Habitat-dependent trophic transfer of legacy and emerging halogenated flame retardants in estuarine and coastal food webs near a source region

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) compare the levels and profiles of HFRs in estuarine and coastal areas; (2) investigate the trophic-transfer behavior of HFRs in two food webs near the source region; and (3) estimate the factors influencing the bioaccumulation of HFRs in estuary–sea ecosystems.

Procedure

Sample collection

Water, sediment and aquatic organism samples were collected from XRE in November 2019 and from LZB in November 2020, respectively. The sample area was showed in Figure S1 in Supporting Information (SI). The aquatic organisms in XRE 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), and conch (Glossaulax didyma) (n = 4)), and four fish species (catfish (Zoarces slongatus) (n = 5), mullet (Sphyraenus) (n = 5), sea perch (Lateolabrax japonicas) (n = 5), and flatfish (Pleuronectiformes) (n = 1)). The organisms in LZB included phytoplankton (n=3), zooplankton (n=3), invertebrates (including clam (Meretrix meretrix) (n = 4), oyster (Ostrea gigas) (n = 4), Japanese stone crab (Charybdis japonica) (n = 4), sea snail (Rapana venosa) (n = 4), bay scallop (Argopecten irradians) (n = 4), octopus (Octopus variabilis) (n = 4) and sea cucumber

(Stichopus japonicus) (n = 4)), and five fish species (tongue sole (Cynoglossus semilaevis) (n = 4), goby (Acanthogobius ommaturus) (n = 4), finespotted flounder (Pleuronichthys cornutus) (n = 4), sea perch (Lateolabrax japonicas) (n = 4) and jacopever (sebastes schlegeli) (n = 4)). Fishes and invertebrates were collected with a bottom trawl. All samples were freeze in the refrigerator and then transported to the laboratory. The muscle of fish and soft part of invertebrates were dissected. All biota samples were freeze-dried, homogenized, and stored at -20 °C until analysis.

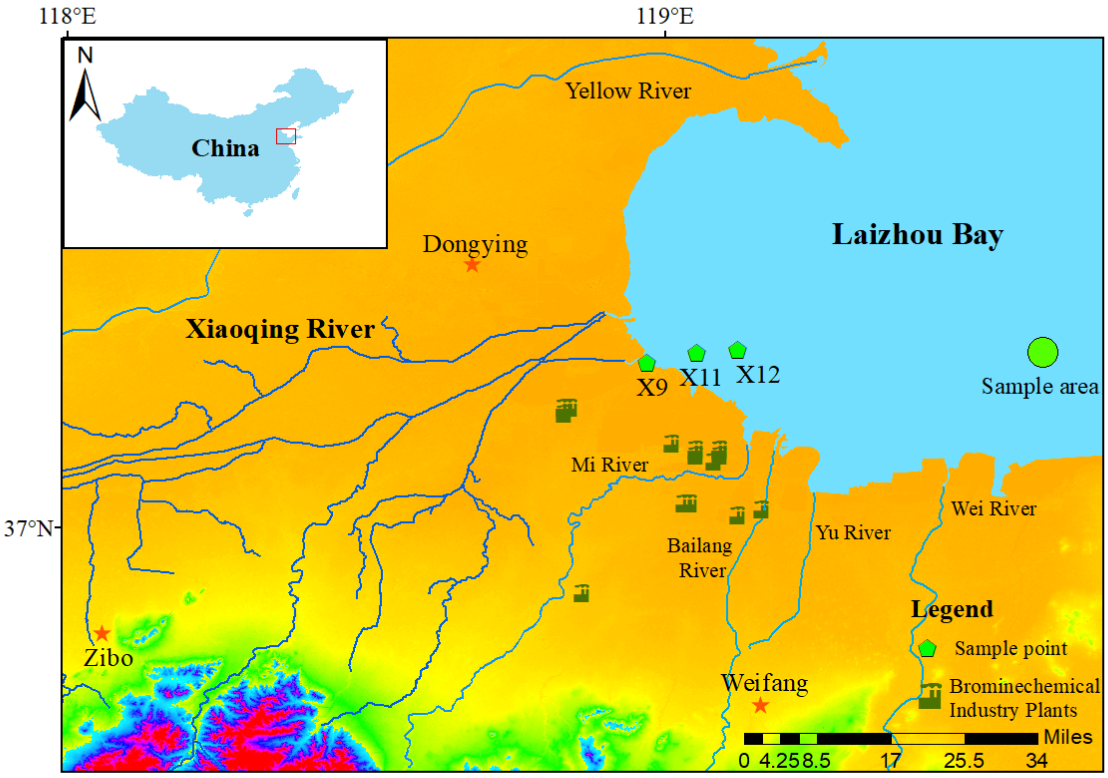

Figure 1. Map of sampling locations in the Xiaoqing River estuary and Laizhou Bay

Results

Concentrations and profiles of HFRs in water and sediment

The mean value of ∑HFRs concentrations in seawater of XRE was 6390 (range from 6050 to 6730) pg/L and DBDPE accounts for a large proportion (52.9%), followed by BDE-209 (36.5%), BDE-47 (4.12%) and BDE-28 (2.83%). The present results in water are comparable to those measured in the downstream of Xiaoqing River in 2017 (Liu et al., 2021). The concentration and relative abundance of HFR congeners in seawater and sediment are presented in Figure 1 and 2. The concentrations of total

HFRs in seawater of LZB ranged from 142 to 1109 pg/L with an average concentration of 428 pg/L, which is lower than that in XRE. This might be ascribed to the point inputting contamination in river mouth and the seawater dilution effecting in bay. BDE-209, DBDPE, syn-DP and anti-DP were identified in all seawater samples of LZB and they were the dominant substances, which accounted for mean 20.6%, 18.7%, 11.7% and 30.4% of total HFRs, respectively. The high levels of BDE-209 and DBDPE could be attributed to their large production in this region. Higher level of DPs was observed in seawater of LZB (mean: 180 pg/L) than those in XRE (59.9 pg/L), suggesting the existence of additional DPs source in LZB.

The concentration of ∑HFRs in sediment of XRE and LZB ranged from 14.3 to 35.9 ng/g dw and from 4.57 to 10.5 ng/g dw, respectively. ∑HFRs are higher in XRE (mean value: 26.7 ng/g dw) than those in LZB (mean value: 8.69 ng/g dw), and are much higher than those in sediments of Yellow Sea (mean value: 2.62 ng/g) and East China Sea (mean value: 0.59 ng/g) (Li et al., 2019). In XRE, BDE-209 is the predominant compound (93.9%) and DBDPE accounts only for a small proportion (4.97%), while in the LZB, DBDPE is the dominant compound (65.6%), followed by BDE-209 (25.4%). DP levels in the sediment of LZB (mean: 64.2 pg/g dw) are equivalent to that in Sishili Bay (mean: 69.9 pg/g dw), and slightly higher than that in Jiaozhou Bay (mean: 24.7 pg/g dw) and Taozi Bay (mean: 40.4 pg/g dw) (Zhao et al., 2011).

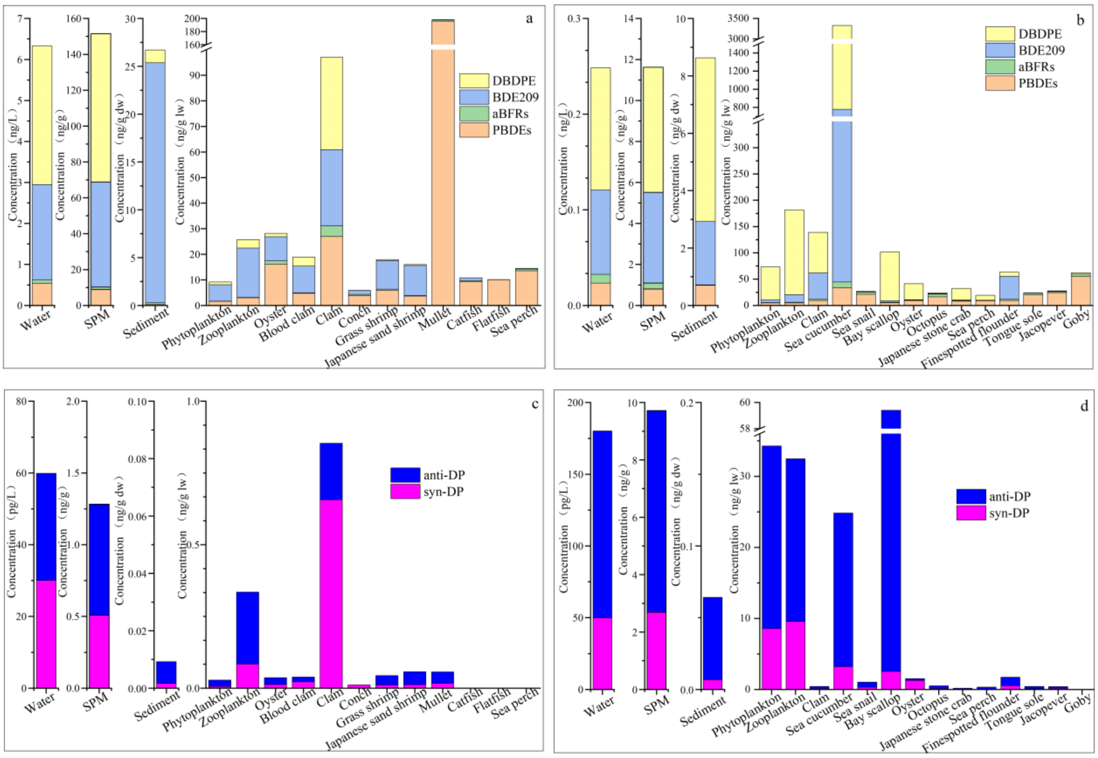

Figure 2. Comparison of HFRs in samples obtained from XRE (a, c) and LZB (b, d).

Note: PBDEs represent the sum concentration of BDE-28, -47, -100, -99, -154, -153 and -183, aBFRs refer to the sum concentration of PBT, PBEB, TBP-DPTE, HBB, EHTBB and BTBPE.

Comparison of HFRs concentration in organisms from two coastal zones

The relative abundance of HFRs in aquatic organisms was shown in Figure 2. In XRE, the mean value of ∑HFRs in organisms ranged from 5.90 (conch) to 198 ng/g lw (mullet) as showed in Table 1 and Figure 1. The detection rate of BDE-28, BDE-47 and PBT was the highest (100%), while BDE-209 and DBDPE had the lower detection frequency (78.9% and 31.6%, respectively). The predominant compound was BDE-209, with a mean abundance of 40.6%, followed by BDE-28 (22.4%), BDE-47 (18.5%) and BDE-153(4.94%). PBT was detected in all species with an average concentration of 0.34 ng/g lw. Syn-DP and anti-DP were mainly detected in invertebrates and planktons, although the maximum concentration was less than 1 ng/g lw. In organisms of LZB, the ∑HFR concentrations ranged from 19.6 ng/g lw in sea perch to 3360 ng/g lw in sea cucumber (Figure 1 and Table 2). HFR level in sea cucumber was one order of magnitude higher than that in other organisms (mean: 82.4 ± 85.7 ng/g lw). The detection frequency for BDE-28, BDE-47, PBT, syn-DP, anti-DP, BDE-209 and DBDPE were all higher than 70%. DBDPE contributed the most proportion (40.7%) of ∑HFRs, followed by BDE-47 (17.6%), BDE-28 (11.3%), BDE-209 (10.8%) and DPs (7.12%). Similarly, DPs were predominantly accumulated in organisms with low trophic levels. Our results are comparable to that reported in Pearl River estuary, China (Xiang et al., 2006), and lower than that in an estuarine food web of Ariake Sea, Japan (Kobayashi et al., 2015), while much higher than that in Bohai Bay (Shao et al., 2016), Liaodong Bay, China (Ma et al., 2013) and three regions in Japan (Ashizuka et al., 2008).

HFRs concentrations and profiles varied greatly among the different groups of biotas. In two coastal zones, the levels of BDE-209 and DBDPE in benthic invertebrates were significantly higher than those in fish. In estuary, BDE-209 is the predominant compound in invertebrates, while DBDPE is the primary contributor in benthos of the bay. In estuary, all HFR concentrations in different groups of organisms (mean value) followed the order: bivalves > crustacean > plankton > fish (except for mullet) > gastropods, which analogous to the results in the bay, holothuroidea > bivalves > plankton > crustacean > fish > cephalopod > gastropods. ∑HFRs concentrations in invertebrates (mean value: 30.8 ng/g lw in estuary and 539 ng/g lw in bay) were generally higher than those in fish (except for mullet) (mean value: 11.8 ng/g lw in estuary and 41.6 ng/g lw in bay), which could attribute to the following factors, including different habitat, feeding habits and metabolic mechanism of HFRs in organisms. Bivalves are all filter feeders and mainly feed on plankton, diatom and organic detritus, attaching in sediments regularly. Crustaceans are omnivorous and mainly feed on plankton, bivalves, while gastropod is carnivorous and mainly feed on bivalve mollusks. The behavior of sea cucumber is resembled with that of bivalve, usually feeding on algae, organic detritus and micro-organisms in sediments and they can ingest sediments with organic matters abundant. Therefore, invertebrates had more chance to contact with sediment, indicating that besides absorption from seawater, ingesting sediment may contribute an additional pathway for HFRs accumulation. And the low TL organisms probably had inefficient metabolism and excretion for exogenous substances. Furthermore, lipid/protein ratio of different species, hydrological condition, selection of biotas (whole tissue of invertebrate and fish muscles) would also affect HFRs concentration levels of organisms. And the relative abundance of sea cucumber was resembled with that of sediment, suggesting that was impacted by habitat surroundings.

It can be seen clearly that species- and habitat dependent accumulation for organisms through HFRs distribution as described in the following. The fish with the highest concentration was detected in mullet (mean: 198 ng/g lw) of estuary, with BDE-28 and BDE-47 occupying a large proportion of the total concentrations (Table S3). This might ascribe to the fact that mullet is the only herbivorous fish and trophic level is relatively lower among fishes, mainly feeding on lower level living creatures (plankton, diatom and organic detritus). The phenomenon was consistent with the results that the highest HFRs value was also observed in mullet from Yellow River Delta, China (Zhang et al., 2020). Our result was also in line with that reported in estuary of Mihe River, where mullet showed the highest levels of hexabromocyclododecane (HBCD) (Zhang et al., 2018), demonstrating bioaccumulation ability of mullet for hydrophobic substances. The highest HFRs residue in invertebrates was observed in sea cucumber (2627-4671 ng/g lw) of bay (Table S4), with BDE-209 and DBDPE accounting largely of the total HFRs concentrations (21.9% and 76.1%, respectively), which may be associated with their long-term exposure to sediment. Conch had the lowest HFRs level among these species, which opposite to the results that the highest poly- and perfluoroalkyl substances (PFAS) concentration was detected in gastropod reported previously from the same batch samples in estuary (Li et al., 2021). And the relatively lower HFRs concentrations were found in gastropods (conch in estuary and sea snail in bay) in present study. This could be ascribed to the different physicochemical properties of contaminants, bioavailability and metabolism mechanism in vivo for organisms. Organic substances usually accumulate in organisms through partition to lipid component or combining with proteins. Conch had high protein and low fat, and PFAS prefer to bind with protein, while HFRs have affinity ability with lipid compartment (Li et al., 2021). Among the benthos, clam showed the highest ∑HFRs concentrations (mean value: 97.8 ng/g lw) in estuary, comparable to the same species in bay (mean value: 139 ng/g lw). The same is true for oyster in estuary (mean value: 27.5 ng/g lw), which had equivalent ∑HFRs concentration level with that in bay (mean value: 34.3 ng/g lw). The concentration levels of organisms from XRE are comparable to that in LZB, though the seawater of former is more polluted than that of the latter.

In addition, there were also distribution differences in HFRs levels and distinct congener profiles between two coastal zones. Higher concentration of DPs was found in organisms of bay comparing with the estuary. The concentrations of anti-DP were in general greater than syn-DP in organisms, which is similar to isomer profiles reported in green mussels from the south China sea (Sun et al., 2020). Plankton, sea cucumber and bay scallop showed high levels of DPs with high proportion of anti-DP. This suggested that species-specific bioaccumulation and habitat-dependent of DPs between different species regarding the terrestrial input into the bay. $F_{\text{anti-DP}}$ was used to clarify the behavior and fate of DPs in environment and was calculated by following equation: $f_{\text{anti-DP}}$ = anti-DP/(anti-DP + syn-DP) (Zhang et al., 2013). The $f_{\text{anti-DP}}$ values ranged from 0.5 to 1 with a mean value of 0.78, which close to the f_{anti} values of the DP commercial mixtures (0.64-0.80) (Wang et al., 2010). This may suggest that these aquatic organisms have low metabolism mechanism of DPs and there is no selective enrichment for the two DP isomers.

Factors influencing HFRs bioaccumulation for organisms

Factors such as dietary intake, habitat and exposure environment synthetically affect bioaccumulation for various types of organisms in different ways. For zoobenthos, ∑HFRs concentrations followed the order: filter feeding (mean value: 48.3 ng/g lw in estuary and 744 ng/g lw in Bay) > carnivorous (mean value: 5.90 ng/g lw in estuary and 29.3 ng/g lw in Bay) in these two coastal areas. These invertebrates were almost inhabited in the bottom of shallow sea or sand and muddy seafloor. The filter feeding biotas mainly feed on lower level living creatures (plankton, diatom and organic detritus), while the carnivorous invertebrates hunt shellfish and shrimp for food. Thus, feeding habit, prey and habitat may explain the intuitive differences in HFRs compositions among different zoobenthos. Fishes selected were almost lived in the benthic or gravel-associated environment, except for sea perch swimming in middle-upper layer seawater, which are all carnivorous and prey on invertebrates/small fish. Considering different migration behaviors, the ∑HFRs results displayed the following pattern: benthic non-migratory fish (mean value of tongue sole, finespotted flounder and jacopever: 47.1 ng/g lw) > oceanodromous fish (mean value of sea perch: 19.6 ng/g lw) in LZB. Demersal non-migratory fish is more vulnerable to be affected by water pollution from local source owing to the short migration distance and fixed water surroundings. Therefore, non-migratory fish may live in heavier contaminated environment and have higher HFRs levels than oceanodromous fish. Similar trends were also reported in LZB for organophosphate (Bekele et al., 2019) and Cl-PFESA in marine organisms from Bohai Sea, China (Liu et al., 2017). These results suggest that HFRs accumulation in fish is significantly different from that in invertebrates.

The conventional wisdom was that bioavailability of DBDPE was lower than that of BDE-209 owing to its relatively larger molecular weight and volume as compared with BDE-209 (Sun et al., 2020). However, the concentration of DBDPE in invertebrates (especially for bivalve and sea cucumber) was more than twice times higher than that of BDE-209 in this study. In plankton and invertebrates, DBDPE and

BDE-209 were the predominant compounds, which differed considerably with the profiles in fish occupying high trophic levels. BDE-209 and DBDPE were less detected than lower brominated congeners in fishes maybe due to their low bioavailability and fast biotransformation rate in fishes compared to the lower brominated congers. Previous studies have shown that BDE-209 can be metabolized into BDE-154 in common carp (Stapleton et al., 2004a), (Tomy et al., 2004) and some kinds of fish can debrominate BDE 99 to BDE-47 (Stapleton et al., 2004b), which may be the reason for low level of BDE-209 found in fish. Thus, BDE-209 may be transformed into low brominated congeners through metabolism in fishes with high TLs, while invertebrates have weaker metabolism capacity of BDE-209. This composition pattern was in agreement with the results from Taihu Lake (Zheng et al., 2018).

These two coastal zones share similarities but also exhibit differences, as the different physical hydrological conditions, salinity and nutrients. The major differentiator is as follows: (1) BDE-209 is the main substance in sediments and benthic invertebrates of estuary, while DBDPE is the primary contributor in the bay, reflecting a dependence on living habitat. This may be related to the different species of organisms, hydrodynamic conditions (salinity and nutrients, etc.) in the coastal waters, the complexity of estuarine environment and peripheral source inputting; (2) The higher level of DPs is observed in bay, suggesting the existence of DPs inputting from extra land-based source. The similarities lie in: The levels of BDE-209 and DBDPE in benthic invertebrates were significantly higher than those in fish, and the predominant compounds of fish in these two coastal zones are low bromine PBDEs. There may be possible links between invertebrates and sediments due to intimate contact, whereas fish pollution is the result of synthesized factors considering their wide swimming range. The distinct HFRs accumulation patterns may be the results of comprehensive factors i.e. feeding habit, habitat, migration behavior, exposure pathway, bioavailability and metabolic degradation in organisms of estuary-sea ecosystem (Jin et al., 2016).

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 2021 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.

References

Ashizuka, Y., Nakagawa, R., Hori, T., Yasutake, D., Tobiishi, K., Sasaki, K., 2008. Determination of brominated flame retardants and brominated dioxins in fish collected from three regions of Japan. Molecular Nutrition & Food Research 52, 273-283.

Bekele, T.G., Zhao, H., Wang, Q., Chen, J., 2019. Bioaccumulation and Trophic Transfer of Emerging Organophosphate Flame Retardants in the Marine Food Webs of Laizhou Bay, North China. Environ Sci Technol 53, 13417-13426.

Jin, X., Lee, S., Jeong, Y., Yu, J.-P., Baek, W.K., Shin, K.-H., Kannan, K., Moon, H.-B., 2016. Species-specific accumulation of polybrominated diphenyl ethers (PBDEs) and other emerging flame retardants in several species of birds from Korea. Environmental Pollution 219, 191-200.

Kobayashi, J., Imuta, Y., Komorita, T., Yamada, K., Ishibashi, H., Ishihara, F., Nakashima, N., Sakai, J., Arizono, K., Koga, M., 2015. Trophic magnification of polychlorinated biphenyls and polybrominated diphenyl ethers in an estuarine food web of the Ariake Sea, Japan. Chemosphere 118, 201-206.

Li, Y., Yao, J., Zhang, J., Pan, Y., Dai, J., Ji, C., Tang, J., 2021. First Report on the Bioaccumulation and Trophic Transfer of Perfluoroalkyl Ether Carboxylic Acids in Estuarine Food Web. Environ Sci Technol.

Li, Y., Zhen, X., Liu, L., Tian, C., Pan, X., Tang, J., 2019. Halogenated flame retardants in the sediments of the Chinese Yellow Sea and East China Sea. Chemosphere 234, 365-372.

Liu, L., Zhen, X., Wang, X., Zhang, D., Sun, L., Tang, J., 2021. Spatio-temporal variations and input patterns on the legacy and novel brominated flame retardants (BFRs) in coastal rivers of North China. Environmental Pollution 283.

Liu, Y., Ruan, T., Lin, Y., Liu, A., Yu, M., Liu, R., Meng, M., Wang, Y., Liu, J., Jiang, G., 2017. Chlorinated Polyfluoroalkyl Ether Sulfonic Acids in Marine Organisms from Bohai Sea, China: Occurrence, Temporal Variations, and Trophic Transfer Behavior. Environ Sci Technol 51, 4407-4414.

Ma, X., Zhang, H., Yao, Z., Zhao, X., Wang, L., Wang, Z., Chen, J., Chen, J., 2013. Bioaccumulation and trophic transfer of polybrominated diphenyl ethers (PBDEs) in a marine food web from Liaodong Bay, North China. Marine Pollution Bulletin 74, 110-115.

Shao, M., Tao, P., Wang, M., Jia, H., Li, Y.-F., 2016. Trophic magnification of polybrominated diphenyl ethers in the marine food web from coastal area of Bohai Bay, North China. Environmental Pollution 213, 379-385.

Stapleton, H.M., Alaee, M., Letcher, R.J., Baker, J.E., 2004a. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (Cyprinus carpio) following dietary exposure. Environmental Science & Technology 38, 112-119.

Stapleton, H.M., Letcher, R.J., Baker, J.E., 2004b. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (Cyprinus carpio). Environmental Science & Technology 38, 1054-1061.

Sun, R., Pan, C., Peng, F., Wu, Y., Chen, X., Mai, B., 2020. Alternative halogenated flame retardants (AHFRs) in green mussels from the south China sea. Environmental Research 182.

Tomy, G.T., Palace, V.P., Halldorson, T., Braekevelt, E., Danell, R., Wautier, K., Evans, B., Brinkworth, L., Fisk, A.T., 2004. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (Salvelinus namaycush). Environmental Science & Technology 38, 1496-1504.

Wang, D.-G., Yang, M., Qi, H., Sverko, E., Ma, W.-L., Li, Y.-F., Alaee, M., Reiner, E.J., Shen, L., 2010. An Asia-Specific Source of Dechlorane Plus: Concentration, Isomer Profiles, and Other Related Compounds. Environmental Science & Technology 44, 6608-6613.

Xiang, C.-h., Luo, X.-j., Yu, M., Meng, X.-z., Mai, B.-x., Zeng, E., 2006. Distribution of polybrominated diphenyl ethers in aquatic species from the Pearl River Estuary. Huan jing ke xue= Huanjing kexue 27, 1732-1737.

Zhang, H., Wang, P., Li, Y., Shang, H., Wang, Y., Wang, T., Zhang, Q., Jiang, G., 2013. Assessment on the Occupational Exposure of Manufacturing Workers to Dechlorane Plus through Blood and Hair Analysis. Environmental Science & Technology 47, 10567-10573.

Zhang, Y., Lu, Y., Wang, P., Shi, Y., 2018. Biomagnification of Hexabromocyclododecane (HBCD) in a coastal ecosystem near a large producer in China: Human exposure implication through food web transfer. Science of the Total Environment 624, 1213-1220.

Zhang, Z., Tong, X., Xing, Y., Ma, J., Jiang, R., Sun, Y., Li, J., Li, X., Wu, T., Xie, W., 2020. Polybrominated diphenyl ethers, decabromodiphenyl ethane and dechlorane plus in aquatic products from the Yellow River Delta, China. Marine Pollution Bulletin 161.

Zhao, Z., Zhong, G., Moeller, A., Xie, Z., Sturm, R., Ebinghaus, R., Tang, J., Zhang, G., 2011. Levels and distribution of Dechlorane Plus in coastal sediments of the Yellow Sea, North China. Chemosphere 83, 984-990.

Zheng, G., Wan, Y., Shi, S., Zhao, H., Gao, S., Zhang, S., An, L., Zhang, Z., 2018. Trophodynamics of

Emerging Brominated Flame Retardants in the Aquatic Food Web of Lake Taihu: Relationship with Organism Metabolism across Trophic Levels. Environmental Science & Technology 52, 4632-4640.