

TROPHODYNAMICS OF POLYBROMINATED DIPHENYL ETHERS AND METHOXYLATED POLYBROMINATED DIPHENYL ETHERS IN A MARINE FOOD WEB

KUN ZHANG,[†] YI WAN,[†] LIHUI AN,[†] and JIANYING HU*[†][†]College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

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Abstract—The current study measured the concentrations of 14 polybrominated diphenyl ethers (PBDEs) and eight methoxylated polybrominated diphenyl ethers (MeO-PBDEs) in a marine food web and estimated their trophic magnification factors (TMFs), to highlight the differences between invertebrates, fish, and seabirds. Concentrations of PBDEs were orders of magnitude greater in seabirds (184.07 ± 161.63 ng/g lipid wt) compared with invertebrates and fish (19.01 ± 14.14 ng/g lipid wt). Although the congener profiles in invertebrates, fish, and juvenile seabirds were dominated by BDE-47, the contributions of BDE-99 and BDE-153 in adult seabirds were also significant. Unlike PBDEs, however, higher average MeO-PBDE concentrations were detected in fish (126.27 ± 189.27 ng/g lipid wt) and bivalves (15.96 ± 11.82 ng/g lipid wt) than in seabirds (2.61 ± 2.87 ng/g lipid wt). Correlations between lipid-normalized PBDE concentrations and trophic levels confirmed that seven PBDE congeners were magnified in the invertebrate-fish-seabird food web and that PBDE concentrations increased at a much greater rate across trophic levels in seabirds than in invertebrates and fish. This result indicates that estimating TMFs of PBDEs separately for seabirds, invertebrates, and fish is preferable. For MeO-PBDEs, no significant relationships were obtained in the invertebrate-fish-seabird food web. Environ. Toxicol. Chem. 2010;29:2792–2799. © 2010 SETAC

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants used in a wide range of textiles, construction materials, and electronic equipment [1]. They are believed to leach easily into the environment over their life cycle as commercial products [2], and they have been detected in different environmental media since they were first reported in fish from the Visken River, Sweden [3]. Increasing evidence indicates that these compounds can disturb thyroid homeostasis, leading to adverse effects on an organism's health, including neurodevelopment deficits and reduced reproductive success [4–6]. A recent study on kestrels (*Falco sparverius*), for example, found that exposure to the PBDE technical mixture DE-71 at environmentally relevant concentrations affected the timing and frequency of reproductive courtship behaviors [7].

In recent decades, studies have shown that PBDEs pose an environmental threat to organisms occupying high trophic levels, such as birds [8–10]. Dietary accumulation or biomagnification of PBDEs, in addition to lipid–water partition, can cause stepwise enrichment with increasing trophic levels in food webs [11]. Therefore, scientific research and environmental policies have focused on PBDE biomagnification to assess the ecological risks of chemicals, and several papers have reported on trophic magnification behaviors in food webs using archived samples [12,13]. For example, in an aquatic food web consisting of six species of fish, zooplankton, and mussels in Lake Winnipeg, Canada, the trophic magnification factors (TMFs) of BDE-47 and BDE-209 were 1.5 and 3.6, respectively [13]. Wan et al. [12] investigated the trophodynamics of PBDEs

in a marine food web consisting of zooplankton, mussels, fish, and seabirds and reported relatively high TMFs for BDE-28 (3.57), BDE-47 (7.24), BDE-100 (3.37), and BDE-119 (2.60) [12]. When seabirds were excluded from the analysis, however, only BDE-47 exhibited trophic magnification (TMF 4.85). Both papers came to the conclusion that BDE-47 exhibited the greatest trophic magnification among those PBDEs usually detected in food webs and that the trophic magnification behaviors of other PBDEs were dependent on food web type (i.e., invertebrate–fish only or invertebrate–fish–seabird), even though the trophic levels of seabirds were similar to those of some fish species. The greater, specific stepwise enrichment with trophic levels for some persistent organic pollutants such as polychlorinated biphenyls also has been observed in birds and marine mammals when compared with a food web consisting of aquatic organisms [14,15]. Studies of biomagnification of PBDEs in birds or mammals are therefore important in assessing their environmental risks.

Several papers have highlighted the occurrence and sources of methoxylated polybrominated diphenyl ethers (MeO-PBDEs) in freshwater and marine environments. Teuten et al. [16] identified two MeO-PBDEs (2'-MeO-BDE-68, 6-MeO-BDE-47) isolated from a True's beaked whale as naturally produced by analyzing their natural abundance radiocarbon content [16]. Methoxylated polybrominated diphenyl ethers also may be formed through methylation of hydroxylated PBDEs or PBDEs by intestinal or sedimentary microflora [17]. Several studies have evaluated the trophic magnification potential of MeO-PBDEs, and significant biomagnification of 2'-MeO-BDE-68 (TMF 2.3) and 6-MeO-BDE-47 (TMF 2.6) have been observed in a Canadian Arctic marine food web ($p < 0.05$). Fish muscle, seabird liver, and seal blubber were used in this study; the use of different tissues within a simple food web may have confused the interpretation of the trophic transfer behaviors of the MeO-PBDEs [18].

All Supplemental Data may be found in the online version of this article.

* To whom correspondence may be addressed

(hujy@urban.pku.edu.cn).

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Liaodong Bay is an enclosed inner sea in northern China and an important spawning and feeding ground for many fish species. Large quantities of wastewater from coastal cities are discharged into the bay, resulting in heavy pollution and potentially threatening the marine ecology. In the current study, we analyzed 14 PBDEs and eight MeO-BDEs in 14 aquatic organisms. The trophic levels of all organisms were determined using nitrogen isotopes. The relationships between contaminant concentrations and trophic levels were analyzed in an aquatic organism-only food web and an aquatic organism-seabird food web. Trophodynamics of PBDEs and MeO-PBDEs in the different food webs were compared to clarify the food web-specific trophic magnification of these compounds.

MATERIALS AND METHODS

Sample collection

Liaodong Bay is located in the north region of the Bohai Sea, northern China, with an approximate area of 10,000 km² and maximum depth of 32 m. As shown in Figure 1, seabirds were sampled along the coast of Liaodong Bay (40°52'N; 121°51'E) in November 2006. Both black-tailed gulls and black-headed gulls are resident seabirds in Liaodong Bay [19]. They build their nests on the coast and feed mostly on insects, crustaceans, and fish [19]. Aquatic food web components (excluding seabirds) were collected in November 2006 in Liaodong Bay (40°42'N; 121°46'E). This food web included three mollusk species (short-necked clam [*Ruditapes philippinarum*], *Macra quadrangularis* [*Macra veneriformis* Reeve], and rock shell [*Rapana venosa*]), two crustacean species (mole cricket [*Upogebia major* de Haan] and Chinese mitten-handed crab [*Eriocheir sinensis* H. Milne Edwards]), nine fish species (red-eye mullet [*Liza haematocheila*], goby [*Synechogobius hasta*], small yellow croaker [*Pseudosciaena polyactis*], China anchovy [*Thrisa kammalensis*], half-smooth tongue sole [*Cynoglossus semilaevis*], Japanese Spanish mackerel [*Scomberomorus niphonius*], flathead fish [*Platycephalus indicus*], black spot-fed bass [*Lateolabrax japonicus*], and spotted maigre [*Nibea albiflora*]), and two seabird species (black-tailed gull [*Larus crassirostris*], and black-headed gull [*Larus ridibundus*]). Seabirds were captured with a trap, and invertebrates and fish were caught with a bottom trawler. All samples were stored at -20°C before analysis. The whole bodies of zooplankton, soft tissues of invertebrates, and muscles of fish and seabirds were used for the PBDE, MeO-PBDE, and isotope analysis.

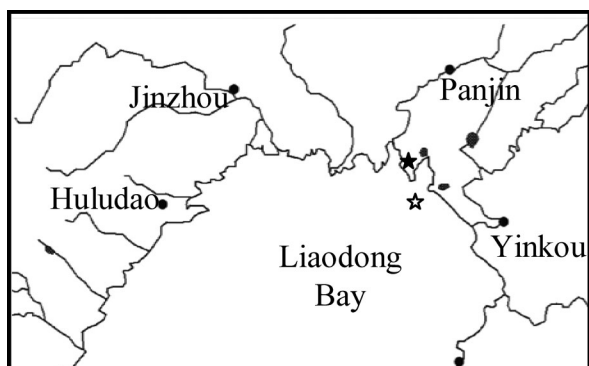


Fig. 1. Location of sampling sites. Black star=sampling locations of seabirds; white star=sampling locations of fish and invertebrates in Liaodong Bay, north China.

Chemicals

Fourteen PBDEs (BDE-28, BDE-47, BDE-66, BDE-71, BDE-75, BDE-99, BDE-100, BDE-118, BDE-119, BDE-138, BDE-154, BDE-153, BDE-138, and BDE-183) and eight MeO-PBDEs (5-MeO-BDE-47, 6-MeO-BDE-47, 6'-MeO-BDE-49, 2'-MeOBDE-68, 5'-MeO-BDE-100, 4'-MeO-BDE-103, 4'-MeO-BDE-101, and 5'-MeO-BDE-99) were selected as target compounds because of their reported worldwide abundance. The PBDE standards and surrogate standards (BDE-85) were obtained from AccuStandard. The MeO-PBDEs were obtained from Wellington Laboratories. All solvents (dichloromethane, acetone, and hexane) were pesticide grade, purchased from Fisher Scientific. Sodium sulfate and silica gel (approximately 100–200 mesh size) were purchased from Beijing Chemical Reagent.

Analysis of PBDEs

Details of PBDE determinations in biota samples and quality assurance/quality control procedures have been described previously [12]. The soft tissues of mollusks and crustaceans and the muscles of fish and seabirds were first freeze-dried. Approximately 1 to 5 g dry samples were then spiked with surrogate standards (BDE-85) and Soxhlet-extracted with a mixture of dichloromethane and hexane (3:1) for 24 h. One fifth of the extracts were used to determine the lipid content by rotary evaporating to dryness and heating at 65°C for approximately 30 min, after which the lipid content was determined gravimetrically, calculated on a wet weight basis. The remaining extract was concentrated and subjected to a glass column packed with 1 g Na₂SO₄ and 8 g acidified silica (48% H₂SO₄). After the application of the sample, the column was eluted with 15 ml hexane and 10 ml dichloromethane.

Gas chromatography-mass spectrometry conditions

Identification and quantification of PBDE congeners were performed using a gas chromatography-electron capture negative ionization mass spectrometry (Shimadzu QP 2010 plus). Chromatographic separation was achieved on a DB-5MS capillary column (30 m × 0.25 mm × 0.1 μm film thickness; J&W Scientific). A splitless injector was used and held at 250°C. The temperature program was from 110°C (1 min) to 180°C at the rate of 10°C/min, then increased to 220°C (5 min) at the rate of 5°C/min, and then to 310°C (5 min) at a rate of 20°C/min. The interface and ion temperatures were maintained at 320°C and 280°C, respectively. The carrier gas was helium at a constant flow rate of 2 ml/min. Data acquisition was conducted in selected ion monitoring mode.

Quantitation and quality assurance quality control

The sample pretreatment was conducted in a super clean laboratory. To avoid high brominated flame retardant content in the procedural blanks, all glassware was properly cleaned, and direct exposure of the sample to laboratory air was minimized. A procedural blank was analyzed with every set of seven samples as a check for interference, and the blank concentrations were subtracted from that found in each sample before application of the detection limit. The accuracy and reproducibility of the entire analytical procedure was checked by analyzing biota samples spiked with at least three times the original concentrations. Six replicate spiked samples and one matrix blank sample were analyzed, and the absolute recoveries ranged from 70 ± 10 to 112 ± 9.6% for PBDEs and 93 ± 18 to 99 ± 17% for MeO-PBDEs. The method detection limits were

set as the mean concentrations plus three times the standard deviation in the blank samples, in which BDE-28, BDE-47, BDE-118, and BDE-183 were detected. The tissue and compound-dependent detection limits (ng/g wet wt) for PBDEs ranged from 0.25 to 5.8 pg/g wet weight in crustaceans and fish and from 0.93 to 15 pg/g wet weight in seabirds, and for MeO-PBDEs ranged from 2.5 to 33 pg/g wet weight in crustaceans and fish and 9.3 to 89 pg/g wet weight in seabirds. For results less than the method detection limits, half of the method detection limit was assigned to avoid missing values.

Stable nitrogen isotope analysis and calculations of trophic level

The samples were homogenized and freeze-dried to constant weight and then were extracted with methanol for approximately 12 h to remove lipids and reduce variability caused by isotopically lighter lipids [20]. After drying at 80°C for 4 h, the samples (approximately 0.5 mg set in Sn capsules) were combusted at 1,000 to 1,050°C, and organic material was oxidized to various nitrogen-bearing gases and water. The carrier gas was passed through a reduction furnace packed with elemental copper and a water trap, which converted nitrogen in the samples to N₂. Nitrogen gas was then carried through the interface (ConFlo III, Finnigan MAT) and analyzed using a mass spectrometer (Thermo Delta plus, Finnigan MAT). Stable isotope values were expressed as

$$\delta^{15}\text{N} = \left(\frac{{}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}}}{{}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}}} - 1 \right) \times 1,000 (\text{‰}) \quad (1)$$

The ¹⁵N/¹⁴N standard values were based on atmospheric N₂ (air). In marine ecosystems, long-lived primary consumers can be used to qualify ¹⁵N baselines because of their lower temporal isotopic signature variability compared with primary producers and detrital energy sources [21]. In the current study, short-necked clams (*Ruditapes philippinarum*) were used to estimate the ¹⁵N baseline and were assumed to represent the trophic position 2.0 because they are filter feeders [21]. With the exception of seabirds, the trophic positions of aquatic organisms were calculated by the relationship proposed in Fisk et al. [22].

$$\text{TL}_{\text{consumer}} = 2 + (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{Ruditapes philippinarum}}) / 3.8 \quad (2)$$

where $\delta^{15}\text{N}_{\text{Ruditapes philippinarum}}$ was determined as 8.98 and the trophic enrichment factor of $\delta^{15}\text{N}$ was 3.8 [20]. For seabirds, the more appropriate diet–tissue fraction factor was 2.4 [23], and the relationship was modified as follows:

$$\text{TL}_{\text{seabird}} = 3 + (\delta^{15}\text{N}_{\text{seabird}} - \delta^{15}\text{N}_{\text{Ruditapes philippinarum}} - 2.4) / 3.8 \quad (3)$$

A linear regression model was used to describe biomagnifications of persistent organic pollutants across trophic levels.

Biomagnification factor calculations

The TMFs can be estimated using the following relationship [12]. The concentration levels of PBDEs on a liquid basis were used to reduce the variance introduced by liquid content in the statistical analysis.

$$\text{Log PBDEs concentration} = a + b \text{TL} \quad (4)$$

where TL is the trophic level of a food web organism, *b* is the slope, and *a* is the constant.

Some quantified PBDE congeners were below the detection limit and so were replaced by 0.5 detection limits to avoid missing values. The *b* in Equation 4 was used to calculate the TMF using the following equation:

$$\text{TMF} = 10^b \quad (5)$$

Statistical analysis

Before statistical analyses, the PBDE concentrations were log-transformed. Linear regression analysis was used to determine relationships between the log-transformed PBDE concentrations and trophic level. When the *p* value was below 0.05, the linear regression was regarded as significant. All analyses were conducted using SPSS 15.0.

RESULTS AND DISCUSSION

Trophic levels of organisms in the marine Liaodong Bay food web

The $\delta^{15}\text{N}$ ratio is an indicator of trophic level (different food preferences), because ¹⁵N is successively enriched relative to ¹⁴N in food chains [21]. The $\delta^{15}\text{N}$ ratio values of the 23 seabirds ranged from 10.50‰ (juvenile black-tailed gulls) to 15.76‰ (adult black-headed gulls). The wide ranges in the seabird $\delta^{15}\text{N}$ ratios can be used to reflect the effects of the trophic position on the accumulation of PBDEs. For Liaodong Bay invertebrates and fish, the $\delta^{15}\text{N}$ ratio ranged from 5.63‰ in *Mactra quadrangularis* to 14.14‰ in the black spot-fed bass. Based on Equations 1 and 2 and the trophic level of short-necked clams (2.0), the trophic levels calculated from the $\delta^{15}\text{N}$ ratios were 3.78 ± 0.26 (mean \pm standard deviation) for black-headed gulls and 3.62 ± 0.30 for black-tailed gulls, which indicated that these two species were the top predators. The trophic levels for invertebrates and fish ranged from 2.0 ± 0.12 (short-necked clam) to 3.36 ± 0.06 (black spot-fed bass). *Mactra quadrangularis*, the short-necked clam, and the rock shell represent the second trophic level (TL range, 1.12–2.09), and the Chinese mitten-handed crab and the mole cricket were intermediate between the second and the third trophic level (TL 2.54–3.14), which is consistent with their carnivorous feeding habits [24,25]. The trophic levels of fish species ranged from 1.93 to 3.41 because of their different feeding habits. The food web structure in the current study is consistent with previous reports that used traditional stomach content analysis. For example, the trophic levels of small yellow croaker and black spot-fed bass calculated by nitrogen stable isotope ratios were 2.85 ± 0.13 and 3.36 ± 0.06 , respectively, which is comparable to those obtained from traditional stomach content analysis (2.99 and 3.37, respectively) [25]. The trophic levels were also consistent with prey–predator relationships, as shown in Figure 2 [25]. For example, mole cricket and rock shell have a direct prey–predator relationship, and there is approximately one order of magnitude between their calculated trophic levels.

Residue levels in Liaodong Bay food web

Table S1 in the Supplemental Data shows the concentrations of PBDEs in muscle samples of organisms collected from Liaodong Bay. Fourteen identifiable tri- to hepta-PBDE congeners (BDE-28, -47, -66, -71, -75, -77, -99, -100, -118, -119, -138, -153, -154, and -183) were detected in the samples. The BDEs-28, -47, -100, -99, -153, and -154 were detected in all seabird samples, whereas only BDE-28 and -47 were detected in all invertebrate and fish samples. When the concentrations were expressed on a lipid weight basis, the concentrations in the

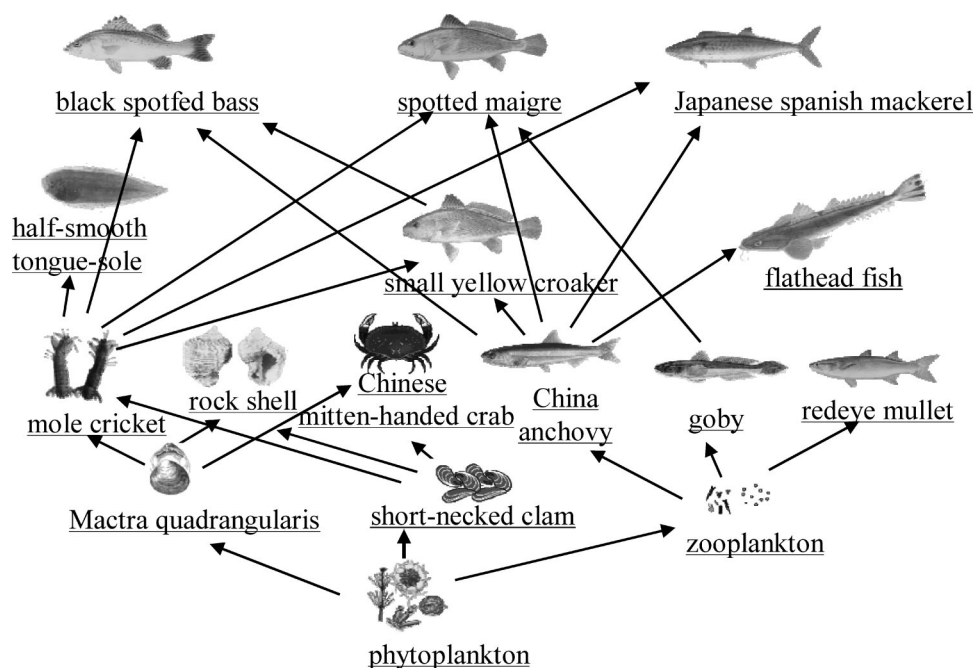


Fig. 2. Prey-predator relationships among invertebrates and fish collected in Liaodong Bay, north China.

seabirds ranged from 4.54 ng/g lipid weight (juvenile black-tailed gulls) to 520.16 ng/g lipid weight (adult black-headed gulls) and ranged from 2.74 ng/g lipid weight (mole cricket) to 49.26 ng/g lipid weight (spotted maigre) in aquatic organisms (Table S1). The mean concentration of total PBDEs in seabirds from the current study (184.07 ± 161.63 ng/g lipid wt) was much higher than those in herring gulls sampled in Bohai Bay (32.8 ± 5.1 ng/g lipid wt) adjacent to Liaodong Bay [12,26] and in black guillemots (*Cephus grylle*) from Greenland ($0.74\text{--}6.7$ ng/g wet wt) [27], but much lower than those in birds of prey from Northern China ($12,300$ ng/g lipid wt) [28] and in cormorants (*Phalacrocorax carbo*) from England and Wales ($1.8\text{--}140$ ng/g wet wt) [29]. The sum concentrations of PBDEs and the BDE-47 concentration in short-necked clams were 12.02 ± 8.93 ng/g lipid weight and 2.00 ± 2.04 ng/g lipid weight, respectively, which were comparable to those in bivalves of a Canadian Arctic marine food web (Σ PBDEs: 5.4 ng/g lipid wt; BDE-47: 2.9 ng/g lipid wt), much higher than those from Bohai Bay (Σ PBDEs: 0.32 ng/g lipid wt; BDE-47: 0.14 ng/g lipid wt), and much lower than those in mussels from Lake Winnipeg (BDE-47: 21.11 ng/g lipid wt) [12,13,26]. The concentrations in fish were higher than those from Bohai Bay and lower than those from the Pearl River Estuary, South China [12,30]. The PBDE concentrations in organisms from the present study appeared to be at a moderate level compared with other aquatic organisms around the world.

For MeO-PBDEs, the highest average concentrations were detected in fish (126.27 ± 189.27 ng/g lipid wt), followed by bivalves (15.96 ± 11.82 ng/g lipid wt), seabirds (2.94 ± 2.70 ng/g lipid wt), and crustaceans (2.44 ± 0.71 ng/g lipid wt), and were much higher than those in a Canadian Arctic food web [18]. Of the eight MeO-PBDEs, only 2'-MeO-BDE-68, 6-MeO-BDE-47, and 4'-MeO-BDE-103 were detected in seabirds, with concentrations of ND-8.61, ND-3.04, and ND-2.93 ng/g lipid weight, respectively, whereas all target MeO-PBDEs, except for 5'-MBDE-100, appeared in invertebrates and fish. For invertebrates and fish, 6-MeO-BDE-47 exhibited the highest concentration ($0.71\text{--}331.45$ ng/g lipid wt) among MeO-

PBDEs, followed by 2'-MeO-BDE-68 (ND \pm 267.62 ng/g lipid wt) and 4'-MeO-BDE-103 (ND \sim 9.78 ng/g lipid wt). These relatively low seabird MeO-PBDE concentrations in comparison with bivalves and fish have also been reported in the Canadian Arctic marine food web [18].

Profiles

Figure 3 shows the PBDE profiles in organisms from Liaodong Bay. In invertebrates and fish, BDE-47 was predominant among the 14 target PBDEs, with an abundance of $34.5 \pm 10.9\%$ of the total PBDEs concentration, and the other five major congeners (BDE-28, BDE-99, BDE-100, BDE-153, and BDE-154) were of a similar level, accounting for $8.9 \pm 5.2\%$, $6.9 \pm 5.5\%$, $7.1 \pm 2.9\%$, $5.4 \pm 3.1\%$, and $8.0 \pm 4.3\%$ of the total PBDE concentration, respectively. Relatively high proportions of high brominated PBDEs were found in mollusks compared with other species, which could be explained by the filter-feeding habits of mollusks, resulting in congener profiles similar to those in sediment. The profiles of PBDEs in juvenile black-tailed gulls were similar to those in invertebrates and fish, with BDE-47 being the dominant congener ($46.8 \pm 9.0\%$ of Σ PBDEs), followed by BDE-153 ($9.1 \pm 3.4\%$), BDE-154 ($8.7 \pm 2.2\%$), BDE-99 ($8.6 \pm 3.2\%$), BDE-100 ($7.5 \pm 2.3\%$), and BDE-28 ($6.5 \pm 2.8\%$). In adult black-tailed and black-headed gulls, BDE-47 was still the most dominant congener ($32.1 \pm 8.3\%$), but the contributions of BDE-99 and BDE-153 increased to $20.0 \pm 9.2\%$ and $22.0 \pm 9.8\%$, respectively. The profile of PBDEs in juvenile black-tailed gulls was similar to those in aquatic birds from Bohai Bay [12] and Belgium [31], whereas those in adults were similar to profiles observed in terrestrial birds [32]. The different profiles of PBDEs in aquatic and terrestrial birds has been attributed to congener-specific dietary exposure between aquatic and terrestrial systems or differences in PBDE biotransformation capacities between avian species, particularly for BDE 99 [32,33]. However, the considerable differences in individual profiles within the same population of black-tailed gulls may not be solely related to

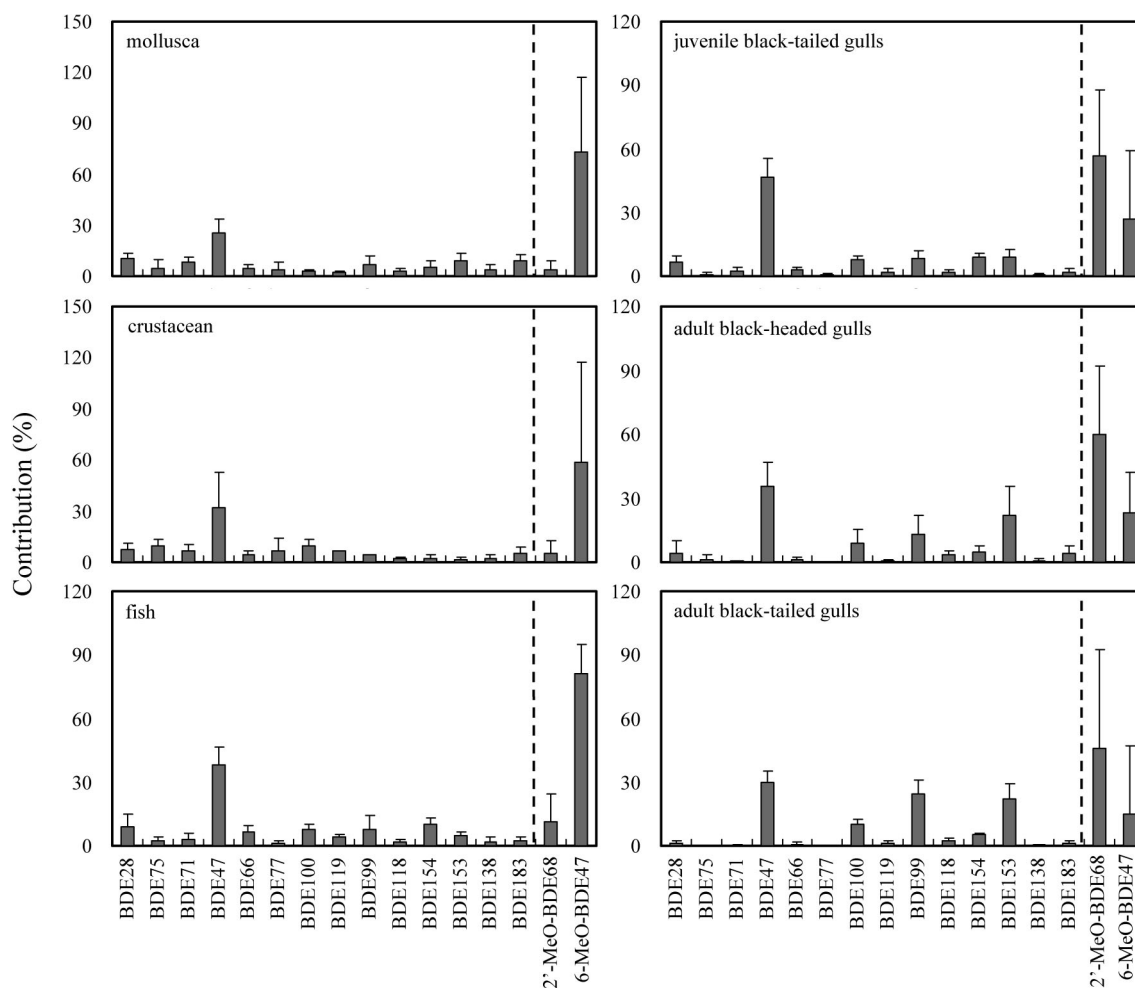


Fig. 3. Polybrominated diphenyl ether (PBDE) profiles in organisms collected from Liaodong Bay, north China. The error bars represent the standard deviation of the contributions of PBDE congeners to Σ PBDEs among nine mollusk samples, nine crustacean samples, 27 fish samples, five juvenile black-tailed gulls, seven adult black-headed gulls, and 11 adult black-tailed gulls.

the different habitats and metabolism capabilities of seabirds in the current study.

The profiles of MeO-BDEs in aquatic organisms were different from those of seabirds (Fig. 3), with 6-MeO-BDE-47 the dominant congener among the eight target MeO-BDEs in all invertebrate and fish samples and accounting for $76.2 \pm 27.2\%$ of the total MeO-BDE concentrations. In seabirds, the contribution of 6-MeO-BDE-47 relative to the total MeO-PBDEs concentration decreased to $20.2 \pm 27.8\%$, whereas 2'-MeO-BDE-68 became the dominant congener ($56.2 \pm 38.4\%$).

Biomagnification behaviors of PBDEs in the food web

To investigate the biomagnification behavior of PBDEs in the food web, a regression analysis was conducted between trophic levels and concentrations of different PBDE congeners in organisms from the Liaodong Bay food web to estimate TMFs (Fig. 4). In the aquatic invertebrate–fish food web, only, the lipid normalized concentrations of BDE-47, BDE-100, and BDE-119 increased significantly with increasing trophic level, with TMF values of 3.91 ($p=0.022$), 3.71 ($p=0.022$), and 3.14 ($p=0.033$), respectively. The TMF of BDE-47 was comparable to that reported in the Bohai Bay food web in north China (4.85) and in Lake Winnipeg, Canada (5.2), indicating similar biomagnification behavior of BDE-47 in both freshwater and marine invertebrates and fish [12,13]. In the

invertebrate–fish–seabird food web, the TMFs of BDE-47, BDE-100, and BDE-119 increased to 6.56, 7.66, and 3.79 ($p=0.005$), respectively, when compared with TMFs in the aquatic-only food web. In addition, correlations between concentrations of BDE-99, BDE-153, and BDE-154 and trophic level were statistically significant with TMFs of 10.02, 6.12, and 5.01, respectively (Table 1). This indicates that TMFs determined using single regressions for the entire food web were likely overestimated for invertebrates and fish and underestimated for seabirds.

For MeO-PBDEs, the concentrations of 2'-MeO-BDE-68 and 6-MeO-BDE-47 increased slightly with TL in invertebrates and fish (Fig. 5). However, no statistically significant relationships were obtained ($p>0.05$) in the invertebrate–fish food web. This result differs from the Canadian Arctic marine food web, where these two chemicals exhibited significant concentration increases across trophic levels with TMFs of 2.3 and 2.6, respectively [18]. This may be because organs with preferential accumulation of MeO-PBDEs were analyzed in high trophic level organisms, with tissue-specific compositions reported in previous papers [18,34]. Similar to those in the Canadian Arctic marine food web, the concentrations of 6-MeO-BDE-47 and 2'-MeO-BDE-68 in seabirds were less than or comparable to those in fish and invertebrates, possibly because of higher excretion or metabolism. Up to now, the origin of MeO-PBDEs

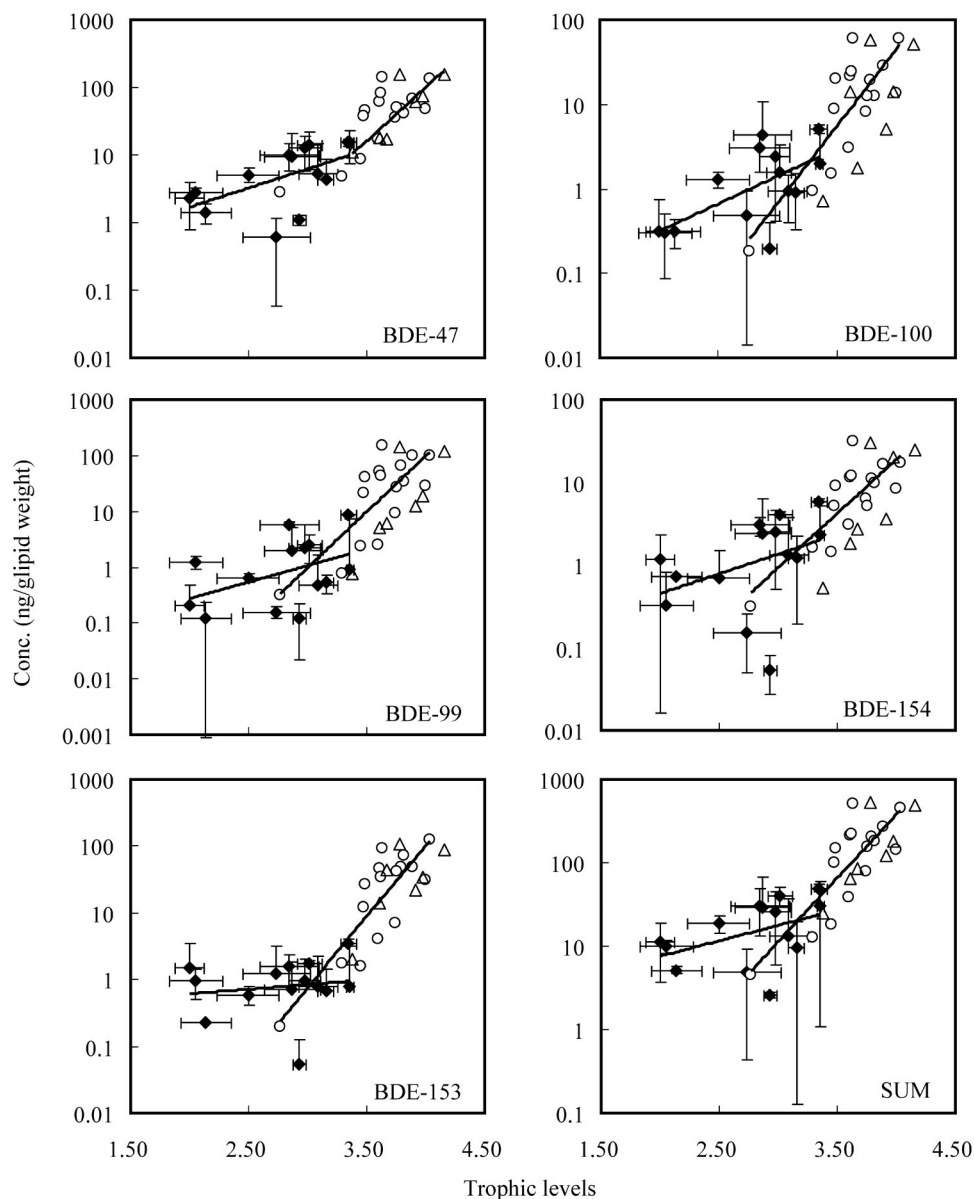


Fig. 4. Relationships between concentrations of five major polybrominated diphenyl ether (PBDE) congeners and Σ PBDEs (ng/g lipid wt) and trophic levels in invertebrates and fish (black diamonds), black-tailed gulls (white circles), and black-headed gulls (white triangles) in Liaodong Bay, north China.

detected in organisms is not well understood. Some MeO-PBDEs are reported to be of natural origin, such as sponges, algae, and acorn worms [16]. Another possible source of MeO-PBDE residue is from direct methoxylation or a two-step hydroxylation followed by methylation of PBDEs [35]. However, no reports have been published of MeOBDEs as metabolites after exposure of PBDEs to microsomes in rainbow trout (*Oncorhynchus mykiss*), chickens (*Gallus gallus*), and rats (*Rattus norvegicus*) [36]. Conversely, if they are metabolites of hydroxylated PBDEs or PBDEs, the results from the current study suggest a low biotransformation capability of PBDEs in seabirds, which was supported by the high biomagnification of PBDEs in seabirds as described previously.

Biomagnification behaviors of PBDEs in seabirds

Considering the importance of seabirds in assessing the biomagnification of PBDEs through a food web, we conducted a regression analysis between concentrations of PBDEs in 23

seabirds and their trophic levels. Of the 14 PBDEs, concentrations of BDE-47, -77, -99, -100, -118, -119, -138, -153, -154, and -183 significantly increased with trophic level ($p < 0.05$), as shown in Figure 4, and their TMF values were 19.54 ($p < 0.001$), 8.43 ($p = 0.021$), 84.72 ($p < 0.001$), 51.76 ($p < 0.001$), 79.62 ($p < 0.001$), 19.01 ($p = 0.020$), 17.70 ($p = 0.009$), 97.05 ($p < 0.001$), 23.77 ($p < 0.001$), and 13.68 ($p = 0.001$), respectively (Table 1). These TMF values were much higher than those estimated from the whole food web, which may be related to the different assimilation capability of seabirds compared with invertebrates and fish [14]. In addition, the TMFs of these PBDEs were related to their bromine atom numbers (Fig. 6); the TMFs of PBDEs increased with bromine atoms up to 5, and then tended to decrease from penta-BDEs. The increase of magnification potential with degree of bromination or $\log K_{OW}$ (approximately 5.84–6.76 for tetra-BDEs, 7.27–7.49 for penta-BDEs) was attributable to the slow rate of chemical elimination in organisms. For chemicals with

Table 1. Parameters of regression analyses between logarithm of concentration polybrominated diphenyl ethers (PBDEs) and trophic levels, and trophic magnification factors (TMFs)

	Invertebrates and fish			Combined food web			Seabirds		
	r^2	TMF	p	r^2	TMF	p	r^2	TMF	P
BDE-28	0.033	1.47	0.533	0.124	1.90	0.181	0.119	3.20	0.106
BDE-47	0.364	3.91	0.022	0.58	6.56	0.001	0.65	19.54	<0.001
BDE-66	0.151	2.65	0.170	0.20	2.55	0.079	0.12	5.09	0.107
BDE-77	0.098	0.38	0.276	0.01	0.80	0.153	0.23	8.43	0.021
BDE-99	0.153	3.21	0.167	0.42	10.02	0.006	0.53	84.72	<0.001
BDE-100	0.365	3.71	0.022	0.59	7.66	0.001	0.56	51.76	<0.001
BDE-119	0.327	3.14	0.033	0.50	3.79	0.002	0.23	19.10	0.020
BDE-118	0.014	1.35	0.685	0.24	3.85	0.057	0.64	79.62	<0.001
BDE-138	0.09	0.39	0.296	<0.001	1.15	0.852	0.29	17.70	0.009
BDE-153	0.012	1.36	0.711	0.27	6.12	0.041	0.67	97.05	<0.001
BDE-154	0.101	2.77	0.269	0.28	5.01	0.034	0.57	23.77	<0.001
BDE-183	0.065	0.53	0.38	0.04	1.59	0.49	0.44	13.68	0.001
Sum	0.196	2.37	0.113	0.46	4.81	0.004	0.65	29.17	<0.001

p values shown in italics represent statistically significant increases or decreases of the lipid equivalent concentration (i.e., <0.05); underscored p values represent congeners without significant correlations in combined food web but having statistically significant concentration increases with trophic levels in seabirds.

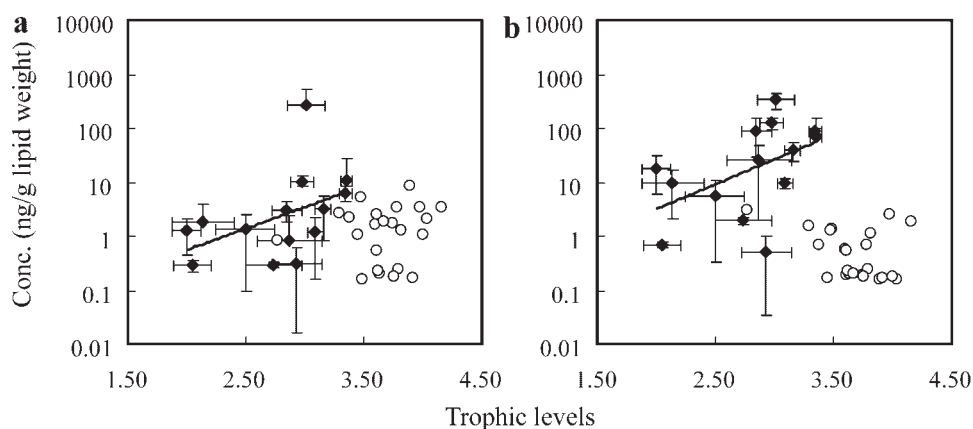


Fig. 5. Relationships between concentrations of methoxylated polybrominated diphenyl ether congeners and trophic levels in invertebrates and fish (black diamonds) and seabirds (white circles) in Liaodong Bay, north China. (a) 2'-methoxylated polybrominated diphenyl ether (MeO-BDE) 68; (b) 6-methoxylated polybrominated diphenyl ether (MeO-BDE) 47.

high bromine atom numbers or high log K_{OW} (7.58–7.89 for hexa-BDEs and 8.3 for BDE-183), the relatively low magnification was possibly caused by low dietary absorption efficiencies, as exemplified by the similar relationship observed

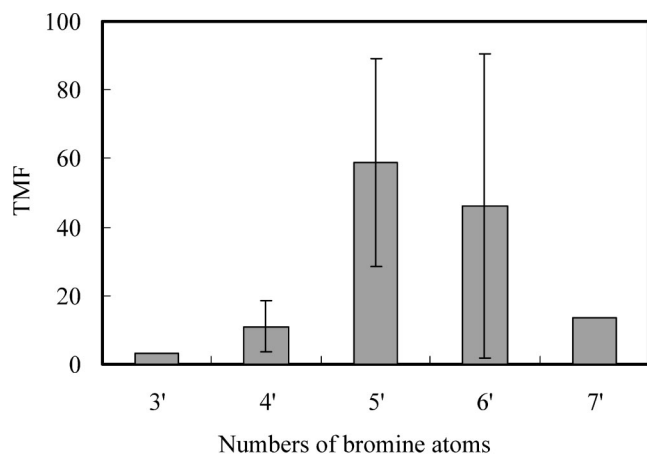


Fig. 6. Relationship between trophic magnification factors (TMF) in seabirds and number of bromine atoms of polybrominated diphenyl ethers (PBDEs) congeners in the Liaodong Bay marine food web.

between the degree of magnification for polychlorinated biphenyls in a food web from Twelve Mile Creek and log K_{OW} values [14,37]. These congener-specific biomagnifications for PBDEs in seabirds were the main reason that the profiles in adult seabirds were different from those of the juvenile seabirds, invertebrates, and fish observed in the current study.

The PBDEs with the same bromine atoms, such as BDE-99, -118, -100, and -119 (penta-BDEs), have different TMFs. The TMFs of BDE-99 and BDE-118 with adjacent bromine in the meta-para position (TMF = approximately 79.62–84.72) were much higher than those of BDE-100 and BDE-119 (TMF = approximately 19.10–51.76). This phenomenon was also observed in BMF studies of polychlorinated biphenyls, in which polychlorinated biphenyl-99 and -100 with adjacent chlorines were more recalcitrant to biotransformation via oxidation, resulting in their high degree of biomagnifications [38]. In invertebrates and fish, however, high TMFs were found for BDE-100 and BDE-119 (approximately 3.14–3.71, $p < 0.05$) compared with BDE-99 and BDE-118 ($p > 0.05$). The congener and species-specific difference between seabirds was also found in a study on accumulation of PBDEs in a marine food chain [39]. In that study, the measured accumulations of BDE-99 and BDE-100 were lower than predicted in fish species but higher in birds and marine mammals. The possible reason for this could

be the debromination of BDE-99 in some fish species [40], which has been related to the fact that BDE-99 does not magnify through a marine food web [12]. The results from the current study indicate that low metabolic capability and high assimilability in birds may be the major reasons for the high degree of magnification of PBDEs in seabirds compared with invertebrates and fish, and for the different patterns between aquatic and terrestrial birds. In conclusion, we propose that TMFs of PBDEs should be estimated separately for seabirds, invertebrates, and fish to avoid either overestimation or underestimation.

SUPPLEMENTAL DATA

Table S1. Biological parameters and PBDE concentrations of 16 marine organisms. (14 KB DOC)

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