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LEVELS OF POLYBROMINATED DIPHENYL ETHER (PBDE) AND NON-PBDE FLAME RETARDANTS IN CHICKEN AND FISH SAMPLES FROM AN ELECTRONIC WASTE PROCESSING AREA IN NORTHERN VIETNAM

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Introduction

A broad array of flame retardants (FRs) have been used for several decades to reduce the flammability of polymeric materials in electronic products in order to pass fire safety regulations[1]. Evidence about environmental and human contamination with polybrominated diphenyl ether (PBDE) technical formulations has been generated in response to concerns about the adverse environmental and human health impacts of PBDEs[2]. Strict bans have been imposed on the worldwide use of PBDEs in electronic products during the past decade[3,4], and then non-PBDE FRs, such as other brominated FRs (BFRs), dechlorane plus (DP), monomeric organophosphorus FRs (m-PFRs), and oligomeric organophosphorus FRs (o-PFRs) were introduced as alternatives for PBDEs[5]. However, little is known about environmental and human contamination with non-PBDE FRs. Our earlier studies[6–9] reported that primitive processing to recover recyclable/reusable materials of electronic wastes (e-wastes) and uncontrolled dumping of non-recyclable materials in an informal e-waste processing area in northern Vietnam resulted in causing environmental, livestock, and fish contaminations with PBDEs and non-PBDEs. The widespread occurrence of PBDEs and non-PBDEs in floor dusts, surface soils, and locally produced foods might have caused human exposure to PBDEs and non-PBDEs in the e-waste processing area. Special attention should be paid to the levels of PBDEs and non-PBDEs in the environment, livestock, and fish in order to understand the potential human exposure to PBDEs and non-PBDEs from e-waste processing activities. To provide data on the levels of PBDEs and non-PBDEs in livestock and fish, this study measured PBDEs and non-PBDEs in the chicken and fish samples from the e-waste processing areas in northern Vietnam.

Materials and methods

Sample collection and pretreatment.

Samples of chicken and fish were collected from an e-waste processing area in Bui Dau (Cam Xa, Hung Yen province), northern Vietnam. Five samples of chicken egg, with each sample consisting of three eggs from a sampling site, five samples of chicken muscle, five samples of chicken liver, and five samples of chicken skin were purchased in January 2014. In addition to the samples of chicken, five samples of fish in a farming pond were purchased in December 2014. Fifteen samples of fish in the river that flows through the e-waste processing area in Bui Dau were collected at the same time. Following collection, the samples of chicken egg were boiled on location in a large pan for 8 minutes at 100 °C and then cooled to room temperature. The yolks of the boiled eggs were separated from albumens. The samples of chicken egg yolks, chicken muscles, chicken livers, chicken skins, and fish muscles were stored in amber glass bottles at −20 °C until chemical analysis.

Chemical analysis.

13 PBDE congeners (BDE-28, 47, 49, 99, 100, 153, 154, 183, 196, 197, 206, 207, and 209), six other BFRs (TBBPA, PBBZ, HBB, BEH-TEBP, BTBPE, and DBDPE), two DP isomers (syn-DP and anti-DP), eight m-PFRs (TCEP, TCIPP, TDCIPP, TPHP, MPDPP, EHDPP, TMPP, and TDMPP), and three o-PFRs (PBDPP, BPA-BDPP, and PBDMPP) were selected for the target analysis of PBDEs and non-

PBDEs based on results of environmental occurrence in our earlier studies[6–9], current understanding of potential replacements for PBDEs[5], health concerns[5], and analytical capability.
Following homogenization and freeze-drying, approximately 5 g of each sample was extracted using a rapid solvent extractor (SE-100; Mitsubishi Chemical Analytech Co., Ltd.) with acetone:n-hexane (1:1, v/v) mixture and toluene. The crude extract was evaporated to 10 mL and stored at 4 °C until cleanup. Two different methods were used for cleanup of the extracts. A portion of the crude extract for the measurement of PBDEs, PBBZ, HBB, BEH-TEBP, BTBPE, DBDPE, and DPs was spiked with the ^{13}C-labeled internal standards ($^{13}C_{12}$-PBDE congeners, $^{13}C_6$-HBB, and $^{13}C_{12}$-BTBPE) and was passed through a gel permeation chromatography column packed with S-X3 Bio-Beads (Bio-Rad Laboratories, Inc.) with ethyl acetate:cyclohexane (1:1, v/v) mixture. The elutate was evaporated to 0.1 mL, and redissolved in 1 mL of n-hexane. Subsequently, the eluate was passed through a glass column packed with activated florisil with n-hexane and dichloromethane, and then subjected to measurement using an electron ionization-quadrupole mass spectorometer equipped with a gas chromatography system (5973 MSD/6890 GC; Agilent Technologies Inc.) with an Agilent DB-5MS capillary column. A portion of the crude extract for the measurement of TBBPA and PFRs was spiked with four deuterium-labeled PFRs (TCEP-d_{12}, TPHP-d_{15}, TMPP-d_{21}, and TDMPP-d_9) and was evaporated to 0.1 mL and redissolved in 1 mL of acetonitrile. Subsequently, the extract was passed through a glass column packed with Discovery® DSC-18Lt (Sigma-Aldrich Corp.) with acetonitrile. The eluate was evaporated to 0.5 mL, and then subjected to measurement using an electronspray ionization-tandem mass spectrometer (Quattro Ultima; Waters Corp.) equipped with ultra-high-performance liquid chromatography system (Agilent Technologies Inc.) with an Agilent ZORBAX Eclipse Plus C18 RRHD column.

Results and discussion
All 32 FR compounds targeted in this study were detected in chicken and fish samples collected from the e-waste processing area in Bui Dau, northern Vietnam (Table 1). The concentrations of PBDEs in chicken egg yolk, chicken muscle, chicken liver, chicken skin, pond fish muscle, and river fish muscle ranged from 53−8600, 62−3500, 10−14000, 9.0−2800, <6.5−36, and 43−2300 ng/g lipid weight (lw), whereas those of non-PBDEs ranged from 80−2800, 410−5600, 70−25000, 33−4300, 160−770, and 210−4200, respectively. The levels of non-PBDEs in chicken and fish samples were comparable to those of PBDEs. The concentrations of PBDEs in chicken and fish samples varied by more than about 2−3 orders of magnitude among sampling sites (Table 1). Deca-BDE (i.e., BDE-209) was abundant among PBDE congeners in chicken and fish samples, accounting for 36−100% and 8.0−80% of the sum of PBDE congeners in chicken and river fish samples, except for those of pond fish samples. Of the investigated non-PBDEs, DPs, and TPHP were dominant in chicken samples, whereas TBBPA, DBDPE, DPs, TCEP, TCIPP, and TPHP were dominant in fish samples (Table 1). As same as the concentrations of PBDEs, those of DPs and TPHP in chicken and fish samples also varied by more than about 2−3 orders of magnitude among sampling sites. The difference among sampling sites suggests that the concentrations of PBDEs and non-PBDEs and the contribution ratios of Deca-BDE of the sum of PBDE congeners in chicken and fish samples might reflect the concentrations of PBDEs and non-PBDEs in the environments, where the chickens and fishes were raised. Our earlier studies reported that the concentrations of PBDEs, DPs, and TPHP in soils around e-waste processing workshops in January 2012 ranged from 68–9200, 0.50–65, and 11–3300 ng/g dry weight (dw) and those in river sediments around workshops at the same time ranged from 90–320, 1.0–6.7, and 4.3–38 ng/g dw, respectively. The results of this study indicate that elevated concentrations of PBDEs and non-PBDEs in the surrounding environments around the e-waste processing workshops resulted in their accumulations in locally produced foodstuffs such as meats and eggs.
According to Environmental Health Criteria of World Health Organization[10], each commercial PBDE technical formulations, Penta-BDE, Octa-BDE, and Deca-BDE has been incorporated into different polymeric materials such as high-impact polystyrene (HIPS), acrylonitrile–butadiene–styrene, wire and cable insulation, and electrical and electronic connectors, and Deca-BDE of the three PBDE technical formulations has been mainly used in HIPS of TV cabinets, TV back covers, and electrical appliance housings. Deca-BDE was mainly found in polymeric materials of e-wastes, such as Cathode Ray Tube monitors and TVs, and household appliances for high temperature applications, according to the results of a previous study investigating the presence of PBDEs in mixed plastics from waste electrical and electronic equipment[11]. According to a manual of DP reported from OxyChem[12], DPs are used as an additive for polymeric materials, such as electrical wire and cable coatings, and computer connectors. TPHP itself has been used as a flame retardant and plasticizer[13], whereas the presence of TPHP has been

confirmed as an impurity of PBDPP and BPA-BDPP technical formulations in polymeric materials of electronics housings[14]. The applications of PBDEs, DPs, and TPHP to polymeric materials in electronic products suggest that open storage of large amounts of polymeric materials along the roadsides, dismantling of printed circuit boards and electrical wires and cables outside workshops to recover noble metals in the backyard of domestic buildings, and e-waste processing-associated wastewater might contribute to elevated concentrations of PBDEs, DPs, and TPHP in chickens and fishes.
It is noteworthy that levels of o-PFRs in chicken and fish samples were 1−3 order of magnitude lower than those of PBDEs, other BFRs, DPs, and m-PFRs (Table 1), even though the concentrations of o-PFRs were higher than those of PBDEs, other BFRs, DPs, and m-PFRs in the environments around e-waste processing workshops. The results of this study indicate lower bioaccumulation potential of o-PFRs compared with other FRs. Ballesteros-Gómez et al.[15] reported that PBDPP was readily hydrolyzed and gave a variety of degradation products in hydrolysis incubation experiments. However, Jurgens et al.[16] reported that PBDPP was biodegradable, whereas BPA-BDPP was persistent based on the results of mineralization tests using activated sludge samples. Two previous studies about in vivo and in vitro metabolism of PBDPP[15,17] demonstrated that PBDPP was easily metabolized and gave a variety of degradation products. Prior to the metabolization, the potential bioaccessibility of o-PFRs might be lower than those of other FRs. However, little is known about the potential bioaccessibility of FRs, except for PBDEs and TBBPA in house dust[18]. Furthermore, our earlier reports[6,19] described that the presence and potential environmental emissions of o-PFR themselves and low molecular weight impurities should be regarded as risk factors along with processing of e-wastes. Ballesteros-Gómez et al.[20] recently reported elevated concentrations of an o-PFR impurity in indoor dust samples on and around electronics, and suggested that o-PFR impurities appear to migrate easily into the environment. However, little is known about human exposure to o-PFR themselves and impurities. Additional studies are needed to assess the actual human exposure to PBDEs and non-PBDEs in environmental and food samples.

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Table 1. Concentrations (ng/g lipid weight) of PBDEs, other BFRs, DPs, m-PFRs, and o-PFRs in chicken and fish samples collected from an e-waste processing area in Bui Dau, northern Vietnam.

	Chicken												Pond fish			River fish		
	Egg york (n = 5)			Muscle (n = 5)			Liver (n = 5)			Skin (n = 5)			Muscle (n = 5)			Muscle (n = 15)		
	Min.	Median	Max.	Min.	Median	Max.	Min.	Median	Max.	Min.	Median	Max.	Min.	Median	Max.	Min.	Median	Max.
Polybrominated diphenyl ethers (PBDEs)																		
BDE-28	<0.38	<0.38	<0.38	<3.0	<3.0	<3.0	<1.5	<1.5	<1.5	<0.38	<0.38	1.0	0.25	0.64	4.8	0.68	13	59
BDE-47	<0.38	1.0	5.0	<3.0	5.9	350	<1.5	4.0	140	1.0	3.0	440	2.2	3.8	18	7.9	71	370
BDE-49	<0.38	<0.38	1.0	<3.0	<3.0	64	<1.5	<1.5	21	<0.38	<0.38	82	0.95	1.2	4.6	1.3	17	77
BDE-99	1.0	3.0	6.0	<3.0	8.1	520	<1.5	3.0	180	<0.38	5.0	570	<0.26	<0.26	0.52	0.52	5.4	79
BDE-100	<0.38	1.0	2.0	<3.0	<3.0	45	<1.5	3.0	31	<0.38	1.0	50	<0.20	0.42	1.7	1.2	8.4	41
BDE-153	1.0	5.0	25	<6.0	15	180	<3.0	16	110	<0.75	19	170	<0.23	<0.23	<0.23	2.6	15	110
BDE-154	<0.75	1.0	2.0	<6.0	<6.0	42	<3.0	<3.0	17	<0.75	2.0	41	1.0	1.9	7.3	7.8	54	410
BDE-183	2.0	8.0	32	<6.0	6.8	81	<3.0	6.0	120	<0.75	6.0	81	<0.65	<0.65	<0.65	<0.65	2.0	75
BDE-196	1.0	20	52	<6.0	13	33	<3.0	22	46	<0.75	15	38	<1.7	<1.7	<1.7	<1.7	<1.7	7.9
BDE-197	1.0	7.0	17	<6.0	<6.0	31	<3.0	7.0	41	<0.75	7.0	30	<1.8	<1.8	<1.8	<1.8	<1.8	18
BDE-206	4.0	160	700	<15	45	66	<7.5	84	360	<1.9	49	100	<3.9	<3.9	<3.9	<3.9	<3.9	56
BDE-207	3.0	120	410	<15	100	230	<7.5	160	390	<1.9	91	170	<4.0	<4.0	<4.0	<4.0	<4.0	25
BDE-209	39	1500	7400	62	1800	3100	10	2300	13000	8.0	1000	1400	<6.5	<6.5	<6.5	8.4	73	1400
Σ13PBDEs	53	1900	8600	62	2500	3500	10	3400	14000	9.0	1700	2800	<6.5	7.8	36	43	250	2300
Other brominated flame retardants (Other BFRs)																		
TBBPA	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<15	<15	310	<15	19	190
PBBZ	0.19	0.96	1.9	<1.5	<1.5	<1.5	<0.36	<0.36	3.7	<0.5	<0.5	2.0	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
HBB	<1	1.1	2.1	<1.5	<1.5	10	<0.36	<0.36	11	<0.3	0.49	5.8	<1.8	2.2	4.1	<1.8	2.2	5.3
BEH-TEBP	<1.3	<1.3	2.0	<6.5	<6.5	<6.5	<1.5	<1.5	<1.5	<1.3	<1.3	<1.3	<33	<33	<33	<33	<33	<33
BTBPE	<2.8	18	160	<3.1	46	100	<0.7	12	130	<0.62	25	100	<7.5	<7.5	<7.5	<7.5	<7.5	<7.5
DBDPE	<2.5	<2.5	62	<7.5	<7.5	<7.5	<3.0	<3.0	<3.0	<2.8	<2.8	<2.8	<34	<34	<34	<34	37	2600
Other BFRs	<7.0	22	230	<40	46	100	<20	<20	130	<7.0	33	100	<34	<34	310	<34	96	2800
Dechlorane plus isomers (DPs)																		
syn-DP	3.4	390	560	<1.6	7.6	1400	<0.36	6.8	8100	<0.32	0.38	790	<0.19	0.38	10	2.2	130	430
anti-DP	9.1	950	1800	<1.6	26	1600	7.5	21	17000	<0.32	1.6	3000	<0.19	0.31	14	2.4	140	520
DPs	13	1300	2400	<1.6	34	3000	7.5	28	25000	<0.32	2.0	3800	<0.19	0.67	24	4.6	270	880
Monomeric organophosphorus flame retardants (m-PFRs)																		
TCEP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	29	54	85	<15	46	160
TCIPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	68	170	290	63	130	300
TDCIPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<10	21	40	12	27	79
TPHP	<7.0	240	560	350	1900	3600	60	280	330	<7.0	100	680	9.2	28	94	43	92	230
MPDPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	6.1	12	31	11	24	68
EHDPP	<7.0	<7.0	<7.0	<40	<40	62	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	<5.0	12	<5.0	<5.0	11
TMPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	12	61	11	37	94
TDMPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	<5.0	<5.0	<5.0	<5.0	7.9
m-PFRs	<7.0	240	560	410	1900	3600	60	280	330	<7.0	100	680	140	300	570	180	400	720
Oligomeric organophosphorus flame retardants (o-PFRs)																		
PBDPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	8.0	9.5	<5.0	6.1	8.2
BPA-BDPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	<5.0	5.3	<5.0	<5.0	10
PBDMPP	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	<5.0	<5.0	<5.0	<5.0	9.3
o-PFRs	<7.0	<7.0	<7.0	<40	<40	<40	<20	<20	<20	<7.0	<7.0	<7.0	<5.0	8.0	15	<5.0	6.8	18