Assessment of polybrominated diphenyl ethers in East Asian finless porpoises from the East China Sea

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Highlights:

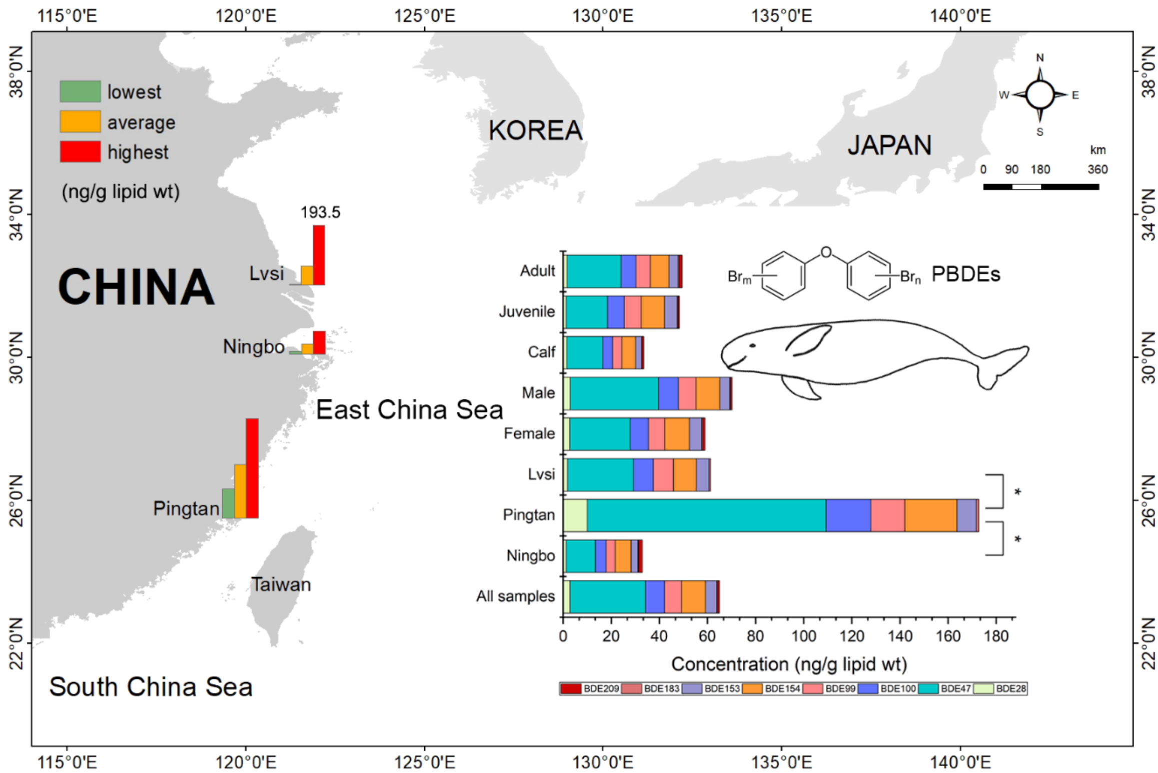
a. PBDE levels were firstly measured in East Asian finless porpoise blubbers from the East China Sea.

b. BDE47 was the highest concentrated congener detected in this study.

c. The contaminant levels showed significant spatial variations in distribution.

d. Combined risk assessments suggested that porpoises had a low health risk from PBDEs.

18 **Graphical Abstract** (colour printing)**:**



19

Abstract:

Despite that certain polybrominated diphenyl ethers (PBDEs) have been banned for years, PBDEs still have the potential to cause harm to marine fauna, due to their persistence and bioaccumulation features. East Asian finless porpoises (EAfps) are one of the most threatened coastal cetaceans in the East China Sea (ECS). As apex predators, they are also marine ecosystem sentinels. In this study, fifty-six blubber tissue samples from EAfps in the ECS were collected during 2009-2011. Eight typical PBDEs (BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209) were screened using gas chromatography/mass spectrometry methods. This study represents the first attempt to explore the PBDE accumulation characteristics in finless porpoises in this region. All congeners targeted were detected in our analysis, and the concentration of ΣPBDEs ranged from 2.2 ng/g to 321.4 ng/g, which was lower than the concentration in other populations and in most other cetaceans. BDE 47 was the major congener, representing ~48.3 % of the ΣPBDEs in all samples, followed by BDE154, BDE100 and BDE99. The abundance of PBDEs in the Pingtan porpoise (172.8 ng/g) was significantly larger than in Lvsi (61.2 ng/g) and Ningbo (32.9 ng/g). Pearson correlation analysis showed a significant relationship between body length and the PBDE concentration in the male group. We propose that porpoises had a low health risk from the studied PBDEs according to our combined risk assessments. However, long-term surveillance of the EAfps is still necessary due to their long-time exposure to PBDEs, which are not completely banned.

Keywords: health risk; polybrominated diphenyl ether; the East Asian finless porpoise; the East China Sea

1. Introduction

In the past decades, the exposure of persistent organic pollutants (POPs) in the marine environment has become a serious anthropogenic threat to the survival and the sustainability of cetacean populations (Hall et al. 2006, Yordy et al. 2010b). Polybrominated diphenyl ethers (PBDEs) are well-known POPs that exist widely in the environment and biota along with organochlorine pesticides and polychlorinated biphenyls (Hu et al. 2008). PBDEs have been widely used in industrial products, such as electronic materials, plastics and consumer products, since they are excellent flame retardants (De Wit 2002). However, the health hazards of these chemicals have also attracted increasing scrutiny due to the evidence of their hormone-disrupting effects and carcinogenicity. PBDEs are present widely in coastal and offshore environments and in aquatic mammals in China (Xian et al. 2008, Lam et al. 2009, Li et al. 2012, Lin et al. 2012). The extensive concentration of PBDEs found in the Chinese environment and human breast milk has raised concern as well (Li et al. 2008, Shi et al. 2013).

Cetaceans occupy top trophic positions and have a long lifespan. High concentrations of lipophilic POPs are generally prone to accumulate in the thick subcutaneous lipid layer of cetaceans (Moon et al. 2010, Yordy et al. 2010a, Alonso et al. 2014, Pinzone et al. 2015), thus cetacean blubber is a useful agent for monitoring contaminants. Bioaccumulation of organic pollutants in cetaceans off China coastal waters has been partially reported (Ramu et al. 2005, Hung et al. 2006, Gui et al. 2014a, b, Zhu et al. 2014, Zeng et al. 2015). In China, the East Asian finless porpoise (EAfp, *Neophocoena sunameri*), one of three finless porpoises species (Zhou et al. 2018), is distributed widely in the north of the South China Sea, East China Sea (ECS) and Yellow Sea. It has been classified as “Vulnerable” in the IUCN (the International Union for Conservation of Nature and Natural Resources) Red List of threatened species. Assessment research of the POPs exposure in finless porpoises has been conducted in Japan, Korea, South China and Hong Kong coastal waters (Ramu et al. 2006, Park et al. 2010, Isobe et al. 2011, Zhu et al. 2014). However, the accumulation characteristics and effects of PBDEs on finless porpoises of ECS have not been reported yet.

The objectives of this study were to: 1) establish an analytical method to detect PBDEs in the blubber of the EAfps from the ECS, 2) to examine the PBDE concentrations in relation to sex, age, region, and body length, and 3) to evaluate porpoise health risks from PBDEs through multiple risk assessments.

2. Materials and Methods

2.1 Sampling collection

A total of 56 porpoise specimens were collected in Lvsi, Ningbo, and Pingtan from the ECS, which is the routine habitat of the porpoises. All porpoises were accidentally killed during fishing activities or stranded dead from 2009 to 2011. The body length of the collected porpoises was measured (Table 1). The necropsies of porpoises were performed, and the blubber samples were taken to be wrapped in tinfoil and stored at -

20 °C until further analysis.

2.2 Chemicals

The eight authentic PBDE (BDE28, 47, 99, 100, 153, 154, 183 and 209) standards plus BDE77 and BDE118 were obtained from AccuStandard, Inc. (NewHaven, CT, USA). Anhydrous sodium sulphate Na_2SO_4, NaCl, concentrated sulfuric acid H_2SO_4, hexane, acetonitrile and isopropanol of analytical grade were purchased from the Shanghai Chemical Company (Shanghai, China), and ^{13}C-PCB28, ^{13}C-PCB114, ^{13}C-BDE118 and ^{13}C-BDE209 were purchased from Cambridge Isotope Laboratories, Inc. of the USA. ^{13}C-PCB28, ^{13}C-PCB114 and ^{13}C-BDE118 were used as surrogates, and ^{13}C-BDE209 was used as an internal standard.

	Pingtan	Ningbo	Lvsi	All samples
Sampling years	2010	2009-2011	2009	2009-2011
Sample numbers (male/female)	9 (6/3)	28 (15/13)	19 (9/10)	56 (30/26)
Age groups (Calf/Juvenile/Adult)	1/1/7	13/9/6	1/7/11	15/17/24
Body length (m)	116.9 (84.5~160.0)	114.7 (64.8~153.5)	140.0 (76.0~187.5)	123.6 (64.8~187.5)

Table 1. Biometry of the finless porpoise populations in the three offshore areas.

2.3 PBDEs determination and quality control

PBDEs in the blubber samples were detected in accordance with EPA 8270d. The details are described below.

2.3.1 Sample extraction

After thawing and homogenization, 2-5 g of the blubber sample were accurately weighed and placed in a centrifuge tube with a lid. Then, 40 mL of n-hexane/isopropanol (1:1) mixed solvent were added to the tube, which was shaken vigorously for 2 hours. The sample was centrifuged at 3500 rpm for 10 min, and the solvent was transferred to the second centrifuge tube. Thirty mL n-hexane/isopropanol (1:1) mixed solution were added to the centrifuge tube for repeating extraction, and the two extracts were merged. Then, 20 mL of 0.5 % NaCl solution was added to the second tube, and the extraction was performed by shaking and centrifugation, respectively. Finally, the extract in the n-hexane phase was collected and dried with anhydrous sodium sulphate.

2.3.2 Fat determination of the samples

The above extract was transferred to the weighed flat-bottomed flask, evaporated by rotary evaporation with a temperature $\leqslant$ 35 °C, and concentrated to near dry. With the assistance of nitrogen gas blowing, the weight of the extract sample was nearly constant by multiple weighing, so the fat content in the sample was determined by the percentage or weight.

2.3.3 Sample purification

Due to the high ratio fat content in the blubber samples, a 0.5 g fat sample was weighed and placed in a glass tube. After adding 20 ng of BDE118 and ^{13}C-BDE209 (standards for purification process), the fat sample was dissolved in 2 mL n-hexane, and then 2 mL concentrated sulfuric acid was added to remove the fat with careful shaking of the glass 2-3 times (1~2 min each). After the mixture stood for a few minutes, it was centrifuged at 2500 rpm for 10 minutes, and the acid solution was discarded. The extract in n-hexane was treated with concentrated sulfuric acid 2-4 times until the colour of the added acid did not change. The organic phase was then transferred to a glass tube, and the acid was not transferred to the new glass tube.

Approximately 1.5 mL of the above organic phase was added to 0.8 mL of acetonitrile solution saturated with n-hexane, which was fully shaken and centrifuged at 2000 rpm for 5 min. This step of the extraction was repeated twice, and the extracts in acetonitrile were transferred to a sample bottle. Then, the acetonitrile extract was blown slightly when dried with nitrogen gas. Twenty nanograms of BDE77 and PCB209 (standards for sample analysis) were added to the sample bottle, and the total volume was brought to 0.1 mL with n-hexane. The lid of the sample bottle was screwed shut, and the samples were stored at 4 °C before analysis.

2.3.4 Quality control

There were four ways to ensure the measurement quality: 1) a blank experiment, to determine if the test process has a significant influence on the results; 2) a parallel experiment, to examine the stability of the analysis method and operation and to lower down the error rate; 3) a recovery experiment, to determine whether the method could be directly employed. When the rate is <50 % or ＞130 %, the measurement would be corrected based on the difference; and 4) internal standard experiment, to obtain the response of the native compound corrected against the response of the respective internal standard. In general, the recoveries of spiked internal standards of PBDEs are higher than 60 % and lower than 130 %, which is satisfactory for quality control. The detailed processes for quality control have been described in the Supplementary materials (Suppl) S 1.

2.3.5 Sample analysis

High resolution gas chromatography-mass spectrometry (GC-MS, Agilent 7890A GC/Jms-Q1000GC) was used to quantify the target compounds in this study. A 30-m-long DB-5MS (Agilent, USA) column with a 0.25-mm internal diameter and 0.25-μm film thickness was used. Ultrapure helium (99.999 %) was used as the carrier gas with a constant flow rate of 1.0 mL/min. The injection volume was 1.0 μL. The temperatures of the splitless injector and transfer line were set at 280 °C and 300 °C, respectively. The oven temperature was programmed as follows: initial temperature set at 80 °C for 2 min, ramping at 20 °C/min to 150 °C and ramping at 5 °C/min to 300 °C holding for 10 min. The total running time was 40 min, and the volume injected into the injector was 1 μL. Based on the standard addition recoveries, including the blank addition, sample addition and calibration curves of PBDEs, the targeted PBDEs were measured.

2.4 Statistical analysis

We examined the difference of PBDE concentrations in males and females using an independent samples t-test, LSD and Bonferroni tests were conducted to determine the relationship between contaminant levels and age (calf, juvenile and adult), and a Kruskal Wallis test was used to examine the difference in pollutant levels in Pingtan, Ningbo, and Lvsi samples. The data for the age classified groups were transformed by Log function. Principal component analysis (PCA) was used to interpret the relationship between the contamination in the blubber and geographical locations, and data from all eight congeners in each sample individual were included in the PCA. A Pearson's correlation test was applied to analyse the pairwise correlation between finless porpoise body length and PBDE concentrations in female samples, male samples, and all samples group. Three age stages were classified according to the body length method proposed by Gao and Zhou (1993), i.e., for males: body length (cm) $\leqslant$ 117 (calf), 117-134.5 (juvenile), $\geqslant$ 134.5 (adult); for females: body length (cm) $\leqslant$ 117 (calf), 117-136 (juvenile), $\geqslant$ 136 (adult). A Spearman correlation matrix was applied to test the inter-correlation of BDE congeners. The above statistical analysis was performed in SPSS version 24.0 and RStudio.

2.5 Risk assessment

Equation (1) and (2) were used to assess the PBDE toxicity in finless porpoises through test animal thresholds. The Lowest Observed Adverse Effect Level (LOAEL) and No Observed Adverse Effect Level (NOAEL) (Sample et al. 1996) were applied to estimate the toxic hazards caused by PBDEs in finless porpoises, and the functions were derived as follows (the health risk from PBDEs is deemed to be potentially present if the PBDE levels in finless porpoises are above the $NOAEL_d$):

$$LOAEL_d = LOAEL_t \left(\frac{BW_t}{BW_d}\right)^{1/4} \qquad (1)$$

$$NOAEL_d = {}^{LOAEL_d}/_{10} \qquad (2)$$

Furthermore, the health risk through the food chain is also estimated here (Equation (3) and (4)), RQ (Risk Quotient, Hung et al. 2004) is derived as an assessment value, if RQ＞1, indicating that there may be toxic effects from PBDEs, and the relative equations are:

$$MAC_{diet} = \frac{NOAEL_d \times BW_d \times AT}{IR \times FI \times EF \times ED} \qquad (3)$$

$$RQ = \frac{Concentration\ of\ PBDEs\ in\ prey}{MAC_{diet}} \qquad (4)$$

where $LOAEL_d$ ($mg/kg \cdot day^{-1}$) = daily dose levels normalized to the body weight of the dolphin, $LOAEL_t$ ($mg/kg \cdot day^{-1}$) = daily dose levels normalized to the body weight of the test animal, BW_t (kg) = the body weight of the test animal, BW_d (kg) = the body weight of dolphin, only adult body weight value was used in this study for the convenience of calculation, MAC_{diet} (mg/kg) = maximum allowable concentration of PBDEs from diet, AT (day) = average time under exposure, IR (kg/day) = ingestion rate, FI = fraction ingested, EF (days/year) = exposure frequency, ED (year) = exposure duration, RQ = risk quotient. The PBDE data of the test animal is referenced from mice (Sample et al. 1996), and the parameters used in this study are shown in Suppl Table S 2.1.

3. Results and Discussion

3.1 PBDE congener profiles in finless porpoises

All eight BDE congeners were detected in the blubber samples. The total concentrations of the eight BDEs (ΣBDEs) was 65 ng/g lipid wt, on average, ranging from 2.2 to 321.4 ng/g lipid wt (Table 2). The samples from Pingtan showed the highest PBDE concentration, with 172.8 ng/g lipid wt, and those from Ningbo accumulated the least.

In the eight detected BDE homologues, BDE47 had the highest bioaccumulation of congeners in the three regions, followed by BDE154, BDE100 and BDE99 (Table 2, Fig. 3). The bioaccumulation concentration of BDE47 accounted for approximately 48.3 % of the total BDE concentration.

The coastal ECS region is the most industrialized area in China, and there are many light industry-related (such as furniture, textile and electronics) factories. BDE47 is one of the most important penta-products of PBDEs, it is generally used in flame retard polyurethane foams in furniture, carpet underlay and bedding (Alcock et al. 2003, Li et al. 2012). Other research work also indicated that BDE47 has become the main homologous pollutant of PBDEs on a global scale for the marine environment (Lee and Kim 2015). Our result implies that the contamination of BDE47 may be a result of e-wastes from the wide ranging penta-PBDE-using factories in the ECS region, especially in Fujian province.

It should be noted that highly brominated BDEs are easily debrominated to lower brominated congeners by a photocatalytic reduction, while lower brominated congeners are more difficult to reduce because of their low electron affinity (Lei et al. 2016a, Lei et al. 2016b), which might be the reason that BDE47 (a moderately brominated congener) had the highest accumulation in this study, while BDE183 (a higher brominated congener) had the lowest accumulation. BDE-47, BDE-153, and BDE-154 congeners were also detected in fishes from ECS (Wang et al. 2007), and they were predominant in fish samples (Peng et al. 2007), indicating that PBDEs accumulated in finless porpoises through the food chain.

	Lowest (ng/g)	Highest (ng/g)	Mean (ng/g)
BDE28	0	20.5	2.8
BDE47	0	196.9	31.4
BDE100	0.4	35.4	7.9
BDE99	0	34.6	7
BDE154	0	48.9	10
BDE153	0	41.3	4.5
BDE183	0	2.3	0.5
BDE209	0	16.7	0.8
ΣPBDEs (Pingtan)	94.8	321.4	172.8
ΣPBDEs (Ningbo)	8.4	74.8	32.9
ΣPBDEs (Lvsi)	2.2	193.5	61.2
ΣPBDEs (All samples)	2.2	321.4	65

Table 2. PBDE levels in the East Asian finless porpoise in this study.

3.2 Regional comparison of PBDE concentrations

The highest mean concentration of PBDEs from finless porpoises in Pingtan was 172.8 ng/g, followed by Lvsi samples (61.2 ng/g) and Ningbo samples (32.9 ng/g). The abundance of BDE47 and BDE28 in Pingtan samples was dramatically greater than those from Lvsi and Ningbo (Fig. 3). The PCA results showed that PC1 accounted for 64.8 % of the total variance, PC2 consisted of 14.3 %, and PC3 consisted of 11.4 %. PC1 had positive associations with all of the congeners except BDE209. This indicated that BDE209 may have a different source. PC2 had the strongest positive correlation with BDE28, while it had the strongest negative correlation with BDE209. PC3 had the strongest negative correlation with BDE209 and BDE28. In addition, samples from Lvsi and Ningbo generally merged on the plot, and the Pingtan cluster was isolated from the other two clusters (Fig. 1). The Kruskal Wallis test showed that the PBDE concentration in Pingtan porpoises is significantly greater than porpoises from Lvsi ($P < 0.05$) and Ningbo ($P < 0.001$), yet no such difference between Ningbo and Lvsi samples was found ($P > 0.05$).

In our study, the highest ΣPBDEs bioaccumulation concentration in ECS finless porpoises was significantly lower compared with those of finless porpoises reported in Hong Kong (Ramu et al. 2006), Korea (Bukyeong et al. 2010) and Japan (Isobe et al. 2011, Nomiyama et al. 2011) (Fig. 2). In comparisons with other global cetaceans, the finless porpoise had a lower concentration level. The harbour porpoise from the UK (Law et al. 2002), the bottlenose dolphin and false killer whale from the USA (Fair et al. 2010, Bachman et al. 2014), the Indo-Pacific humpback dolphin from Hong Kong (Kajiwara et al. 2006) and the Beluga (Pinzone et al. 2015) showed much higher PBDE levels (＞1000 ng/g) than those found in this study. The variations of PBDE levels could be affected by both biotic factors (prey distribution, reproductive status) and abiotic factors (species, food habitat, geographical variation, and source and use of contaminant). Some research documented that the sediment in ECS had a low level of PBDE contamination between 2010 – 2011 compared with other nations / regions, and concentrations in ECS were lower than those in 2006 - 2007 as well (Li et al. 2012, Wang et al. 2016). The occurrence of this phenomenon might be ascribed to the local restriction on using PBDEs and the dilution/diffusion effects of former contaminants by marine currents (Salvado et al. 2012). In our work, the PBDE levels in Pingtan samples were significantly higher than those in Lvsi and Ningbo, yet no latitudinal differences in PBDE abundance in the marine sediments were found along the coast of ECS (Li et al. 2016, Wang et al. 2016). We speculate that this is related to pollutant usage, porpoise foraging habits, prey distribution, and individual metabolism rate.

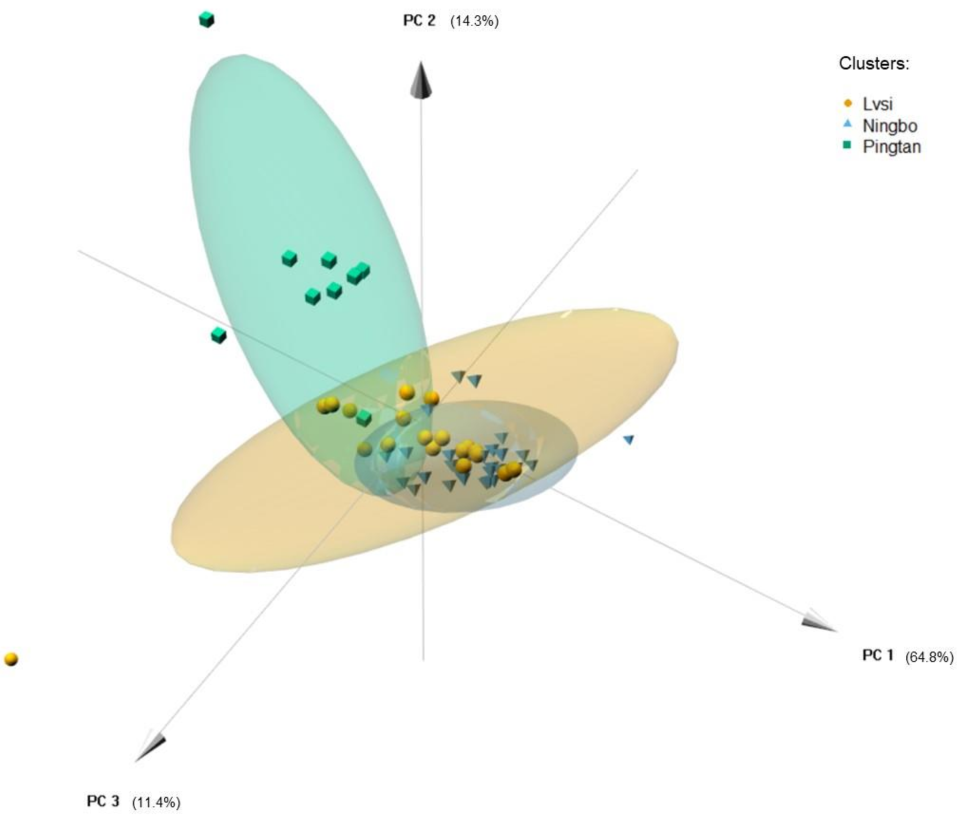


Fig. 1. Plot of the first three principal components after PCA of the analysed PBDE congeners in the blubber of finless porpoise from Lvsi, Ningbo and Pingtan. (colour printing)

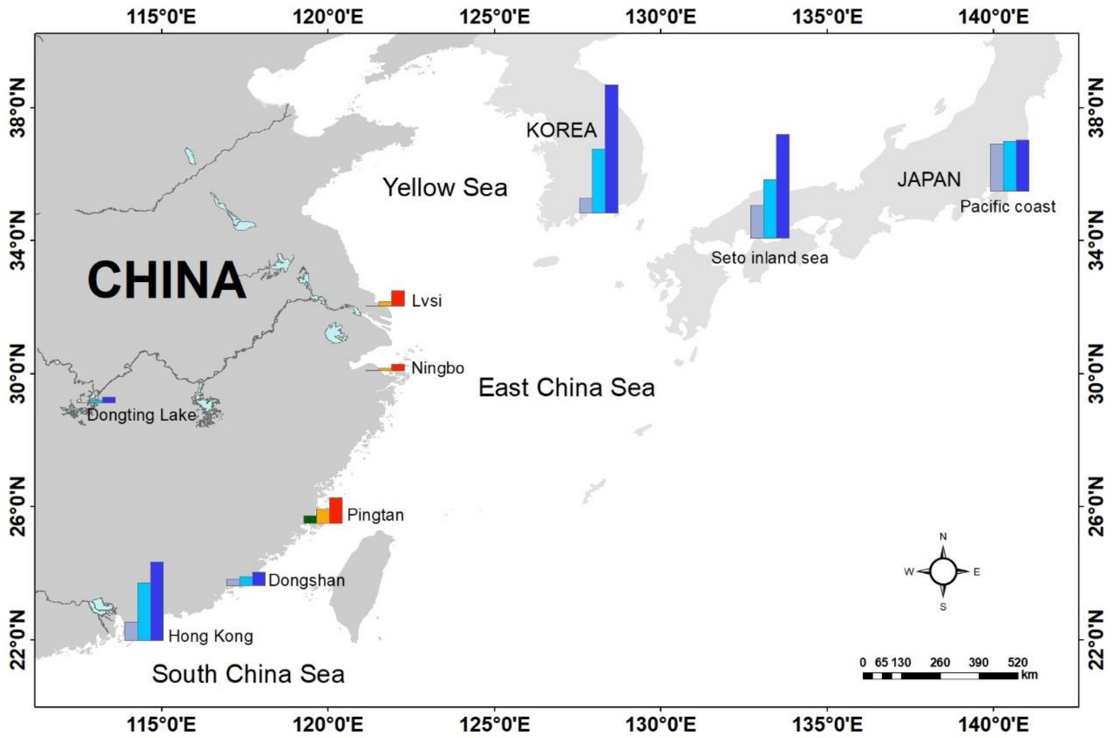
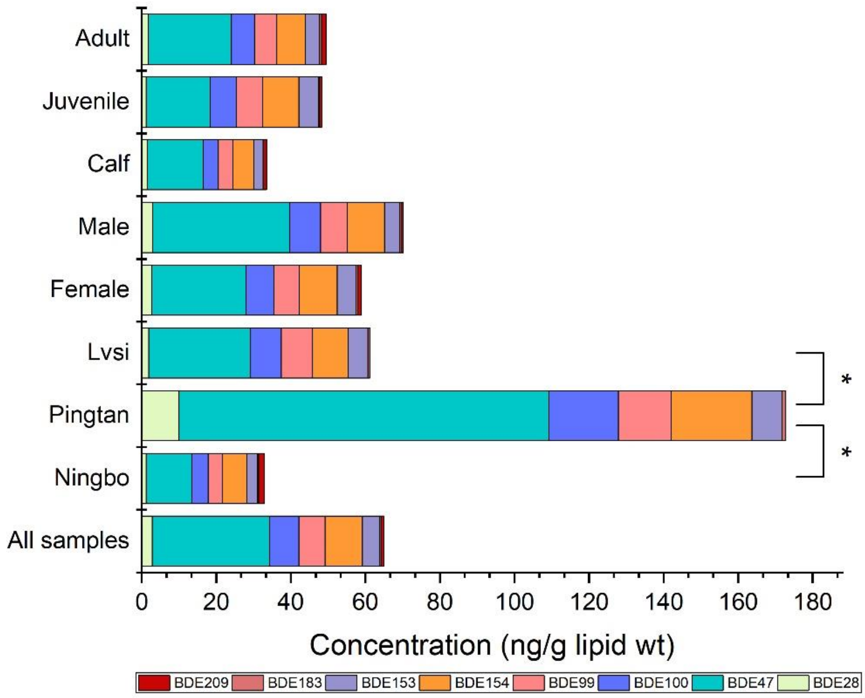


Fig. 2. Concentrations of ΣPBDEs (ng/g lipid wt) in finless porpoise blubber from different countries/regions. The three columns in each region represent the lowest, mean, and highest values. Data from Ningbo, Lvsi and Pingtan are from this study, and data from the other sites are cited from published reports (Kajiwara et al. 2006, Ramu et al. 2006, Park et al. 2010, Yang et al. 2008). (colour printing)

3.3 Sex/age related variations of PBDE accumulation

Given that there is a significant ΣBDE concentration difference between Pingtan and the other two regions, age-related data were analysed from Ningbo and Lvsi. The distribution of PBDEs in different age/sex groups is shown in Fig. 3. Male samples had higher ΣBDEs concentration than female, an independent samples t-test showed a nonsignificant difference in PBDE concentration in the sexual variations ($P > 0.05$). In the eight detected BDE homologues, BDE47 had the greatest bioaccumulation, followed by BDE 154, 100 and 99 in both female and male samples. The calves had lower PBDEs levels than juveniles or adults. Adults had slightly higher concentrations than juveniles, yet there was no significant concentration difference among these three groups ($P > 0.05$).



* : The significance level is 0.05.

Fig. 3. Concentration and compositions of ΣPBDEs in blubber tissue from finless porpoises and variations based on sex, age and sample region group. Calf, juvenile and adult data are from Ningbo and Lvsi. (colour printing)

We did not find notable difference of PBDE distribution in males and females in the present study. This might be because our sample size and gender ratio of different regions were on a small scale, but PBDE accumulation differences do exist between genders. Some earlier research reported that organic pollutants in female whales could be transferred to the next generation during reproduction and lactation through the placenta and breast milk (Yogui et al. 2011a, Leonel et al. 2012, Barbosa et al. 2018). However, with a lack of reproductive transmission, the pollutants in males could not be transferred to the next generation, so they remained at a relative higher concentration in the lipid compared to females. The similar concentrations in juveniles and adults might be attributed to the maternal transfer in adult females and the high metabolism rate of juveniles.

3.4 Variation of PBDE accumulation is related to body length and inter congener correlations

Generally, there was no significant correlation between body length and PBDE levels ($P>0.5$, Fig. 4c). To determine the association difference between females and males, the samples were further divided into two groups based on gender. Fig. 4a and 4b illustrated that there was a significant positive correlation between PBDE concentration and body length in males ($r=0.459$, $P=0.024$), whilst there was no significant correlation in females ($P>0.05$). In our study, Spearman correlation matrix results (Fig. 5) suggested that all of the congener concentrations had pairwise correlations with each other (except for BDE209/BDE154, $P > 0.05$, BDE209/BDE153, $P > 0.05$ and BDE209/BDE183, P=0.05), of which BDE99/BDE100 (r=0.93, P=0.00), BDE153/BDE154 (r=0.93, P=0.00), BDE100/BDE47 (r=0.90, P=0.00) and BDE99/BDE47 (r=0.89, P=0.00) had the highest positive correlation. BDE209 had negative correlations with all of the other congeners, among which BDE28 (r=-0.51, P=0.00) and BDE47 (r=-0.40, P=0.00) had the greatest association with BDE209.

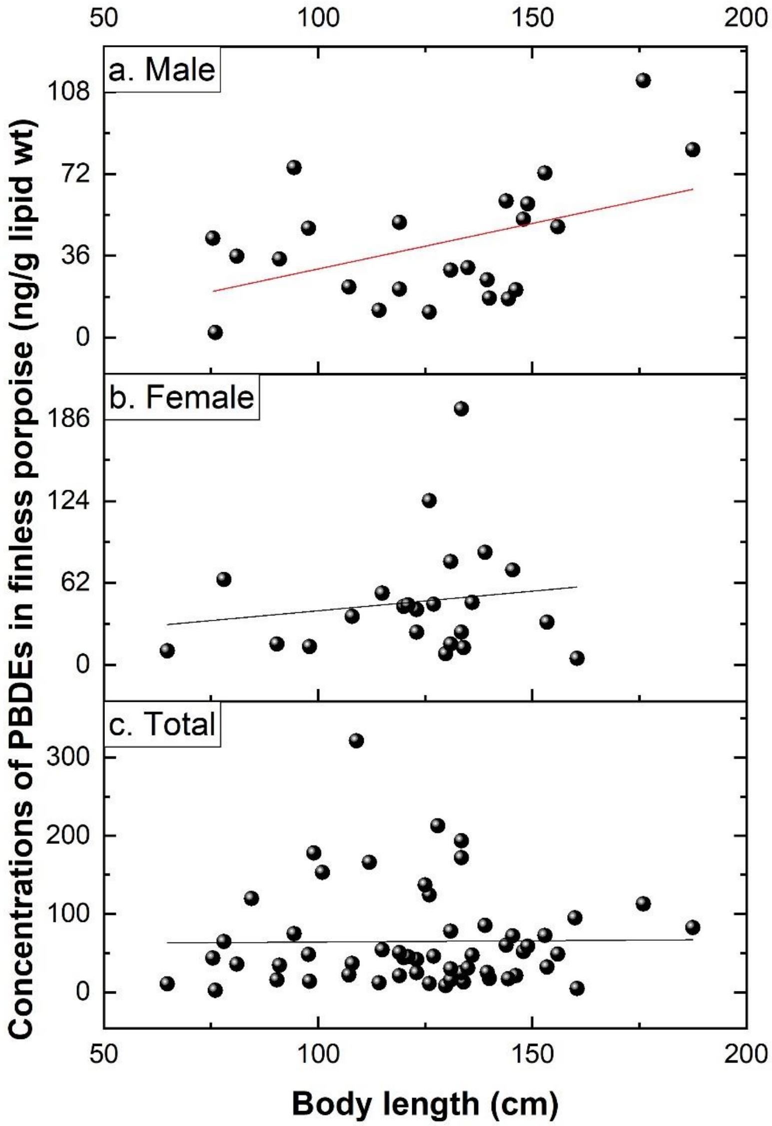


Fig. 4. Correlations between porpoise body length (cm) and the PBDE concentration

(ng/g) in male samples, female samples and all samples. (colour printing)

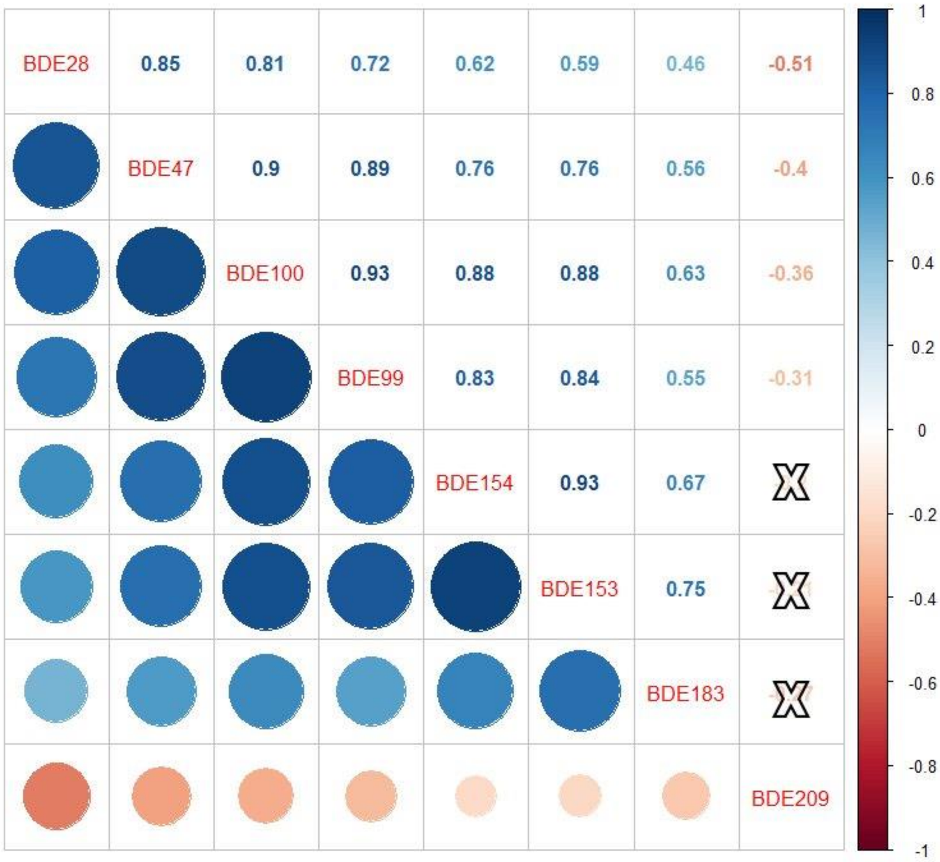


Fig. 5. Correlation matrix among the PBDE congener levels in the blubber of the finless porpoise (Cross mark "╳" means P ⩾ 0.05, no significant difference between the two congeners). (colour printing)

Body size, including body length, represents the nutrition status of the finless porpoise, and it is frequently used in correlation tests to determine pollutant accumulation. The positive correlation between PBDEs and body length in males is consistent with the results in other studies (Park et al. 2010, Bachman et al. 2014). It was reported that the PBDE levels decreased as the body size of mature female cetaceans increased because of the transfer and elimination of organic pollutants through pregnancy and lactation (Leonel et al. 2012, Barbosa et al. 2018). No significant correlation between body length and PBDE levels was found in the female group in our study, which agrees well with other reports. The interelement correlation matrix reveals the congener degradation and interrelation patterns in part. PBDE congeners can degrade from higher brominated to lower brominated congeners. BDE209 is the most brominated congener, and its negative correlation with most of the other congeners may account for the degradation process in the finless porpoise. Commercial pentaBDE is a technical mixture of different PBDE congeners, with BDE-47 (-tetra) and BDE-99 (-penta) being the most abundant (United Nations Environment Programme 2007). In this study, we found a significant high correlation among BDE99 (penta-), BDE100 (penta-) and BDE47 (tetra-). The concentrations of BDE153 (hexa-) and BDE154 (hexa-) reflect PBDE degradation features too.

3.5 Potential health risk assessment for EAfps

Data on the toxicological effects of organic pollutants in the EAfp remain scarce due to sampling challenges and ethical restrictions over conducting experiments. Thus, we calculated and estimated the PBDE toxicity in the finless porpoise via laboratory animal models (mice in this study). The $NOAEL_d$s calculated for each congener are presented in Suppl Table S 2.2. Marine mammals including whales have a relatively higher body fat percentage compared to other animals. The research found that the blubber of sperm whales comprised nearly one-third of their body weight (Lockyer 1991), and the calves of harbour porpoises allocated the greatest percentage of blubber (approximately 37 % of the body mass) (Mclellan et al. 2002). Considering the lipid percentage in blubber and the body fat rate in other cetaceans, the PBDE levels in the finless porpoise did not reach $NOAEL_d$ in the studied regions. Three main prey of the finless porpoise in the ECS were selected in this study, and the total concentrations of PBDEs in the prey were used to estimate the RQ. The PBDEs levels in the prey were far lower than the MAC_{diet} calculated. Meanwhile, by referring to the PBDE concentrations from sea water and surface sediments of the ECS, the data showed that PBDE levels in this region are generally lower compared to other regions (Li 2014).

Comparison of toxic reference values and pathological correlation studies are the main method of assessing health risks. We employed different methods to assess the potential health risk here (Suppl Table S 2.2). The results suggested that the finless porpoise of the ECS is barely influenced by PBDE toxic effects. The estimation through test animals seems to be more conservative compared to the result calculated through the food chain. It is noted that although a factor of 10 is usually used in calculating NOAEL based on LOAEL, the actual NOAEL might only be slightly lower than the experimental LOAEL (Sample et al. 1996). In addition, in contrast to NOVELs and MACs of congener BDE-99, -47, and -153, BDE209 has much higher values because higher brominated congeners are known to be less toxic to organisms (Eriksson et al. 2004).

One study revealed that when the BDE congener concentration increased, reactive oxygen species (ROS) levels, thiol levels and phagocytosis were all affected in harbour seal cells in vitro. The toxicity was most obvious when the concentration of PBDE congeners (BDE-47, -99 and -153) was high (⩾ 12 μM) (Frouin et al. 2010), suggesting that if the concentration of pollutants increases in the marine environment of the ECS, the concentration of pollutants might increase, which would possibly threaten the survival of the finless porpoise. Thus, it is necessary to carry out continuous monitoring of organic pollutants in the finless porpoises of the ECS, especially monitoring of the lower brominated congeners.

Conclusions

PBDE concentrations in EAfp blubbers from the ECS are reported for the first time. The major congeners of PBDEs are detected, indicating widespread contamination in the ECS. Nevertheless, the contamination levels are low compared to the PBDE levels in marine mammals from Japan, Korea and Hong Kong. The pattern of contamination indicates that penta-BDE commercial mixtures are a major source of PBDEs to top predators in the ECS. The PBDE levels significantly varied in samples from different regions, which indicates distinct contamination patterns in various industrial areas, finless porpoise foraging habits and metabolism rates. A significant correlation was found between PBDE levels and body length in males, and the inter congener correlation matrix showed the distribution patterns of different brominated - levels of PBDEs. Multiple methods were applied to assess the health risk of finless porpoise from PBDEs; the results suggest that this species is hardly affected by the toxic effects of pollutants in the ECS. Though low concentrations of PBDEs were identified in this study, cetaceans are crucial to the marine environment as biomarkers; hence, continuous monitoring should continue to increase the understanding of the potential hazards of PBDEs to the finless porpoise.

Declaration of interests

None**.**

Acknowledgements

This research was funded by the National Key Program of Research and Development, the Ministry of Science and Technology (2016YFC0503200), the National Natural Science Foundation of China (31630071), NSF of Jiangsu Province of China (BK20171475), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Ocean Park Conservation Foundation Hong Kong, OPCFHK (MM04-1819), and the Major Project of Hydrobios Resources in Jiangsu Province.

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