Occurrence and trophic transfer of halogenated flame retardants (HFRs) in the food web of a heavily contaminated estuary

Yanan Li,[1,2] Jianhui Tang,[1]

[1]CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Shandong Laboratory of Coastal Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, 264003, China

[2]University of Chinese Academy of Sciences, Beijing, 100049, China

Aim

This research aims to (1) investigate the current status of halogenated flame retardants (HFRs) in aquatic biota, (2) evaluate the trophodynamic behaviors of HFRs, and (3) estimate the potential human health risk related to seafood dietary by local residents.

Procedure

Sample collection

Water, sediment and aquatic organisms were collected from the Xiaoqing River estuary (Fig. 1) in November 2019. The aquatic organisms included phytoplankton (n=3), zooplankton (n=3), invertebrates [including Grass shrimp (Penaeus monodon) (n=4), Japanese sand shrimp (Crangon affinis) (n=4), Clam (Meretrix meretrix) (n=1), Oyster (ostrea gigas) (n=4), Blood clam (Scapharca subcrenata) (n=1), Conch (Glossaulax didyma) (n=4)], and fishes [including Catfish (Zoarces slongatus) (n=5), Mullet (Sphyraenus) (n=5), Sea perch (Lateolabrax japonicas) (n=5), Flatfish (Pleuronectiformes) (n=1)]. Fishes and invertebrates were collected with a bottom trawl. All biota samples were cleaned with Milli-Q water upon capture and their body lengths and weights were recorded. All samples were freeze in the refrigerator and then transported to the laboratory. The muscle of fish and soft part of the invertebrates were dissected. Scalpel, scissors and forceps used were pre-cleaned with Milli-Q water. All biota samples were freeze-dried, homogenized, and stored at −20 ºC until analysis.

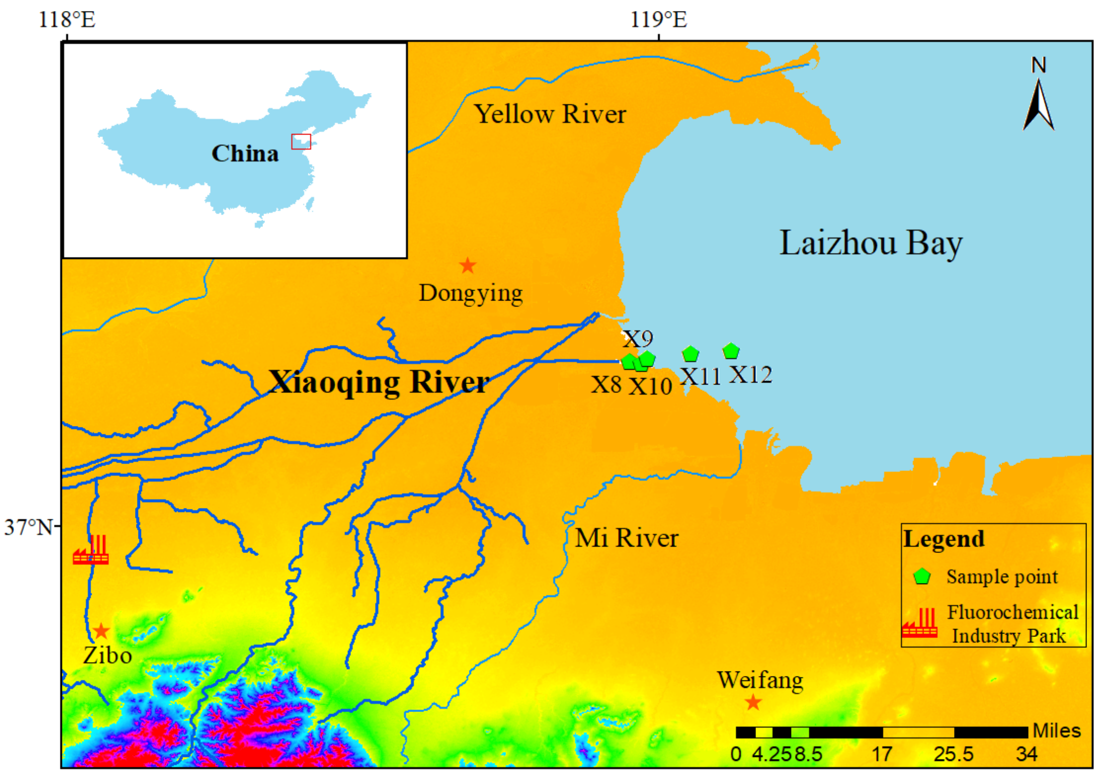

Figure 1. Map of sampling locations in the Xiaoqing River estuary

Results

Concentrations and profiles of HFRs in water and sediment

The mean value of ∑HFRs concentrations in the water and sediment of Xiaoqing River estuary, China, was 683.22 (range from 641.32 to 725.12) pg/L and 1778.64 (range from 954.06 to 2387.04) pg/g dw, respectively. The concentrations of HFR congeners in seawater and sediment are presented in Figure 2. BDE209 and DBDPE were the dominant congeners in sediments and seawater. The high detection level of BDE209 and DBDPE could be attributed to frequent use and emission of Deca-BDE in this region. In seawater, DBDPE accounts for a large proportion (49.41%), followed by BDE 209 (34.18%), BDE 28 (7.74%) and BDE 47 (5.06%). The present results in water are comparable to those measured in the downstream of Xiaoqing River in 2014 (Zhen et al., 2018), while the concentrations in sediments are lower than that (Zhen et al., 2018) and Yellow River Estuary (Yuan et al., 2016). Different HFRs profiles in water and sediment may be affected by their logKow (octanol-water partition coefficient).

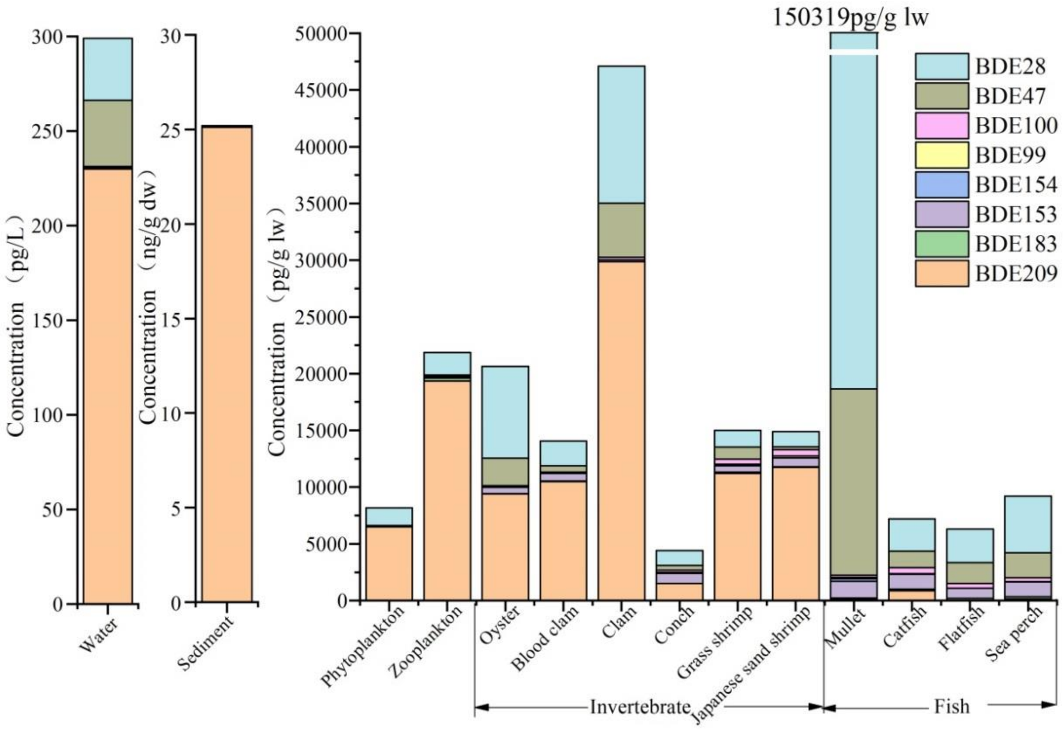

Figure 2. The concentration of HFRs in all aquatic media

HFRs concentrations and profiles in organisms

The concentration of HFRs in all aquatic organisms was shown in Figure 2. All target HFRs were detected in the aquatic organisms. The ΣHFRs in the organisms ranged from 4256.91 (conch) to 603902 pg/g lw (mullet). The highest HFRs residues were detected in mullet (12.34-603.90 ng/g lw), with BDE28 occupying a large proportion of the total concentrations. This might ascribe to the fact that mullet is the only herbivorous fish and mainly feeds on plankton and organic detritus. The detection rate of BDE28, BDE47 and PBT was the highest (100%), while BDE209 and DBDPE had the lower detection frequency (76.47% and 8.82%). The predominant compound was BDE-28, with a mean abundance of 32.29 ± 24.02%, followed by BDE-47 (13.57 ± 11.76%), BDE-209 (30.30 ± 29.89%) and BDE-153(10.47 ± 12.93%) in PBDEs. PBT was detected in all species with an average concentration of 370.8 pg/g lw. Syn-DP and anti-DP were mainly detected in invertebrates and planktons.

All HFR concentrations in organisms followed the order: bivalves > crustacean > plankton > fish (except for mullet) > gastropods, which could relate to their different uptake mechanisms (oyster, blood clam, and clam are all filter feeders). The levels of

BDE 209 in benthic invertebrates were significantly higher than those in fish, especially in clam. The total concentrations of HFRs in bivalves (oyster, blood clam, clam) were higher than shrimps and fishes (except for mullet) in this study, which might result from frequent exposure to sediment (the sink of these substances). Among all PBDEs, the average proportion of BDE28 in fish was significantly higher than those in benthic invertebrates. Overall, benthic invertebrates accumulate more BDE209 than fish, whereas fish exhibit higher BDE28 level than invertebrates. Clam harbored the highest ΣaBFRs (mean value: 40100 pg/g lw) and DPs (mean value: 854 pg/g lw) concentrations, being 1–2 orders of magnitude greater than the other species examined. In contrast, the lowest ΣaBFRs (mean value: 68.5 pg/g lw) concentration was observed in flatfish. Composition profile differences were also observed, with higher proportions of DBDPE in bivalves (clam, oyster, blood clam) than in other species. The different HFRs accumulation characteristics might be attributable to species-specific ecological status such as habitat, feeding habits and trophic level. The bioaccumulation of HFRs in organisms may be a combination of diet and environmental exposure. Our results are comparable to that reported in Pearl River estuary, China (Xiang et al., 2006), while much higher than Bohai Bay (Shao et al., 2016) and Liaodong Bay, China (Ma et al., 2013).

Trophic transfer of HFRs in the food web

For organisms investigated in this study, the measured $\delta^{15}N$ ranged widely from 9.90‰ of oyster to 17.1‰ of Sea perch, and the measured values of $\delta^{13}C$ was in the range of −28.78‰ of oyster to −21.44‰ of Japanese sand shrimp. Estimated TLs ranged from 2.44 ± 0.03 for oysters to 4.33 ± 0.59 for Sea perch. TMFs of HFRs congener in the food web were obtained according to the slope of the regression between log-concentrations (lw) and the TLs of the corresponding organisms. Significant positive relationship ($p < 0.05$) was observed between Log-concentrations (lw) of BDE28 and the TL values. The similar results were also observed on BDE47 and

BDE153. However, significant negative correlation ($p < 0.05$) was observed for correlations between BDE209 and TL values. TMF > 1 indicates that the target substance is considered to be able to biological magnification in the food web, TMF < 1 implys that biological dilution effect has occurred. The results showed that some PBDE congeners could biomagnified with the transfer of food chain, which also confirmed the potential of biomagnification in the food web of Xiaoqing estuary. TMFs were 3.31, 2.88 and 2.69 for BDE28, BDE47 and BDE153, respectively, suggesting that these compounds exhibited significant trophic magnifications in the aquatic food web.

Perspectives in future

The results showed that HFRs were pervasively presented in sediment, seawater, and organisms in this ecosystem. BDE47, BDE28, and BDE209 were detected at high levels in the biotas. BDE47 and BDE28 could biomagnification along the food chain in comparison to that BDE209 exhibited a clear bio-dilution potential. Subsequent research is especially necessary for better understanding the hazards to aquatic biota and ecosystem. Our investigation of HFRs in aquatic organisms provides some meaning for future research.

Due to the pandemic of COVID19, we have not able to visit Ehime University in 2020 to collect environmental and biota samples in the Seto Inland Sea. We hope in the coming year, a comparative investigation can be carried out in the Seto Inland Sea, Japan with those in the Bohai Sea to better understand the distribution, degradation, or bioaccumulation of those emerging contaminants in food webs under different environmental pressures.

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