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RESEARCH ARTICLE

Characterizing PBDEs in fish, poultry, and pig feeds manufactured in China

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Abstract

A total of 53 feeds from 23 brands for four types of animals, i.e., fish, chicken, duck, and pig, as well as six types of raw materials, were bought from Guangxi, Hubei, Anhui, and Guangdong provinces in China and analyzed for polybrominated diphenyl ethers (PBDEs). The raw materials including super fish meal, ordinary fish meal, poultry ore, soybean, stone powder, and rapeseed were selected because they were added to all the animal feeds manufactured. The occurrence of PBDEs was ubiquitous in the feeds and raw materials, with BDE-209 as the most abundant congener. The average concentration of $\sum_8$PBDE was 1.1 and 0.44 ng g^{-1} dry weight in feeds (range 0.25–5.7) and raw materials (range 0.27–0.84), respectively. No statistically significant differences in $\sum_8$PBDE concentrations were observed among the four groups of animal feeds. Feeds from Yangzhiyuan Brand ($n = 11$) contained statistically ($p < 0.01$) lower $\sum_8$PBDE concentrations than all other brands except for Baoshun Brand. Chicken was selected as a representative animal to assess health risk for human exposure to PBDEs via the consumption of chicken raised by the feeds under investigation. Hazard quotients based on per-capita consumption of chicken were all below 1, indicating low potential risk to humans consuming chicken raised with the feeds.

Keywords Polybrominated diphenyl ethers · Animal feed · Raw material · Dietary intake · Risk assessment

Introduction

Consumption of animal-derived foods in China grew rapidly, with an average per-capita fat supply increasing from 4.0 g day^{-1} in 1961 to 59 g day^{-1} in 2013 (Food and Agriculture Organiztion of the United Nations 2017). As a component of diet, food of animal origin is an important source of proteins that are beneficial for growth and development of human body (Foran et al. 2005). However, dietary intake of meat products may pose potential health risk if the foods were contaminated (Foran et al. 2005). Meat products from various regions of the world have been found to contain measurable concentration levels (0.2–23 ng/g wet weight (w/w)) of various organic contaminants (Domingo 2017; Zhou et al. 2012), including polybrominated diphenyl ethers (PBDEs; 0.013–0.19 ng g^{-1} w/w) (Gong et al. 2015).

PBDEs have been widely used as additive flame retardants in numerous commercial and household products (Alonso et al. 2012; Pirard and De Pauw 2007). They can be released to the environment during manufacture and use of PBDEs-containing products, which explains the ubiquity of PBDEs in environmental compartments, wildlife, and humans (de Wit 2002; Hites 2004). Exposure to PBDEs may result in endocrine disruption, developmental neurotoxicity, and thyroid toxicity (Bellés et al. 2010; Kim et al. 2013; Reverte et al. 2014). One of the most important pathways for human exposure to PBDEs is dietary intake of contaminated foods, especially those of animal origin (Bocio et al. 2003; Gong et al. 2015), such as fish, chicken, duck, and pig among others

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(Airaksinen et al. 2015; Cohen et al. 2005; Labunska et al. 2014; Meng et al. 2007; Su et al. 2012; Tao et al. 2017).

It is thus essential to understand the sources of PDBEs in foods of animal origin so that appropriate measures can be implemented to ensure food safety. Animal feeds were found to be one of the most important sources of organic contaminants such as PBDEs in animal products (Fernandes et al. 2016; Guo et al. 2009). For example, fish feeds were demonstrated to be the major source of PBDEs in farmed catfish from Mekong River, Vietnam (Minh et al. 2006) and farmed salmon from Southern Chile (Montory and Barra 2006). Animal feeds are often manufactured from certain types of raw materials such as fishmeal. The production of composite feeds rapidly increased from 0.85 to 200 million tons between 1991 and 2015 in China (Guo et al. 2009; Ministry of Agriculture of the People's Republic of China 2015). Yet animal feeds as an important source of PBDEs in foods have not been adequately assessed. One of the few examples is fishmeal, a raw material for animal feeds, which was found to be contaminated with organic pollutants (Karl et al. 1998). Unintentional contamination of raw materials may also partially result in feed contamination. Assessment of organic contaminants in animal feeds and their raw materials can therefore yield key information for better diagnosing the sources of organic contamination in animal-derived foods, which in turn assists the animal-farming industry in producing quality foods of animal origin. Animal feeds and feed ingredients produced in China have also been sold overseas (Huang et al. 2017; Wang et al. 2018; Workman 2018). Therefore, examining any potential contamination of animal feeds and feed ingredients on Chinese markets is of national and global importance.

The present study was designed to comprehensively investigate the occurrence and profiles of PBDEs in various animal feeds from different brands and producers in China. Super and ordinary fish meals, poultry ore, soybean, stone powder, and rapeseed for brand Yangzhiyuan obtained from Guangdong Province were also included to assess the state of PBDE pollution in feed ingredients and raw materials. A hazard quotient (HQ) model was applied to quantitatively assess the risk of human exposure to PBDEs via consumption of animals (chicken as an example) raised by the feeds under investigation.

Materials and methods

Materials

All standard compounds, including eight target BDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209, sum of which is defined as $\sum_8$PBDE), internal standards (BDE-69, 3-fluoro-2,2′,4,4′,5,6-hexabromodiphenyl ether (F-BDE-139), and 4′,6-difluoro-2,2′,3,3′,4,5,5′,6′-octabromodiphenyl ether (F-BDE-201)), and surrogate recovery standards (BDE-51, BDE-115, and 4′-fluoro-2,2′,3,3′,4,5,5′,6,6′-nonabromodiphenyl ether (F-BDE-208)), were obtained from AccuStandard (New Haven, CT, USA). Sulfuric acid was purchased from Damao (Tianjin, China). Dichchloromethane and *n*-hexane of HPLC grade were purchased from Oceanpak (Gothenburg, Sweden), and acetone of analytical reagent grade was purchased from GongDong Hing Wah Science and Technology (Guangdong, China). Bio-beads SX-3 (Bio-Rad Laboratories, Hercules, CA, USA) was purchased from AnPel (Shanghai, China). Acetone was redistilled to remove impurities in an all-glass system before use. Bio-beads were soaked in dichloromethane until use.

Sample collection

A total of 23 brands including 53 chicken, duck, pig, and fish feeds were purchased from Guangxi, Hubei, Anhui, and Guangdong provinces in China (Table 1). Zhengda, Shuangbaotai, Baoshun, and Yangzhiyuan brands are among the most popular animal feeds in China in terms of Brand Credit Index and sales volume (CNPP 2018). The remaining 19 brands with low sales volume are grouped as brand "others." Six raw materials including super and ordinary fish meals, poultry ore, soybean, stone powder, and rapeseed were commonly used for all the feeds (Berntssen et al. 2010; Torstensen et al. 2008) and obtained locally in Guangdong province (Table 1). Detailed information is presented in Table S1 of the Supplementary Material ("S" indicates tables and figures in the Supplementary Material thereafter). All samples were stored at − 20 °C until analysis.

Sample preparation

The procedures for extraction and purification of PDBEs in animal feeds and raw materials were similar to those described in our previous study (Wang et al. 2017), and only a brief introduction is given here. Samples were ground into fine powders and freeze-dried. Each sample of approximately 50 g was weighed, spiked with known amount of surrogate recovery standards (BDE-51, BDE-115, and F-BDE-208), and Soxhlet extracted for 48 h with 200 mL of hexane/dichloromethane/acetone mixture (2:2:1 in volume). An aliquot (~ 20%) of the extract was retained for lipid measurement. The remaining extract was mixed with sulfuric acid to remove lipid. The upper layer was combined and concentrated to 2 g, and further purified with a gel permeation chromatographic column padded with 6 g of Bio-beads SX-3. The column was eluted with 30 mL of hexane/dichloromethane mixture (1:1 in volume). The 15–30 mL fraction was collected and blown down with a gentle N_2 stream to 100 μL, and spiked with known amounts of internal standards (BDE-69, F-BDE-139, and F-BDE-201) before instrumental analysis.

Table 1 Background information (type, brand, factory location) on the animal feeds and raw materials from Chinese market. Super fish meal and ordinary fish meal were mainly composed of fish. Poultry ore and stone powder were mainly composed of mineral elements necessary for animals. Soybean is dried soybean. Rapeseed was residues produced by oil manufacturing which squeezes oil out rapeseed

Code	Feed	Brand	Factory Location	Code	Feed	Brand	Factory Location
A1	Small chicken	Yangzhiyuan	Guangdong	A31	Small pig	Shuangbaotai	Guangdong
A2	Medium-sized chicken	Yangzhiyuan	Guangdong	A32	Adult pig	Dabeinong	Guangdong
A3	Small chicken	Yangzhiyuan	Guangdong	A33	Small pig	Fuda	Guangdong
A4	Small chicken	Zhengda	Guangdong	A34	Medium-sized pig	Tongwei	Guangdong
A5	Adult chicken	Zhengda	Guangdong	A35	Medium-sized pig	Shuangbaotai	Guangdong
A6	Medium-sized chicken	Others	Guangdong	A36	Medium-sized pig	Shuangbaotai	Guangdong
A7	Medium-sized chicken	Zhengda	Guangdong	A37	Small pig	Jinhaihe	Guangdong
A8	Medium-sized chicken	Zhengda	Guangdong	A38	Medium-sized pig	Yifeng	Guangdong
A9	Medium-sized chicken	Zhengda	Guangdong	A39	Small pig	Yangxiang	Guangxi
A10	Small chicken	Henxing	Guangdong	A40	Small pig	Shuangbaotai	Guangxi
A11	Small chicken	Jinqian	Guangdong	A41	Small pig	Baoshun	Anhui
A12	Medium-sized chicken	Fuda	Guangdong	A42	Small pig	Zhengda	Anhui
A13	Medium-sized chicken	Jiuding	Guangdong	A43	Small grass carp	Yangzhiyuan	Guangdong
A14	Adult chicken	Baoshun	Anhui	A44	Small Tilapia	Yangzhiyuan	Guangdong
A15	Small chicken	Baoshun	Anhui	A45	Medium-sized tilapia	Shuma	Guangdong
A16	Small chicken	Xiangdaluotuo	Anhui	A46	Adult tilapia	Shihai	Guangdong
A17	Small chicken	Xiwang	Anhui	A47	Adult tilapia	Aohua	Guangdong
A18	Small chicken	Liuxin	Anhui	A48	Medium-sized tilapia	Shuma	Guangdong
A19	Small duck	Yangzhiyuan	Guangdong	A49	Adult tilapia	Shihai	Guangdong
A20	Adult duck	Yangzhiyuan	Guangdong	A50	Medium-sized tilapia	Zhengda	Guangdong
A21	Adult duck	Yangzhiyuan	Guangdong	A51	Medium-sized tilapia	Yuehai	Guangdong
A22	Medium-sized duck	Zhengda	Guangdong	A52	Adult tilapia	Zhengda	Guangdong
A23	Medium-sized duck	Xiangdaluotuo	Anhui	A53	Medium-sized tilapia	Yinong	Hubei
A24	Medium-sized duck	Xiwang	Guangxi	A54	Poultry ore	Yangzhiyuan	Guangdong
A25	Medium-sized duck	Bole	Anhui	A55	Ordinary fish meal	Yangzhiyuan	Guangdong
A26	Medium-sized duck	Xiangdaluotuo	Anhui	A56	Stone powder	Yangzhiyuan	Guangdong
A27	Small pig	Yangzhiyuan	Guangdong	A57	Soybean	Yangzhiyuan	Guangdong
A28	Medium-sized pig	Yangzhiyuan	Guangdong	A58	Rapeseed	Yangzhiyuan	Guangdong
A29	Adult pig	Yangzhiyuan	Guangdong	A59	Super fish meal	Yangzhiyuan	Guangdong
A30	Medium-sized pig	Xiwang	Guangdong				

Instrumental analysis

Sample analyses were carried out with an Agilent 7890A gas chromatograph coupled to a 5975C mass spectrometer in the electron capture negative ionization mode. A DB-5HT capillary column (15 m × 0.25 mm i.d; 0.1 μm thickness) was used for chromatographic separation. The column oven temperature was initially held at 80 °C for 1 min, programmed to 200 °C at 30 °C min^{-1} (held for 4 min), increased to 260 °C at 10 °C min^{-1} (held for 1 min), and finally ramped to 310 °C at 15 °C min^{-1} (held for 5 min). Sample injection (1 μL) was accomplished with an autosampler in the splitless/split mode. Ultrahigh purity methane was used as reagent gas and ultrahigh purity helium was used as carrier gas. The ion source and interface temperature were maintained at 200 and 250 °C, respectively. Quantitative analysis was conducted in the selected ion monitoring mode.

Quality control and quality assurance

One procedural blank, one matrix blank, two spiked blanks, and two matrix spiked samples were analyzed for each batch of 20 field samples. The recoveries of the surrogate standards, BDE-51, BDE-115, and F-BDE-208, were 94 ± 12%, 100 ± 13%, and 88 ± 18% in field samples and 93 ± 11%, 108 ± 7%, and 82 ± 6% in blank samples, respectively. The concentrations of BDE congeners in feed samples were all normalized to dry sample weights unless specially specified. The reporting limits for tetra- to octa-BDEs and BDE-209 were 0.01 and 0.1 ng g^{-1}, respectively, for 50-g dry sample weight.

Only BDE-28 and BDE-99 were detected in blank samples with average concentrations of 0.01 and 0.11 ng g^{-1}, respectively. Concentrations of PBDEs in all samples were blank corrected, but not corrected for surrogate standard recoveries.

Data analysis

Concentration levels were log-transformed and subject to an analysis of variance (ANOVA, Minitab 17.0) to investigate if there are any potential differences in levels of PBDEs among different categories of animal feeds and among different brands.

Chicken was used as an example to evaluate the risk of human exposure to PBDEs via consumption of animals raised by the feeds under investigation. The estimated daily intake (EDI; ng (kg bw)$^{-1}$ day^{-1}) of PBDEs was calculated using

$$EDI = T \times C \times R \times M/(W \times BW) \qquad (1)$$

where T is the total amount of feeds consumed by chicken (5570 g w/w) (Ministry of Agriculture of the People's Republic of China 2004); C is the concentration of a target compound in feeds (ng g^{-1} w/w; Table S3); R is the uptake rate by animals, which was defined as 80% for chicken (Pirard and De Pauw 2007); M is the per-capita consumption of chicken meat (37.8 g day^{-1}) (Food and Agriculture Organiztion of the United Nations 2015); W is the average weight of an animal species for sale (2460 g) (Ministry of Agriculture of the People's Republic of China 2004); and BW is the human body weight assumed to be 70 kg for adults.

Health risk of human exposure to PBDEs through the consumption of chicken can be evaluated by the hazard quotient (HQ) (US EPA 1989):

$$HQ = EDI/RfD \qquad (2)$$

where EDI is the estimated daily intake (ng (kg bw)$^{-1}$ day^{-1}) and RfD is the chronic oral reference dose of PBDEs established by the US EPA (Table S4) (US EPA 2014). An HQ value greater than 1 suggests potential health risk (US EPA 1989).

Results and discussion

Occurrence of PBDEs in animal feeds

BDE-209 was detected in all the animal feeds and raw materials, whereas the other seven PBDE congeners were detected at a frequency range of 11 to 79% (Table S2). No significant correlation ($p > 0.05$) was observed between lipid contents and concentrations of PBDEs in animal feeds. Consequently, all measured concentrations were normalized to dry sample weight unless specified. Concentrations (range, average, and median) of BDE-209 and $\sum_8$PBDE are summarized in Table 2.

Table 2 Detection frequencies (det., %) and concentrations (ranges, averages (ave.) ± standard errors (st. err), and medians) of BDE-209 and $\sum_8$PBDE (ng g^{-1} dry weight) in animal feeds of different brands. $\sum_8$PBDE is the sum of BDE-28, 47, 99, 100, 153, 154, 183, and 209. Concentrations below reporting limits were replaced with zero when $\sum_8$PBDE is calculated

	All (n = 53)		*Shuangbaotai (n = 4)*	
	BDE209	$\sum_8$PBDE	BDE-209	$\sum_8$PBDE
Det. (%)	100	100	100	100
Range	0.25–5.4	0.25–5.7	0.52–0.83	0.63–0.96
Ave. ± st. err	1.0 ± 0.13	1.1 ± 0.13	0.67 ± 0.075	0.81 ± 0.077
Median	0.69	0.72	0.67	0.81
	Zhengda (n = 9)		*Baoshun (n = 3)*	
	BDE209	$\sum_8$PBDE	BDE209	$\sum_8$PBDE
Det. (%)	100	100	100	100
Range	0.42–1.6	0.43–1.74	0.25–1.0	0.25–1.2
Ave. ± st. err	1.0 ± 0.16	1.1 ± 0.17	0.56 ± 0.22	0.65 ± 0.27
Median	1.1	1.2	0.45	0.53
	Yangzhiyuan (n = 11)		*Others (n = 26)*	
	BDE209	$\sum_8$PBDE	BDE209	$\sum_8$PBDE
Det. (%)	100	100	100	100
Range	0.25–0.36	0.28–0.49	0.25–5.4	0.32–5.7
Ave. ± st err	0.30 ± 0.011	0.36 ± 0.020	1.4 ± 0.22	1.5 ± 0.23
Median	0.30	0.34	1.26	1.33

The concentrations of $\sum_8$PBDE ranged from 0.25 ng g^{-1} in a pigling feed of Baoshun Brand to 5.7 ng g^{-1} in a feed for medium-sized tilapia of Shuma Brand (Table S2). The average concentrations of $\sum_8$PBDE in different brands followed the sequence of others (1.5 ng g^{-1}) > Zhengda (1.1 ng g^{-1}) > Shuangbaotai (0.81 ng g^{-1}) > Baoshun (0.65 ng g^{-1}) > Yangzhiyuan (0.36 ng g^{-1}) (Fig. 1). Animal feeds of Yangzhiyuan Brand contained statistically lower $\sum_8$PBDE levels than others, Zhengda, and Shuangbaotai brand (Fig. 1; ANOVA, $p < 0.01$). This result is beneficial for farmers and producers as they can choose less contaminated feeds. Higher concentrations of $\sum_8$PBDE were found in fish feeds (0.31–5.7; average 1.7 ng g^{-1}), followed by chicken feeds (0.28–3.0; average 1.2 ng g^{-1}), pig feeds (0.25–2.1; average 0.90 ng g^{-1}), and duck feeds (0.34–0.83; average 0.53 ng g^{-1}). The concentrations of $\sum_8$PBDE were not significantly different among different feed types (Fig. 2; ANOVA, $p > 0.05$) but were statistically higher in fish and chicken feeds than in duck feeds when pig feeds were excluded (Fig. 2). Categorized based on sampling locations, 10 animal feeds were from Anhui, three from Guangxi, one from Hubei, and the rest from Guangdong province. The concentrations of $\sum_8$PBDE were not significantly different among feeds manufactured in different provinces. This conclusion was preliminary because sample size from all provinces except for Guangdong was limited. Further investigations are necessary

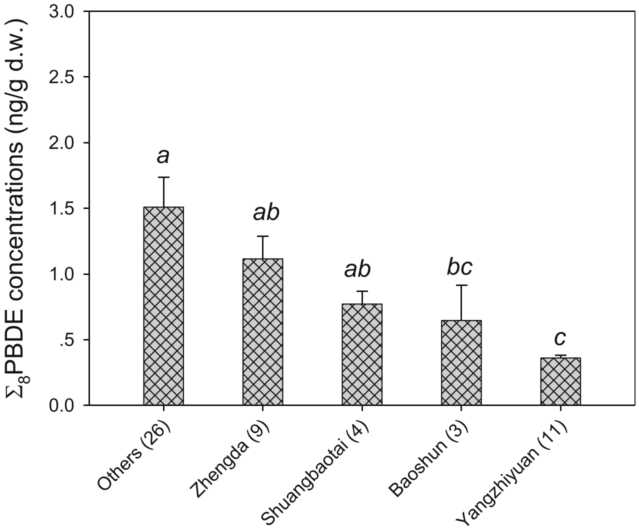

Fig. 1 Concentrations (averages ± standard errors; ng g^{-1} dry weight) of $\sum_8$PBDE (sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) in different brands of animal feeds. The ANOVA results are shown as letters *a*, *ab*, *bc*, and *c* above each bar. $\sum_8$PBDE concentrations which do not share a letter are significantly different from one another ($p < 0.01$)

to comprehensively understand the contamination pattern of animal feeds nationwide.

Concentrations of $\sum_8$PBDE in fish feeds measured in the present study (3.5–77; average 22 ng (g lipid)$^{-1}$) were higher than those found in aquaculture feeds (0.12–7.0; average 2.7 ng (g lipid)$^{-1}$) from Vietnam (Minh et al. 2006) and salmon feeds (8.1–23.9; average 16.6 ng (g lipid)$^{-1}$) from Scotland (Jacobs et al. 2002), but much lower than those in marine compound feeds (4.2–230 ng (g lipid)$^{-1}$), freshwater compound feeds (29–150 ng (g lipid)$^{-1}$), and trash fish (7.2–160 ng (g lipid)$^{-1}$) from South China (Guo et al. 2009). The concentrations of PBDEs on a w.w. basis (0.22–5.1; average 0.97 ng g^{-1}) in animal feeds analyzed in the present study were within the range of salmon feeds (0.49–10.9 ng g^{-1} w.w.) purchased from global suppliers (Hites et al. 2004) and comparable to those found in fish feeds from the UK (1.21–4.46; average 2.25 ng g^{-1} w.w.) (Fernandes et al. 2016) and from Germany (1.1–2.2 ng g^{-1} w.w.) (Suominen et al. 2011) but lower than those found in traditional salmon feeds from Norway (7.3 ng g^{-1} w.w.) (Berntssen et al. 2010). In summary, PBDEs in fish feeds of various brands in China were at the middle level of the global range.

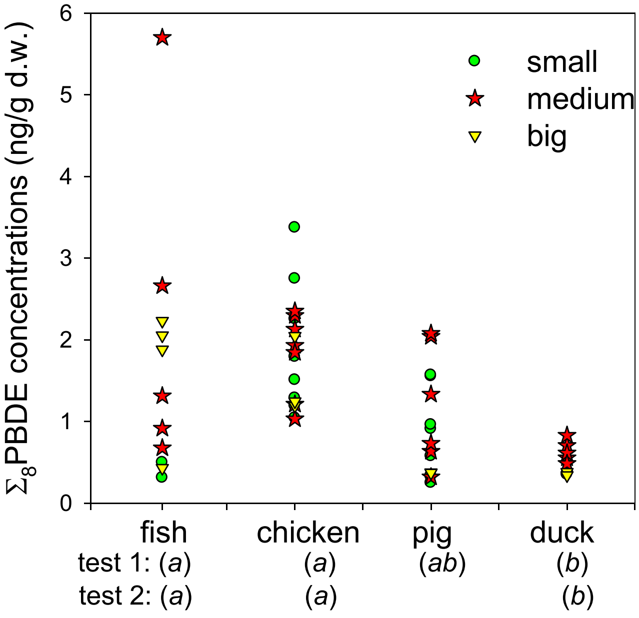

Fig. 2 $\sum_8$PBDE (sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) concentrations (ng g^{-1}) in different types of animal feeds. Letters *a*, *ab*, and *b* indicate the ANOVA results. *Test 1* includes all the four types of animal feeds ($p = 0.058$) and *test 2* excludes pig feeds ($p = 0.043$). Legend small, medium, and big means feeds for different sizes of animals

Concentrations of $\sum_8$PBDE in chicken feeds (0.28–3.0; average 1.2 ng g^{-1}) in the present study were comparable to those in chicken feeds purchased from selected markets in South China (average 1.26 ng g^{-1}) (Zheng et al. 2015), much lower than those in grains (average 13.7 ng g^{-1}) from an e-waste recycling site (Luo et al. 2009). However, the difference was not statistically significant, probably due to small sample sizes. $\sum_8$PBDE concentrations in feeds for chick (1.28 ng g^{-1}), medium-sized chicken (1.20 ng g^{-1}), and adult chicken (0.82 ng g^{-1}) were not statistically different between each other (ANOVA, $p > 0.05$). Similarly, no statistical differences were found for $\sum_8$PBDE concentrations in size-specific fish feeds, pig feeds, and duck feeds (Fig. 2). This lack of statistical significance among size-specific feeds may also be partially due to the limited sample sizes.

Occurrence of PBDEs in raw materials of feeds

Feed ingredients are one of the major sources of organic pollutants in animal feeds, a public health concern required to be addressed (Ábalos et al. 2008; Berntssen et al. 2010; Suominen et al. 2011). To further examine the contributions of raw materials to PBDEs in animal feeds, raw materials commonly used for almost all the feeds were analyzed for PBDEs (Table S2). The average concentrations of $\sum_8$PBDE in super fish meal, ordinary fish meal, poultry ore, soybean, stone powder, and rapeseed were 0.84, 0.48, 0.42, 0.31, 0.29, and 0.27 ng g^{-1}, respectively, which were lower than those in animal feeds (0.25–5.7 ng g^{-1}). A previous study also found that PBDE concentrations in raw materials (0.11–0.82 ng g^{-1}) were lower than those in animal feeds (0.19–9.63 ng g^{-1}) in the UK (Fernandes et al. 2016). Concentrations of PBDEs normalized to w.w. (0.26–0.74, average 0.38 ng g^{-1}) in raw materials measured in the present study were higher than those in fish meal from Peru (0.068 ng g^{-1} w.w.), plant oil mix from Denmark (0.096 ng g^{-1} w.w.), krill from Norway (0.047 ng g^{-1}), and plant meal from Norway (0.11 ng g^{-1} w.w.) (Berntssen et al. 2010).

Compositional profiles

BDE-209 was the most abundant congener in both animal feeds and raw materials, accounting for 65–100% (average 90%) and 60–100% (average 82%) of $\sum_8$PBDE concentrations in animal feeds and raw materials, respectively. This compositional profile (Fig. 3) agreed well with the fact the Deca-BDE commercial mixture has been most widely used in China (Ni et al. 2013). The profiles of PBDEs in the present study were different from those in trash fish, which were predominated by low-brominated BDE congeners (Guo et al. 2009). Previous studies indicated that the uptake of PBDEs with high log K_{ow} (log-normalized octanol–water partitioning coefficients; > 7) was relatively inefficient, whereas low-brominated BDEs were readily bioaccumulated in fish species (Braekevelt et al. 2003; Giulivo et al. 2017), which was corroborated by the higher abundances of lower brominated BDE congeners in trash fish (Guo et al. 2009).

Compositional profiles of PBDEs in feeds and raw materials in the present study were similar to those in marine compound feed, which were dominated by heavily brominated BDE congeners (Guo et al. 2009). This might be because that compound feeds for different animals were manufactured with similar raw materials of different proportions. Compared to aquatic organisms, terrestrial plants have contact with a more variety of environmental media and access to higher brominated diphenyl ethers, such as BDE-209 (Luo et al. 2013). Raw materials are mainly consisted of terrestrial plants, e.g., corn, rapeseed, and soybean meal, which have been found to contain low concentrations of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183 (Berntssen et al. 2010). Both the present study and a previous report (Fernandes et al. 2016) obtained relatively lower concentrations of PBDEs in raw materials than in animal feeds, suggesting external sources such as those incurred during feed manufacturing processes would probably result in increased concentrations of PBDEs in animal feeds.

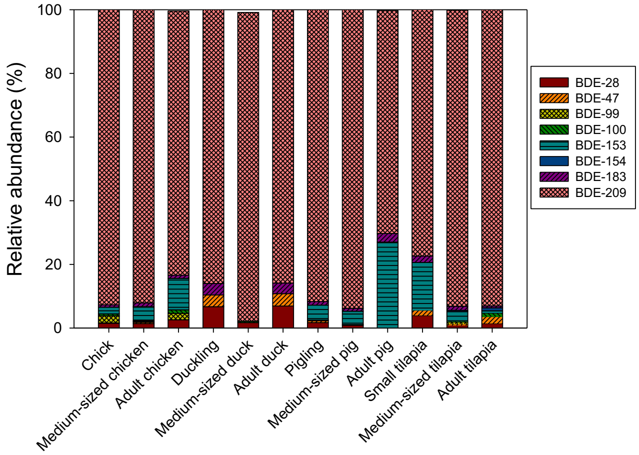

Fig. 3 Relative abundances (%) of BDE congeners in chicken, duck, pig, and fish feeds

Feed manufacturing mainly involves blending, mixing, sterilizing, drying, secondary mixing, and packaging. As a result, PBDEs may enter into manufactured feeds not only from raw materials but also from ambient sources such as air and water during manufacturing processes (Liu et al. 2016; Yang et al. 2015). This scenario may have resulted in varying concentrations of PBDEs in feeds manufactured in different countries (Fernandes et al. 2016). Further investigations of external contamination during feed manufacturing processes are needed.

Human health risk assessment via consumption of chicken

Food consumption has been regarded as the dominant source of human exposure to PBDEs (Kang et al. 2010; Ni et al. 2012). Pork and poultry account for 71 and 74% of meat consumption in developing and developed countries, respectively (Delgado 2003). Poultry consumption was expected to grow at a rate of 3.9% per annum through 2020 in developing countries (Delgado 2003). Statistical data compiled by the Food and Agriculture Organization of the United Nations indicated that chicken meat accounted for up to 80% of the dietary intake of poultry meat around the world (Food and Agriculture Organization of the United Nations n.d.). Therefore, chicken were used as a representative animal to assess exposure risks of PBDEs via food intake with Eqs. 1 and 2. In general, the HQ value of a specific chemical lower than 1 is considered to be free of risk for that chemical and vice versa. In the present study, the hazard quotient values of $\sum_8$PBDE through consumption of chicken raised by animal feeds under investigation were far lower than 1 (6×10^{-5} to 1.1×10^{-3}; Table S5). In our previous study (Wang et al. 2017), chicken were fed with one of the frequently purchased chicken feeds investigated in the present study. Chicken were dissected after 50 days of dietary exposure and analyzed for $\sum_8$PBDEs (Wang et al. 2017). The HQ values of $\sum_8$PBDE for adults via the consumption of chicken leg and breast meat were estimated to be 9.6×10^{-4} and 8.2×10^{-4} (Table S6) (Wang et al. 2017). Obviously, HQ values of $\sum_8$PBDE derived from “real” PBDEs levels in chicken (Table S6) agreed well with those in the present study (Table S5). Apparently, the consumption of chicken raised by the feeds under investigation poses low health risks to consumers. It should be noted that chicken may not be the sole source of human exposure to PBDEs. The combination of chicken with other food items would generate higher HQ values and therefore higher health risk. Control measures to reduce health risk include eliminating any pollutants from feeds and feed ingredients and improving feed manufacturing processes.

Measures to ensure the safety of animal feeds

Animal feed safety is crucial for ensuring food security. Some control measures are outlined below. Two aspects should be taken into account to ensure the safety of animal feeds, i.e., quality of raw materials, and production, packaging, and transportation of feeds. The employment of raw materials free of pollutants is one of the most crucial measures to ensure feed safety. As crops can uptake pollutants from contaminated soils (Huang et al. 2011), farmers should use non-polluted areas for cultivation of plants commonly used as ingredients of animal feeds, including corn, soybeans, and rapeseeds, among others. Local governments and fishmeal suppliers should work together to ensure that non-polluted fish meals are used by manufacturing factories. Feed manufacturing factories should routinely monitor the occurrence of pollutants (e.g., PBDEs) in both domestic and imported raw materials before they can be used. Decontamination technologies should be developed and/or enhanced to reduce pollutant contents in raw materials and feeds. Certain pretreatment methods can be employed to lower pollutant concentrations in feeds and feed ingredients prior to manufacturing. It has been reported that activated carbon (Usydus et al. 2009), supercritical CO_2-extraction (Kawashima et al. 2009), enzymatic treatment (Baron et al. 2007), and short-path distillation technology (Olli et al. 2010) can efficiently reduce the content of organic pollutants, such as PBDEs, polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) in fish oil and fish meal. Finally, external sources, such as air, water, equipment, packaging, distribution, and storage, may introduce PBDEs into feeds. Hence, manufacturing procedures should be conducted with equipment free of contamination in clean environments and use of uncontaminated water. Releases of pollutants from packaging materials also contributed partially to food contamination (Grob et al. 2006; Triantafyllou et al. 2007). Concerted efforts should be directed toward reducing contamination of feeds and raw materials from packaging materials during packaging, distribution, and storage.

Conclusion

The present study presents a detailed dataset and comprehensive analyses of PBDEs in different types of animal feeds and raw materials. PBDEs were detected in all samples of feeds and ingredients, demonstrating the ubiquity of PBDEs, and BDE-209 was the most dominant congener. Concentrations of PBDEs in feeds of low sales volume brands were statistically higher than those of frequently purchased brands. No statistical differences were observed in the concentrations of PBDEs among feeds for fish, chicken, duck, and pig. In addition, the concentrations of PBDEs were greater in feeds than in raw materials, implicating additional sources contributing to the loadings of PBDEs in animal feeds. Health risk assessment with chicken as an example demonstrated that consumption of chicken raised by the feeds under investigation posed low potential risks to consumers. Nevertheless, animal feed safety is crucial for ensuring food security. In all, more concerted efforts should be made to enhance and employ the technologies of decontamination of feeds and raw materials during feed manufacturing processes.

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