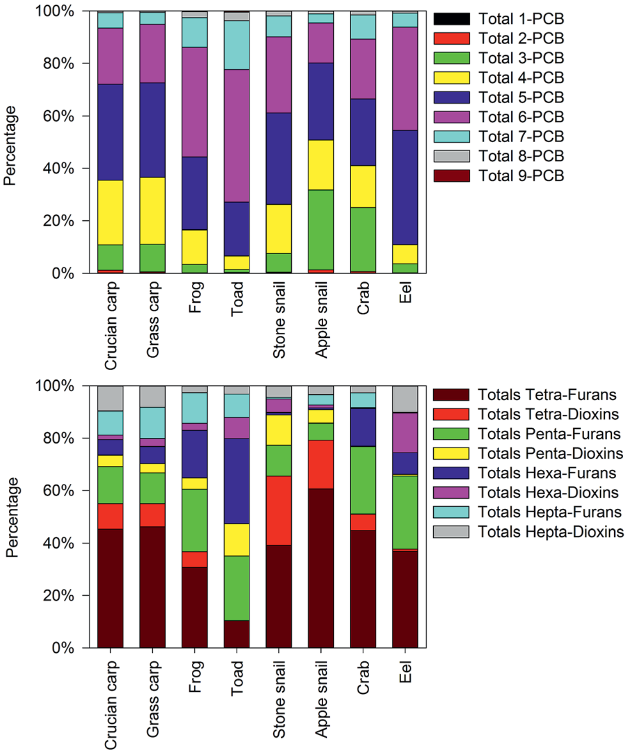

Fig. 1 Homologue profiles of PCBs and PCDD/Fs in aquatic biota species.

The most frequently detected PCDD/Fs congeners were OCDD and OCDF, contributing 96.7 and 91.7% of $\sum_{17}$PCDD/Fs, respectively. Five furan congeners (2378-TCDF, 23478-PeCDF, 123678-HxCDF, 1234789-HpCDF and OCDF) were found in toads, and they had a similar concentration level. The sum of OCDD, OCDF and 2,3,7,8-TCDF represented 82.4, 83.3 and 87.7% of $\sum_{17}$PCDD/Fs in crucian carps, grass carps and eels, respectively. The most dominant congeners in stone snails were OCDD, 1,2,3,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF, occupying 56.4% of $\sum_{17}$PCDD/Fs while the sum of 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD and OCDD contributed 68.3% of $\sum_{17}$PCDD/Fs in frogs. A similar characteristic pattern was reported by Ma *et al.*[33] in frogs. The results indicated that food intake could be the major source of PCDD/Fs in the environmental samples. For tetra- to hepta-furans and dioxins, tetra-furans were the dominant homologues in all biota species (39.1–60.6%), except toads in which penta- and hexa-furans accounted for 57.2% of the $\sum$PCDD/Fs (Fig. 1). Penta-furans contributed 23.8, 25.8 and 27.8% of the $\sum$PCDD/Fs in frogs, crabs and eels, respectively. The percentage of tetra-dioxins in stone snails and apple snails was 26.3 and 18.6%. In contrast, hexa-furans accounted for less than 1% of PCDD/Fs in them. Furthermore, the ratio of furans/dioxins in the biota species was more than 1, with a mean value of 3.9. This result ruled out technical sodiumpentachlorophenolate (Na-PCP) as a possible source of PCDD/Fs. Enriched PCDFs indicated that PCDD/Fs still existed at this e-waste recycling area, possibly due to past primitive combustion activities.[17]

3.3 Bioconcentration of PCBs in aquatic species

The bioconcentration factor (BCF) describes the bioaccumulation tendency for individual compounds in each species.[31] In this paper, BCFs of 25 PCB congeners were calculated as the ratio of the concentrations of each congener both in biota and water samples. The calculated log BCFs of PCBs ranged from 1.0 to 6.6, with the highest value for CB-205 in crucian carp and the lowest value for CB-11 in frog. The ranges of log BCFs were consistent with those reported in wild aquatic species from an e-waste recycling site in South China (2.2–6.5),[9] and from a small lake in Beijing (2.2–5.5),[32] but were lower than those in lake trout from lake Michigan (5.5–8.5).[34] If compounds are regarded as bioaccumulation at BCF > 5000 in aquatic biota species,[32] three PCB congeners (CB-3, -11 and -15) could be excluded from the analyzed PCBs in this study. log BCFs of them were 2.82 ± 0.39, 2.34 ± 0.74, and 2.31 ± 0.73, respectively. The reasons for the low BCFs could be due to the small molecular sizes of the mono- and di-CBs and thus easy to eliminate. On the other hand, high CBs have large molecular sizes, resulting in less bioavailability.[35]

The relationship between log BCFs and log octanol–water partition coefficient (K_{ow}) was adequately described by species-specific parabolic models. log BCFs generally increased at $\log K_{\mathrm{ow}} < 7$, then subsequently declined with further increasing $\log K_{\mathrm{ow}}$ in all species (Fig. 2). A similar pattern was observed between log BCF and the number of chlorine atoms (Fig. 2). These analogous correlations contributed to a significant linear relationship between $\log K_{\mathrm{ow}}$ and the number of chlorine atoms ($R^2 = 0.89$, $p < 0.001$). Similarly, strong parabolic correlations were also observed for individual species, which have been reported in other studies.[14,28,32,36] However, a linear relationship between log BCFs and $\log K_{\mathrm{ow}}$ was observed in phytoplankton, clams and fish for PCBs with up to hexa- or hepta-CBs.[28] Fisk *et al.*[36] observed a linear BCF–K_{ow} relationship with a $\log K_{\mathrm{ow}}$ between 3 and 6 for the Arctic marine zooplankton (*Calanus hyperboreus*).

The curvilinear phenomenon could be attributed to a number of factors, including differences in physicochemical parameters of PCB congeners, various environmental factors in water, octanol being an inaccurate surrogate for lipids, differences in individual species (lengths, sizes, and sex) and biological processes in organisms (such as different metabolism rates of these chemicals).[24,32,36,37] Numerous congeners of these contaminants possessed diverse physical and chemical properties, which make them demonstrate possibly different characteristics in aquatic species. Compared with high CBs, low CBs have relatively low lipid solubility, which means they have relatively high concentrations in water solvent.[9] Furthermore, it is likely that these congeners are easily metabolized and excreted from upper trophic level species.[15] The variation of BCFs might be due to environmental parameters, such as solute effects, pH and buffer capacity of the water phase.[37] The deviations in trends for the highly chlorinated homologues with larger K_{ow} could contribute to the increasing difficulty in the ability of large molecules to migrate across membranes.[28,32] Moreover, the uptake of these high chlorinated homologues with large hydrophobicity may not reach equilibrium between species and water, probably due to limited water solubility.[28,36]

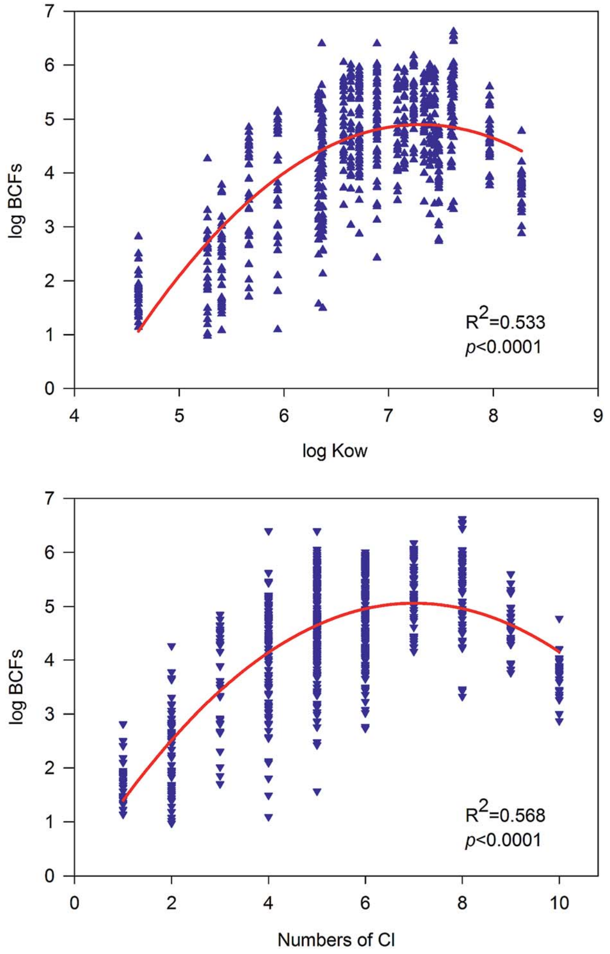

Fig. 2 Dependence of log BCFs of PCBs on $\log K_{\mathrm{ow}}$ and the number of chlorine atoms in all species.

Lipid variations between different species were also major parameters affecting the accumulation of PCBs.[24] If BCFs were calculated based on lipid-normalized concentrations, regression coefficients increased significantly from 0.71 to 0.76 ($p < 0.001$). Another reason could be ascribed to the differences between natural lipids and octanol: the lipid phase has a distinct structure and restricted spatial dimensions, whereas the octanol phase is a bulk phase and lacks structure, induced different activity coefficients and partitioning behaviour,[37] resulting in deflected linear correlations between log BCF and K_{ow}.

3.4 Trophic transfer of PCBs and PCDD/Fs in aquatic species

When PCBs and PCDD/Fs in water are taken in by an organism through dietary uptake, respiration and skin exposure, they may be transferred from one species to another, resulting in biomagnification or dilution through food chains/webs.[22,38] In the present study, regression analysis was conducted in various aquatic species. However, there were no significant correlations between the log-transferred PCB (or PCDD/F) concentrations and trophic levels of biota species (Fig. 3). These results are consistent with those in aquatic species collected from a small lake in Beijing.[32] Fisk *et al.*[22] reported strong positive relationships between the lipid-normalized POP concentration and the trophic level, providing clear evidence of POP biomagnification in Arctic marine food webs.

Several factors such as environmental conditions (the fluctuation of water temperature and pH), physicochemical properties of congeners with selective transformation reactions (*e.g.* metabolism), food chain length and structure of the food web, food habits and other factors could account for this observation.[15,32] Besides, the factors that affected the bioconcentration could also interfere with the biomagnification properties. Thus, the difference in uptake and elimination clearance efficiencies (*e.g.* biodegradation) for specific PCBs or PCDD/Fs might lead to poor correlation.

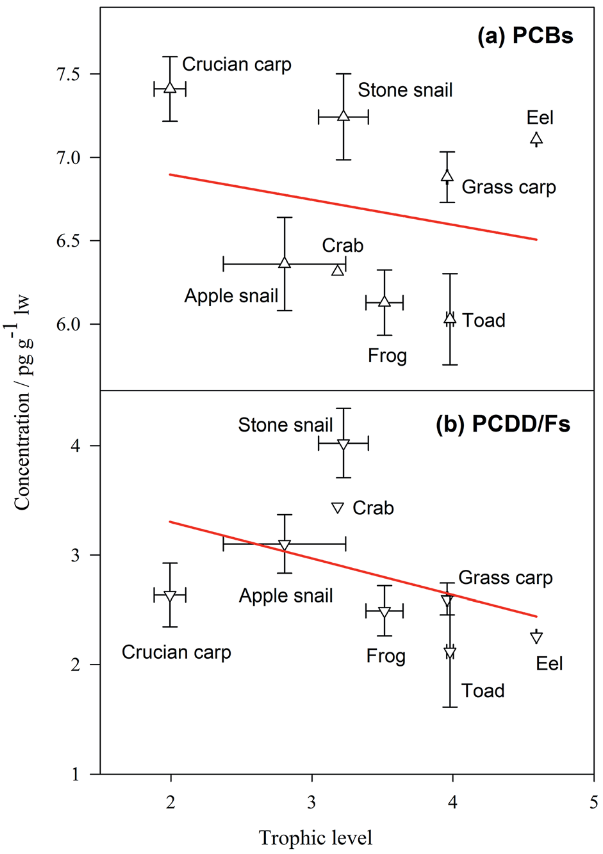

Fig. 3 Relationships between log concentrations of PCBs and PCDD/Fs *versus* trophic levels in aquatic biota species. The red lines represent linear regression equations. A negative correlation was observed in the plot of PCDD/Fs with the trophic level, though it was not statistically significant ($R^2 = 0.52$, $p = 0.07$), whereas no relationship for PCBs ($R^2 = 0.05$, $p = 0.59$) was observed.

4 Conclusions

A wide variety of aquatic biota species from Taizhou, an e-waste recycling area in East China, were investigated. Generally, high levels of PCBs were detected in stone snails and eels. CB-28, -138 and -153 were the dominated congeners in all species. Tetra- to hexa-CBs were the major contributors to the homologues. PCDD/Fs concentrations were at a relatively low level. OCDD and OCDF were the most frequently detected PCDD/F congeners, and tetra-furans were the dominant homologues. Bioconcentration of PCBs was observed in the species, and significant parabolic relationships were found between log BCFs and log K_{ow}, and log BCFs against the number of chlorine atoms. However, statistically significant trophic magnification or dilution of PCBs and PCDD/Fs was not found within the aquatic food webs, which is probably due to the variations in individual species, and differences in the metabolic capacity of the species.

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Notes and references

1 B. H. Robinson, *Sci. Total Environ.*, 2009, **408**, 183–191.
2 L. Chen, C. N. Yu, C. F. Shen, C. K. Zhang, L. Liu, K. L. Shen, X. J. Tang and Y. X. Chen, *J. Soils Sediments*, 2010, **10**, 359–367.
3 UNEP, *Recycling – from e-waste to resources, sustainable innovation and technology transfer industrial sector studies*, Empa, Umicore, UNU, 2009.
4 K. Lundgren, *The global impact of e-waste: addressing the challenge*, International Labour Office (ILO), 2012.
5 J. K. Y. Chan, G. H. Xing, Y. Xu, Y. Liang, L. X. Chen, S. C. Wu, C. C. K. C. Wong, C. K. M. Leung and M. H. Wong, *Environ. Sci. Technol.*, 2007, **41**, 7668–7674.
6 J. J. Fu, Y. W. Wang, A. Q. Zhang, Q. H. Zhang, Z. S. Zhao, T. Wang and G. B. Jiang, *Chemosphere*, 2011, **82**, 648–655.
7 G. F. Zhao, Z. J. Wang, M. H. Dong, K. F. Rao, J. P. Luo, D. H. Wang, J. M. Zha, S. B. Huang, Y. P. Xu and M. Ma, *Sci. Total Environ.*, 2008, **397**, 46–57.
8 H. X. Liu, Q. F. Zhou, Y. W. Wang, Q. H. Zhang, Z. W. Cai and G. B. Jiang, *Environ. Int.*, 2008, **34**, 67–72.
9 J. P. Wu, X. J. Luo, Y. Zhang, Y. Luo, S. J. Chen, B. X. Mai and Z. Y. Yang, *Environ. Int.*, 2008, **34**, 1109–1113.
10 J. H. Jiang, *Acta Oceanol. Sin.*, 2009, **28**, 111–117.
11 G. F. Zhao, Y. Xu, G. G. Han and B. Ling, *Environ. Geochem. Health*, 2006, **28**, 341–351.
12 Q. Zhang, J. J. Ye, J. Y. Chen, H. J. Xu, C. Wang and M. R. Zhao, *Environ. Pollut.*, 2014, **185**, 258–265.

13 M. H. Wong, S. C. Wu, W. J. Deng, X. Z. Yu, Q. Luo, A. O. W. Leung, C. S. C. Wong, W. J. Luksemburg and A. S. Wong, *Environ. Pollut.*, 2007, **149**, 131–140.

14 H. T. Shang, P. Wang, T. Wang, Y. W. Wang, H. D. Zhang, J. J. Fu, D. W. Ren, W. H. Chen, Q. H. Zhang and G. B. Jiang, *Environ. Int.*, 2013, **54**, 50–58.

15 J. P. Wu, X. J. Luo, Y. Zhang, M. Yu, S. J. Chen, B. X. Mai and Z. Y. Yang, *Environ. Pollut.*, 2009, **157**, 904–909.

16 G. F. Zhao, Y. Xu, W. Li, G. G. Han and B. Ling, *Sci. Total Environ.*, 2007, **378**, 281–292.

17 J. J. Fu, T. Wang, P. Wang, G. B. Qu, Y. W. Wang, Q. H. Zhang, A. Q. Zhang and G. B. Jiang, *Chemosphere*, 2012, **88**, 330–335.

18 P. Wang, Q. H. Zhang, T. Wang, W. H. Chen, D. W. Ren, Y. M. Li and G. B. Jiang, *RSC Adv.*, 2012, **2**, 1350–1355.

19 H. X. Liu, Q. H. Zhang, Z. W. Cai, A. Li, Y. W. Wang and G. B. Jiang, *Anal. Chim. Acta*, 2006, **557**, 314–320.

20 P. Wang, H. D. Zhang, J. J. Fu, Y. M. Li, T. Wang, Y. W. Wang, D. W. Ren, P. Ssebugere, Q. H. Zhang and G. B. Jiang, *Environ. Sci.: Processes Impacts*, 2013, **15**, 1897–1903.

21 A. Olsson, K. Valters and S. Burreau, *Environ. Sci. Technol.*, 2000, **34**, 4878–4886.

22 A. T. Fisk, K. A. Hobson and R. J. Norstrom, *Environ. Sci. Technol.*, 2001, **35**, 732–738.

23 J. Starrfelt, K. Borga, A. Ruus and E. Fjeld, *Environ. Sci. Technol.*, 2013, **47**, 11599–11606.

24 G. H. Xing, J. K. Y. Chan, A. O. W. Leung, S. C. Wu and M. H. Wong, *Environ. Int.*, 2009, **35**, 76–82.

25 N. Q. Yang, M. Matsuda, M. Kawano and T. Wakimoto, *Chemosphere*, 2006, **63**, 1342–1352.

26 S. Voorspoels, A. Covaci, J. Maervoet, I. De Meester and P. Schepens, *Mar. Pollut. Bull.*, 2004, **49**, 393–404.

27 N. Bodin, A. Abarnou, A. M. Le Guellec, V. Loizeau and X. Philippon, *Chemosphere*, 2007, **67**, S36–S47.

28 K. Kannan, H. Nakata, R. Stafford, G. R. Masson, S. Tanabe and J. P. Giesy, *Environ. Sci. Technol.*, 1998, **32**, 1214–1221.

29 Y. Yang, Z. Q. Wang, Q. Wang, J. Zhao, Y. J. Yu and D. L. Li, *Asian J. Ecotoxicol.*, 2014, **9**, 133–144.

30 Official Journal of the European Commission, Edition, 2012, pp. L91/91–97.

31 B. Stachel, E. H. Christoph, R. Götz, T. Herrmann, F. Krüger, T. Kühn, J. Lay, J. Löffler, O. Päpke, H. Reincke, C. Schröter-Kermani, R. Schwartz, E. Steeg, D. Stehr, S. Uhlig and G. Umlauf, *J. Hazard. Mater.*, 2007, **148**, 199–209.

32 Y. W. Wang, X. M. Li, A. Li, T. Wang, Q. H. Zhang, P. Wang, J. J. Fu and G. B. Jiang, *Environ. Sci. Technol.*, 2007, **41**, 6026–6032.

33 J. Ma, K. Kannan, J. Cheng, Y. Horii, Q. Wu and W. H. Wang, *Environ. Sci. Technol.*, 2008, **42**, 8252–8259.

34 S. S. Streets, S. A. Henderson, A. D. Stoner, D. L. Carlson, M. F. Simcik and D. L. Swackhamer, *Environ. Sci. Technol.*, 2006, **40**, 7263–7269.

35 J. P. Boon, I. Oostingh, J. Vandermeer and M. T. J. Hillebrand, *Eur. J. Pharmacol., Environ. Toxicol. Pharmacol. Sect.*, 1994, **270**, 237–251.

36 A. T. Fisk, G. A. Stern, K. A. Hobson, W. J. Strachan, M. D. Loewen and R. J. Norstrom, *Mar. Pollut. Bull.*, 2001, **43**, 93–101.

37 M. Müller and M. Nendza, *Literature Study: Effects of Molecular Size and Lipid Solubility on Bioaccumulation Potential*, 2007.

38 A. T. Fisk, R. J. Norstrom, C. D. Cymbalisty and D. C. G. Muir, *Environ. Toxicol. Chem.*, 1998, **17**, 951–961.