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Bioaccumulation of polybrominated diphenyl ethers and several alternative halogenated flame retardants in a small herbivorous food chain

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ABSTRACT

Little is known about the bioaccumulation behavior of polybrominated diphenyl ethers (PBDEs) and other halogenated flame retardants (HFRs) in plants and in herbivores. In the present study, PBDEs and several alternative HFRs (AHFRs) were examined in a small herbivorous food chain (paddy soils–rice plant–apple snails) from an electronic waste recycling site in South China. Mean concentrations of total PBDEs were 40.5, 1.81, and 5.54 ng/g dry weight in the soils, rice plant, and apple snails, respectively. Levels of total AHFRs in the samples were comparable to or even higher than those of PBDEs. The calculated plant to soil concentration ratios for most AHFRs (0.05–3.40) were higher than those for PBDEs (0.02–0.23), indicating the greater bioavailability of the AHFRs in the rice plant. All PBDE congeners and Dechlorane Plus (DP) isomers were biomagnified from the rice plant to apple snails, with mean biomagnification factors (BMFs) of 1.1–5.0.

1. Introduction

Brominated and chlorinated flame retardants are widely added in a variety of consumer products such as textiles and electrical and electronic equipments (EEEs), to improve their resistance to fire (Alaee et al., 2003; de Wit, 2002; Hoh et al., 2006). Most of these halogenated flame retardants (HFRs) are not covalently bound to the materials, and therefore may be leached into the environment during use, following disposal, or during recycling of the related HFR-containing products (de Wit, 2002). In fact, some of these HFRs, e.g., the polybrominated diphenyl ethers (PBDEs), have been demonstrated to be environmentally ubiquitous, bioaccumulative, and toxic, and hence have been regulated or phased out of use recently (UNEP, 2009).

With the bans or regulations on the production and use of commercial PBDEs, some non-regulated HFRs such as Dechlorane Plus (DP), decabromodiphenyl ethane (DBDPE), and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), have been used as alternatives for the discontinued PBDEs in some applications (Covaci et al., 2011). These chemicals have been recently detected in both abiotic and biota matrices from various parts of the world, including the Arctic (Covaci et al., 2011; Xian et al., 2011; Sverko et al., 2011). However, studies on bioaccumulation potentials for the AHFRs are scarce. Field determined bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) indicated that most of these chemicals are highly bioaccumulative, and some of these chemicals may have comparable bioaccumulation potentials with PBDEs (Covaci et al., 2011; Zhang et al., 2011). The calculated predator/prey biomagnification factors (BMFs) suggested that some of these chemicals, e.g., DBDPE and BTBPE, were biomagnified in certain fish species from Lake Winnipeg (Canada) (Law et al., 2006). DP and DBDPE were also demonstrated to be capable of biomagnifying in aquatic food webs (Law et al., 2006; Wu et al., 2010b). The lack of knowledge, combined with recent detection of the AHFRs in the global environmental warrants further investigation into their environmental fate and toxicity.

While considerable work has been conducted on the bioaccumulation of PBDEs in aquatic ecosystems, very little is known about their bioaccumulation behavior in plants and in the herbivorous food chain. Plant constitutes a significant fraction of the total biomass in the environment, and is known to bioaccumulate HFRs such as PBDEs (Mueller et al., 2006; Vrkoslavová et al., 2010; Huang et al., 2010, 2011). Therefore, they may play an important role in the transfer of these chemicals into the food chain. Additionally, bioaccumulation of persistent toxic pollutants such as PBDEs by vegetation is an important process when considering the risks of

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land contamination, and the role of plant in the global cycling of these chemicals. The herbivores consume plants and may bioaccumulate chemicals through plant-herbivore feeding interactions. However, previous bioaccumulation studies on PBDEs mostly focused on the carnivores, the dynamics and bioaccumulation of these chemicals in the bottom part of the food chain, e.g., plants and herbivore animals, have not been adequately investigated in detail.

Apple snails are tropical and sub-tropical freshwater snails, inhabiting a wide range of ecosystems from swamps, ditches, ponds, and paddy fields. They are mainly vegetarian. In paddy fields, they prefer tender leaves of rice plant. Being widely distributed, apple snail has been successfully used as a bioindicator monitoring PBDEs and other organic chemicals in the electronic waste (e-waste) recycling sites in China (Fu et al., 2011). In the present study, we examined PBDEs and several AHFRs including DP, DBDPE, BTBPE, hexabromobenzene (HBB), pentabromotoluene (PBT), and pentabromoethylbenzene (PBEB) in the paddy soils, rice plant (*Oryza sativa*), and apple snails (*Pomacea canaliculata*) collected from an e-waste recycling site in South China. The objectives were to investigate the bioaccumulation behaviors of PBDEs and the AHFRs in the rice plant, and to assess their biomagnification potentials from plant to herbivore animal (apple snails).

2. Materials and methods

2.1. Sample collection and pretreatment

The paddy soils ($n = 12$), leaves of rice plant (*O. sativa*) ($n = 30$), and apple snails (*P. canaliculata*) ($n = 98$) were concurrently collected in 2010, from a paddy field in an e-waste recycling site, South China (latitude 23°36′ N and longitude 113°04′ E). Details of the sampling site have been previously described (Luo et al., 2009). The apple snails were collected by hand. Around the location where the apple snails sampled, tender leaves of rice plant and soils (0–5 cm depth) were taken using stainless scissors and stainless steel shovels, respectively. All the samples were wrapped with aluminum foil, put in polythene zip-bags, and transported to the laboratory in 12 h. At the laboratory, rice plant was rinsed three times with distilled water and blotted with organic chemical free tissue paper. Soft tissue was dissected from the apple snails. All the samples were freeze-dried, ground with agate mortar, and stored <0 °C until analyzed.

2.2. Sample extraction and analysis

The extraction and analysis of the investigated HFRs in the soils, rice plant, and apple snails were according to the previously published methods (Wu et al., 2010a; Chen et al., 2011a), with minor modification. Briefly, subsamples of the lyophilized soils (~2 g), rice plant (~8 g), and apple snails (~1 g) were spiked with surrogate standards (BDEs 77 and BDE 181), homogenized with anhydrous sodium sulfate, and Soxhlet extracted with hexane/acetone (1/1, v/v) for 48 h. An aliquot of the extract of rice plant and apple snails was used for lipid determination gravimetrically. Another aliquot of the extract of rice plant was converted to 60 ml in hexane, and mixed with 60 ml of concentrated H_2SO_4 in a Teflon separatory funnel, shaking for 5 min. This step was repeated three times, and the hexane fractions were combined. The extracts of apple snails used for chemical analysis were subjected to gel permeation chromatography (GPC) for lipid removal. All the extracts were finally purified by passing through a multilayer column packed with neutral silica and acidified silica. Known amounts (40 ng) of internal standards (BDEs 118 and 128) were spiked in the final extracts prior to instrumental analysis.

The octa- to deca-BDE congeners (BDEs 196, 197, 202, 203, 206, 207, 208, and 209), DBDPE, and BTBPE were analyzed using a Shimadzu Model QP2010 gas chromatograph–electron capture negative ionization–mass spectrometer (GC–ECNI–MS), operated in the selected ion monitoring (SIM) mode. A DB-5HT column (15 m × 0.25 mm × 0.10 μm; J&W Scientific) was used for separation. The tri- to hepta-BDE congeners (BDEs 28, 47, 66, 85, 100, 99, 153, 154, and 183), *syn*-DP, *anti*-DP, HBB, PBT, and PBEB were quantified by an Agilent 6890 GC–5975 MS using ECNI in the SIM mode, separated by a DB-XLB column (30 m × 0.25 mm × 0.25 μm; J&W Scientific). Ions *m/z* 79 and 81 were monitored for tri- to nona-BDEs, BTBPE, DBDPE, HBB, PBT, and PBEB. Ions *m/z* 486.7 and 488.7 were monitored for BDE 209 and 653.8 and 655.8 for DP. Details of the GC conditions were described elsewhere (Tian et al., 2012; Wu et al., 2010a).

2.3. Quality assurance and control

The method quality assurance and control was performed by regular analysis of procedural blanks, spiking blanks (a mixture of 10 PBDE congeners and the investigated AHFRs spiked in solvent blanks), and blind triplicate samples. Procedural blanks contained traces of target chemicals, but the levels were less than 1% of the analyzed concentration in the samples. The mean recoveries in the spiking blanks were 77%–91% and 98%–102% for individual PBDE congeners and the AHFs, respectively. The recoveries of surrogate standards were 93% ± 2% (mean ± SE) for BDE 77 and 95% ± 2% for BDE 181. No surrogate or blank corrections were made to the final concentrations. Target chemicals detected in the triplicate samples were consistent (RSD <15%). Instrumental QC was performed by regular injection of solvent blanks and standard solutions.

The limits of quantification (LOQs) were set as the mean values of target compounds detected in the procedural blanks plus three times of standard deviations. For the undetectable compounds in the blanks, the LOQs were estimated from the smallest peak area that could be quantified reliably, which corresponds to a signal-to-noise ratio of 10. The LOQs for PBDEs ranged 0.04–0.79, 0.01–0.20, and 0.03–1.22 ng/g dry weight (dw) in the soils, rice plant, and apple snails, respectively. For the AHFRs, the LOQs ranged 0.01–0.22, 0.01–0.06, and 0.02–0.35 ng/g dw, respectively.

3. Results and discussion

3.1. Levels and congener profiles of PBDEs

The mean and range of concentrations of nine PBDE congeners and total PBDEs (∑PBDEs) in the paddy soils, rice plant, and apple snails were summarized in Table 1. The mean ∑PBDEs concentrations in the paddy soils (40.5 ng/g dw) were comparable to those previously detected in the soils of paddy field (15.6 ng/g dw), vegetable field (34.1 ng/g dw) (Wang et al., 2011), and farmland (42.2 ng/g dw) from the same e-waste recycling region (Luo et al., 2009), and paddy soils from Guiyu (48.2 ng/g dw) and Taizhou (20.9 ng/g dw), another two notorious e-waste recycling regions in China (Leung et al., 2007; Chen et al., 2011b). The ∑PBDEs levels in the paddy soils from e-waste recycling sites

Table 1
Lipid content (% dry weight), water content (%), and concentrations (ng/g dry weight) of PBDEs and the alternative halogenated flame retardants (AHFRs) in the paddy soil, rice plant, and apple snail samples colleted from an electronic waste recycling site in South China.

	Paddy soil ($n = 12$ [6])[a]		Rice plant ($n = 30$ [10])		Apple snail ($n = 98$ [12])	
	Mean	Range	Mean	Range	Mean	Range
Lipid	/	/	0.74	0.61–0.92	0.71	0.54–0.94
Water	84.8	81.4–87.7	68.1	64.4–71.2	80.7	78.6–82.3
PBDEs[b]						
BDE 28	0.22	0.17–0.27	0.06	0.05–0.07	0.10	0.05–0.26
BDE 47	1.42	1.28–1.65	0.37	0.31–0.46	0.53	0.10–1.26
BDE 66	0.31	0.24–0.37	0.07	0.06–0.10	0.18	0.07–0.50
BDE 99	1.37	0.97–2.27	0.17	0.13–0.27	0.60	0.17–1.40
BDE 100	0.30	0.19–0.54	0.03	0.03–0.05	0.16	0.04–0.54
BDE 153	0.72	0.51–1.04	0.02	0.01–0.03	0.17	0.03–0.63
BDE 154	0.44	0.30–0.65	0.01	0.01–0.03	0.17	0.07–0.75
BDE 183	1.03	0.93–1.14	0.06	0.06–0.07	0.50	0.37–0.67
BDE 209	22.5	15.6–29.8	0.71	0.58–0.83	2.24	1.50–5.69
∑PBDEs[c]	40.5	31.2–51.6	1.81	1.30–2.47	5.54	3.04–16.3
AHFRs						
syn-DP	3.66	2.89–4.52	0.23	0.16–0.39	1.12	0.24–3.19
anti-DP	10.8	9.20–12.9	0.89	0.55–1.60	3.06	0.99–6.35
DPDPE	14.7	10.4–18.9	3.59	2.74–4.99	bdl[d]	/
BTBPE	0.03	0.01–0.14	0.03	0.03–0.04	bdl	/
HBB	0.37	0.02–1.40	0.10	0.08–0.12	bdl	/
PBT	bdl	/	0.01	0.006–0.009	bdl	/
∑AHFRs[e]	29.6	25.0–34.5	4.85	3.69–6.68	5.73	0.17–16.8

[a] Number of individual samples collected; figure in the brackets indicates analyzed number of pooled samples.
[b] Only those each accounting more than 3% of total PBDEs in biota samples are listed.
[c] Sum of 18 PBDE congeners measured (BDEs 28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 196, 197, 203, 205, 206, 207, 208, and 209).
[d] Below detection limit.
[e] Sum of the investigated AHFRs.