Environmental Science
Processes & Impacts

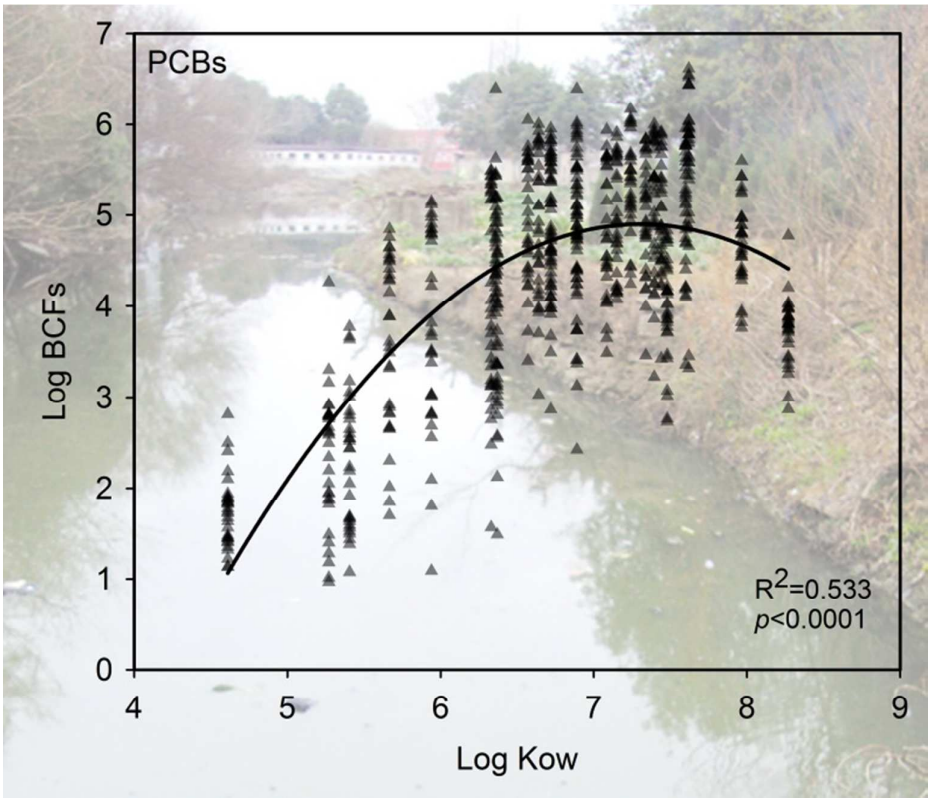
Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Graphical Abstract

The relationship between log BCF of PCBs and their log Kow in all aquatic species



Environmental Impact

E-waste dismantling regions received 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 pollutants (POPs) research. The present study was conducted to investigate the bioconcentration and biomagnification 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 in 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 numbers of chlorines of PCB congeners as well as their log Kows. The present results supplied important information about the bioaccumulation tendency of POPs in aquatic biota species.

Environmental Science
Processes & Impacts

RSCPublishing

ARTICLE

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†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chaofei Zhu[a], Pu Wang[a], Yingming Li[a], Zhaojing Chen[a], Wenjuan Li[a], Patrick Ssebugere[b], Qinghua Zhang[a,*] and Guibin Jiang[a]

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 g^{-1} dry weight (dw). The $\sum_{25}$PCB concentrations in eel was significantly higher than those in other species. The levels for PCDD/Fs changed from 8.13 pg g^{-1} dw in toad to 617 pg g^{-1} dw in stone snail. World Health Organization-toxic equivalents (WHO_{2005}-TEQs) ranged from 2.57 to 2352 pg WHO-TEQ g^{-1} dw with geometric mean value of 64.7 pg WHO-TEQ g^{-1} dw, which greatly exceeded the maximum levels of 4 pg g^{-1} 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 Kow (R^2=0.53, p<0.001), where the maximum value occurred at approximately log Kow of 7. A similar correlation was also found in the plot of log BCF against numbers 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 biotas. 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.

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 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 contamination of the environment[2,6-9]. Once in the environment, the contaminants can accumulate in 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 of 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/or 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 Kow <7, then decreased with further increasing log Kow. Jiang et al.[10] reported BAFs of PCBs in three kinds of prawns 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 Kow with the maximum BSAF at approximate log Kow of 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.

The trophic biomagnification of these contaminants in aquatic food chains or webs were still scare. In the present study, eight aquatic biota species were collected in a small river from 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 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 into 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 (*Eriochei rsinensis*), stone snails (*Bellarnya 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 locks and transported to the analysis laboratory. In the laboratory, samples of similar species and body sizes were classified, and their muscle tissues 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). 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, activation of involved sorbents is 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 clean-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 gravimetric determination of lipid weight. Prior to clean-up, the extract was reconstituted in *n*-hexane and the lipid removed with acidified silica gel. The lipid free extract was purified through a multilayer silica gel column, an alumina column and an activated carbon column in sequence, respectively. PCBs and PCDD/Fs were separated on 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 extract solvent and the extracts were purified followed 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 ≥10,000. A 60m 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, and -180) and some other PCBs (CB-209, -3, -15, -202, -205, -208 and CB-11) 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

$\delta^{15}N$ 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]:

$$\delta^{15}N=[(^{15}N/^{14}N)_{sample} /(^{15}N/^{14}N)_{standard} -1)]\times1000 \quad (1)$$

where $(^{15}N/^{14}N)_{standard}$ values were based on atmospheric nitrogen (air).
Trophic level was determined as the equation below[22].

$$TL_{consumer} = (\delta^{15}N_{consumer} - \delta^{15}N_{baseline})/\Delta\delta^{15}N +2 \quad (2)$$

where $TL_{consumer}$ is the trophic level of biota. $\delta^{15}N_{baseline}$ was the $\delta^{15}N$ of reference species and assumed to occupy trophic level 2. $\Delta\delta^{15}N$ is the isotope enrich 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. 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 g^{-1} 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 contaminants levels, lipid contents and trophic levels of aquatic species are presented in Table 1. The mean $\sum_{25}$PCBs concentrations varied widely from 0.6 (0.25-1.04) $\times10^5$ pg g^{-1} dw in toad to 2.27×10^6 pg g^{-1} dw in eel. 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, $\sum_{25}$PCBs in crucian carp was 1.6 (1-2.15)$\times10^6$ pg g^{-1} dw which was comparable to those in grass carp and silver carp (9.89×10^5 pg g^{-1} dw) in Taizhou e-waste recycling region[11], but one order of magnitude lower than the data in crucian carp[16].

In stone snail the $\sum_{25}$PCBs concentrations (1.07×10^6, range of (0.17-1.6)$\times10^6$ pg g^{-1} dw) were ten times higher than the data in apple snail (8.25×10^4, range of (5.05-14.9)$\times10^4$ pg g^{-1} dw). Σ_{25}PCBs levels in apple snail was equivalent to snail (*Ampullariidae*) observed by Fu et al.[6] While the concentrations in crab 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 $\sum_{25}$PCBs concentrations and lipid contents of aquatic species.

$\sum_{25}$PCBs concentrations in water were 13.4 (10.5-15.3) pg mL^{-1}, which was 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/Fs concentrations were about four orders of magnitude lower than $\sum_{25}$PCBs concentrations in aquatic biota species (Table 1). It should be noted that no significant correlation was observed between PCDD/Fs and PCBs concentrations. The $\sum_{17}$PCDD/Fs concentrations varied from 8.13 (2-13.2) pg g^{-1} dw in toad to 617 (174-1296) pg g^{-1} dw in stone snail. The mean $\sum_{17}$PCDD/Fs concentrations in crucian carp was slightly lower than that in grass carp, but in the range of the data in frog and apple snail. For water samples, only 1234678-HpCDF, OCDF and OCDD were detected, with sum concentrations of 0.02 pg mL^{-1}.

The TEQ values for the Σ(PCDD/Fs and dl-PCBs) in the aquatic species ranged from 2.57 to 2352 pg WHO-TEQ g^{-1} dw (geometric average 65 pg WHO-TEQ g^{-1} 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 literature was difficult due to different units (wet, dry or lipid weight basis), numbers of congeners, specie's life cycle (diet, migratory behaviour and metabolization capacities)[10,27].The TEQ for dioxin-like (dl) PCBs in apple snail was comparable with that in an e-waste recycling area[8]. The TEQ value in eel (1.55 pg WHO-TEQ g^{-1} dw) was lower than that from River Elbe and its tributaries, Germany (0.48-22 pg WHO-TEQ g^{-1} ww)[31]. The TEQs of PCDD/Fs in apple snail were lower than that reported by Liu et al. (75.5 pg WHO-TEQ g^{-1} 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 Σ_{25}PCBs. The indicator PCBs were equally distributed in crucian carp and grass carp. This indicated that they have similar accumulation and absorption patterns. CB-28 accounted for approximately 47.7% of the total indicator PCBs in apple snail and 47.9% in carb while CB-153 represented about 52.2% of those in toad. CB-138 and -153 were the most predominant congeners in frog and eel, accounting for 73% and 70.1% of the total indicator PCBs, respectively. In recent years, CB-11 has attracted great concern due to its unique source and ubiquitous presence in the environment18. In this study, the concentration of CB-11 varied from 5.5 to 1178 pg g^{-1} dw (geometric average of 104 pg g^{-1} dw), occupying less than 1% of the Σ_{25}PCBs.

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

Species	Numbers	lipid content (%)	Trophic levels	$\sum_{25}$PCBs	$\sum_{17}$PCDD/Fs	TEQ [a]
Crucian carp (*Carassius auratus*)	5 (pooled)	6.31±2.78	2.00±0.11	1.6 (1-2.15) $\times10^6$ [b]	28.3(16-55.8)	197(78.5-333)
Grass carp (*Ctenopharyngodon idellus*)	5 (pooled)	16.9±3.56	3.96±0.12	1.32 (0.5-1.92) $\times10^6$	67(33.9-105)	152(58.6-349)
Frog (*Rana plancyi*)	8 (pooled)	7.46±3.20	3.51±0.13	1.38 (0.32-2.8) $\times10^5$	30.4 (12.9-68.3)	39.5(7.29-73.9)
Toad (*Bufo raddei*)	5 (pooled)	6.13±3.35	3.98±0.02	0.6 (0.25-1.04) $\times10^5$	8.13(2-13.2)	2.57(0.3-5.9)
Stone snail (*Bellarnya purificata*)	3 (pooled)	4.80±2.58	3.22±0.18	1.07 (0.17-1.6) $\times10^6$	617(174-1296)	154(14.3-347)
Apple snail (*Ampullaria gigas spix*)	4 (pooled)	3.37±0.56	2.81±0.43	0.83 (0.51-14.9) $\times10^5$	46.6 (18.6-64)	4.25(2.77-5.69)
Crab (*Eriocheir sinensis*)	1 (pooled)	6.58	3.18	1.36 $\times10^5$	183	65.8
Eel (*Monopterus albus*)	1	17.6	4.59	2.27$\times10^6$	31.7	2352

[a] $\sum$TEQ= $\sum$TEQ(PCBs)+$\sum$TEQ(PCDD/Fs);

[b] arithmetic mean , minimum and maximum concentrations are listed.

For mono- to nona-CBs, penta-CBs were the major contributors to the ΣPCBs (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 literature[9,32]. Furthermore, the low (mon-, di-) and high (octa-, nona-) CBs were detected but in small proportions. The percentage of high 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 level (R^2=0.67, p=0.008). This finding could be attributed to differences in trophic position and/or biotransformation and metabolism capacity of species[10,22]. Hexa-CBs contributed 50.5% of the ΣPCBs in toad, in which hepta-CBs had a proportion of 18.7%. Tri-CBs accounted for 30.5% of the ΣPCBs in apple snail and 24.3% in crab. Penta- and hexa-CBs represented 82.9% of the ΣPCBs in eel. The homologue profile for PCBs in crucian carp showed a relatively uniform composition. While for water samples, CB-28 accounted for 42-47.1% of Σ_{25}PCBs; tri- and tetra-CBs occupied 51.2-74.4% of the ΣPCBs.

The most frequently detected PCDD/Fs congeners were OCDD and OCDF, contributing 96.7 and 91.7% of $\sum_{17}$PCDD/Fs, respectively. Five furans congeners (2378-TCDF, 23478-PeCDF, 123678-HxCDF, 1234789-HpCDF and OCDF) were found in toad, and they had the 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 carp, grass carp and eel, respectively. The most dominant congeners in stone snail 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 frog. A similar characteristic pattern was reported by Ma. et al.[33] in frog. 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 homologue in all biota species (39.1-60.6%), except toad in which penta- and hexa-furans accounted for 57.2% of the ΣPCDD/Fs (Fig.1). Penta-furans contributed 23.8, 25.8 and 27.8% of the ΣPCDD/Fs in frog, crab and eel, respectively. The percentage of tetra-dioxins in stone snail and apple snail 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 sodium-pentachlorophenolate (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

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>5,000 in aquatic biota species[32], three PCB congeners (CB-3, -11 and -15) could be excluded from analyzed PCBs in this study. Log BCF of them were 2.82±0.39, 2.34±0.74, 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 the high molecular sizes, resulting in less bioavailability[35].

The relationship between log BCFs and log octanol-water partition coefficient (Kow) was adequately described by species-specific parabolic models. Log BCFs generally increased at log Kow <7, then subsequently declined with further increasing log Kow in all species (Fig. 2). A similar pattern was observed between log BCF and the numbers of chlorines (Fig. 2). These analogous correlations were contributed to a significant linear relationship between log Kow and the number of chlorines (R^2=0.89, p<0.001). Similarly, strong parabolic correlations were also observed for individual

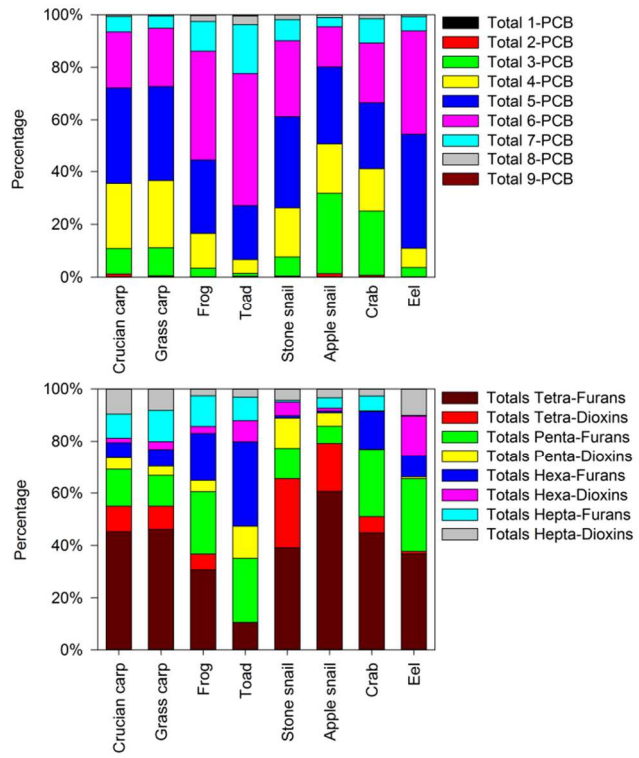


Fig. 1 Homologue profiles of PCBs and PCDD/Fs in aquatic biota species

specie, which have been reported in other studies[14,28,32,36]. However, a linear relationship between log BCFs and log Kow 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-Kow relationship with a log Kow between 3 and 6 for the Arctic marine zooplankton (*Calanushyperboreus*).

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, 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. For low CBs, the relatively low lipid solubility or high water solubility make their relatively higher concentrations in water[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 high chlorinated homologues with larger Kow, could be contributed to the increasing difficulty in the ability of large molecules to migrate across membranes[28,32]. Moreover, the uptake of these higher chlorinated homologues with large hydrophobicity may not reach equilibrium between species and water, probably due to limited water solubility[28,36].

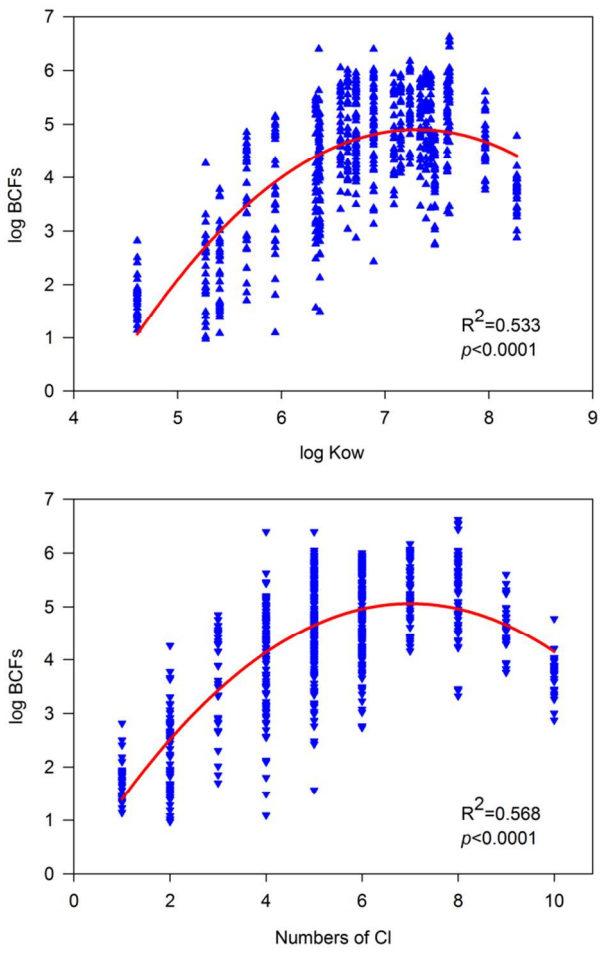


Fig.2 Dependence of log BCFs of PCBs on log Kow and the number of chlorines in all species.

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 differences between natural lipids and octanol: lipid phase has a distinct structure and restricted spatial dimensions, whereas the octanol phase is a bulk phase and lacks of structure, induced different activity coefficients and partitioning behaviour[37], resulting into deflected linear correlations between log BCF and Kow.

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

When PCBs and PCDD/Fs in water are taken in by 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 were conducted in various aquatic species. However, there were no significant correlations between the log-transferred PCBs (or PCDD/Fs) concentrations and trophic levels of biota species (Fig. 3). These results are consistent with those in aquatic species collected from a small

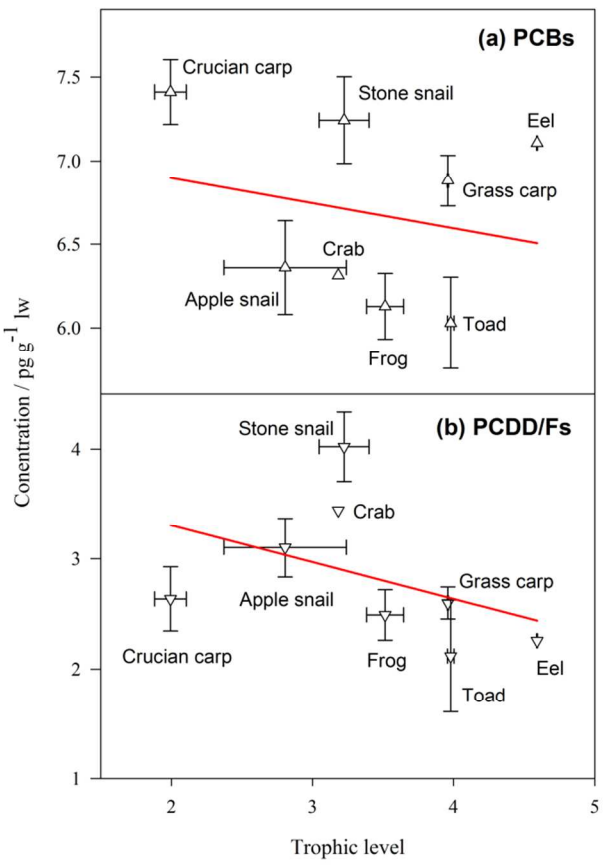


Fig.3 Relationships between log concentrations of PCBs and PCDD/Fs versus trophic levels in aquatic biota species. The red lines represent linear regression equations. The negative correlation was observed in the plot of PCDD/Fs with trophic level, though it was not statistically significant (R^2=0.52,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

lake in Beijing[32]. Fisk et al.[22] reported strong positive relationships between lipid-normalized POPs concentration and trophic level, providing clear evidence of POP biomagnification in Arctic marine food webs.

Several factors such as environment conditions (the fluctuation of water temperature and pH), physiochemical properties of congeners with selective transformation reactions (e.g. metabolism), food chain length and structure of food web, food habits and other factor 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.

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 snail and eel. 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 homologue. Bioconcentration of PCBs was observed in the species, and significant parabolic relationships were found between log BCFs and log Kow, and log BCFs against the numbers of chlorines. However, statistically significant trophic magnification or dilution of PCBs and PCDD/Fs were not found within the aquatic food webs, which is probably due to variation in individual species, and differences in metabolic capacity of the species.

Acknowledgements

Funding for this study was jointly provided by National Natural Science Foundation of China (21277165 and 41276195), Chinese Academy of Sciences (YSW2013B01) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14010100).

Notes and references

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[b] Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda
* E-mail: qhzhang@rcees.ac.cn; Fax: +86-10-62849818; Tel: +86-10-62849818

1. B.H. Robinson, The Science of the total environment, 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, Journal of Soils and 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, Environmental Science & Technology, 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, Science of The Total Environment, 2008, 397, 46-57.
8. H.X. Liu, Q.F. Zhou, Y.W. Wang, Q.H. Zhang, Z.W. Cai and G.B. Jiang, Environment International, 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, Environment International, 2008, 34, 1109-1113.
10. J.H. Jiang, Acta Oceanologica Sinica, 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, Environmental Pollution, 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, Environmental Pollution, 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, Environment International, 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, Environmental Pollution, 2009, 157, 904-909.
16. G.F. Zhao, Y. Xu, W. Li, G.G. Han and B. Ling, Science of the Total Environment, 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 Advances, 2012, 2, 1350-1355.
19. H.X. Liu, Q.H. Zhang, Z.W. Cai, A. Li, Y.W. Wang and G.B. Jiang, Analytica Chimica 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, Environmental Science-Processes & Impacts, 2013, 15, 1897-1903.
21. A. Olsson, K. Valters and S. Burreau, Environmental Science & Technology, 2000, 34, 4878-4886.
22. A. T. Fisk, K. A. Hobson and R. J. Norstrom, Environmental Science & Technology, 2001, 35, 732-738.
23. J. Starrfelt, K. Borga, A. Ruus and E. Fjeld, Environmental Science & Technology, 2013, 47, 11599-11606.
24. G.H. Xing, J.K.Y. Chan, A.O.W. Leung, S.C. Wu and M.H. Wong, Environment International, 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, Marine Pollution Bulletin, 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, Environmental Science & Technology, 1998, 32, 1214-1221.
29. Y. Yang, Z.Q. Wang, Q. Wang, J. Zhao, Y.J. Yu, D.L. Li, Asian Journal of Ecotoxicology, 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, Journal of Hazardous Materials, 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, Environmental Science & Technology, 2007, 41, 6026-6032.
33. J. Ma, K. Kannan, J. Cheng, Y. Horii, Q. Wu and W.H. Wang, Environmental Science & Technology, 2008, 42, 8252-8259.
34. S.S. Streets, S.A. Henderson, A.D. Stoner, D.L. Carlson, M.F. Simcik and D.L. Swackhamer, Environmental Science & Technology, 2006, 40, 7263-7269.
35. J.P. Boon, I. Oostingh, J. Vandermeer and M.T.J. Hillebrand, European Journal of Pharmacology-Environmental Toxicology and Pharmacology Section, 1994, 270, 237-251.
36. A. T. Fisk, G. A. Stern, K. A. Hobson, W. J. Strachan, M. D. Loewen and R. J. Norstrom, Marine Pollution Bulletin, 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, Environmental Toxicology and Chemistry, 1998, 17, 951-961.