Environmental Pollution 283 (2021) 117093

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Spatio-temporal variations and input patterns on the legacy and novel brominated flame retardants (BFRs) in coastal rivers of North China☆

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ARTICLE INFO

*Article history:*
Received 25 December 2020
Received in revised form
2 April 2021
Accepted 3 April 2021
Available online 7 April 2021

*Keywords:*
Halogenated flame retardants
Production
Wet deposition
Biodegradation
High risk

ABSTRACT

Decabromodiphenyl ether (BDE209) has been subject to restrictions since 2018 in developed countries but is still manufacturing in China. Decabromodiphenyl ethane (DBDPE) is widely used as a replacement for BDE209. To better understand the behaviors and fates of these legacy and novel brominated flame retardants (BFRs), water samples were collected from the estuaries of 36 rivers that drain into the Bohai Sea (BS) and North Yellow Sea (NYS) in 2017 and 2018. The results showed that BDE209 was still the predominant compound with a median concentration of 2470 pg $L^{-1}$, whereas DBDPE had a median concentration of 129 pg $L^{-1}$. Spatially, relatively high concentrations were observed in the rivers near Laizhou Bay (LB), which is the manufacturing hub of BFRs. BDE209 concentrations were significantly higher in dry season than in wet season, which indicates a dominant process of dilution by precipitation during the wet season. DBDPE concentration showed no significant seasonal difference. This implies that wet deposition was the major additional source of DBDPE during the wet season, and the concentration increased further during the autumn as a result of a time-lag effect. The BFR concentrations in urban rivers were lower than those reported by a study undertaken in August 2013. An increase in the BFR concentrations in rural rivers since 2013 suggested increases in the use and non-point source emissions of BFRs in some remote aquatic environments. The estimated annual inputs of BDE209 and DBDPE into the BS were ~95.9 kg $yr^{-1}$ and ~26.8 kg $yr^{-1}$, respectively, whereas those into the NYS were ~24.1 kg $yr^{-1}$ and ~8.38 kg $yr^{-1}$. The results revealed an ecological risk of BDE209 in winter especially in the Xiaoqing River, thus suggesting the impact of BDE209 on the aquatic environment and human health.


## 1. Introduction

Brominated flame retardants (BFRs) are chemicals with properties similar to hydrophobic organic pollutants (HOPs), which with high affinity for particles and have raised great concerns over the past decades due to their environmental persistence, long-range transport, bioaccumulation, and toxicity to organisms (Wu et al., 2019). Polybrominated diphenyl ethers (PBDEs), including deca-BDE, have been gradually restricted and phased-out worldwide (UNEP 2018). Previous studies have showed that PBDEs can enter the environment not only by production processes, but also by directly leaching or volatilizing from products as they are addictive BFRs (Wang et al., 2018). Once released, PBDEs could easily migrate to the particle phase in air and water, and thus accumulate in the soil, sediments, and finally posed potential health risks to organism such as cytotoxicity (Tait et al., 2017), thyroid and neuro-developmental effects (Makey et al., 2016). Overall, prevalence contaminations of PBDE have been reported in various countries, e.g. USA (McDonough et al., 2016), Australia (McGrath et al., 2018),

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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https://doi.org/10.1016/j.envpol.2021.117093
0269-7491/

Germany (Vetter et al., 2017), UK (Tao et al., 2017), Canada (Law et al., 2006), or even Africa (Brits et al., 2016). With the phase-out of PBDEs in western countries, several novel brominated flame retardants (NBFRs), such as decabromodiphenyl ethane (DBDPE), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), and hexabromobenzene (HBB), have been used as alternatives in many industrial applications and domestic products, such as plastics, textiles, furniture, and electronic equipment. It is suggested that the molecular and physicochemical similarities of some alternatives to PBDEs might also result in unfavorable environmental fates (Covaci et al., 2011). Several NBFRs have a tendency to bioaccumulate and are potentially toxic owing to their optimum range of $K_{OW}$ (i.e., log $K_{OW}$ of 5–8) for bioaccumulation (Carlsson et al., 2018; Ezechias et al., 2014; Morris et al., 2018). Both legacy and emerging BFRs have been detected in various environments worldwide, and even transported to the polar regions and the deep ocean through the long-range atmospheric transport and ocean current (Brown et al., 2018; Carlsson et al., 2018; Ma et al., 2015).

China is the largest producer and user of BFRs in the world. According to some reports, the production and application of deca-BDE (mainly composed of BDE209) in electronics and electrical equipment are still continuing in China despite its restriction (Chen et al., 2020; Wang et al., 2018). Meanwhile, DBDPE has also been produced in large quantities, especially in the Laizhou Bay (LB) area, owing to the market demand of developed countries to replace deca-BDE. In China, DBDPE concentrations in many environmental components (e.g., air, seawater, and sediment) have been found to exceed those of BDE209 (Chen et al., 2019; Li et al., 2019; Yu et al., 2016; Zhen et al., 2018). Previous study in the Bohai Sea (BS) reported that DBDPE was the dominant compound in both air and seawater samples with the exception of August 2017, when BDE209 concentrations were obviously higher than those of DBDPE in surface seawater (Liu et al., 2020). It is suggested that different input patterns may influence the relative amounts of BDE209 and DBDPE in aquatic environments based on the atmospheric deposition fluexes of these two compounds (Liu et al., 2020). However, the major sources of DBDPE and other BFRs in this rapidly developing region remain unclear due to the lack of studies that have been undertaken in the rivers surrounding the BS.

The BS is a semi-closed water body with a narrow strait to the Yellow Sea, and includes three bays: Liaodong Bay (LDB), Bohai Bay (BB), and LB. Extremely high concentrations of BFRs have been detected in the inland region around the BS and in coastal waters as a result of emissions from manufacturing and consumption (Chen et al., 2019, 2020; Shao et al., 2016; Wang et al., 2017). The Bohai Rim (BR) is surrounded by Tianjin City and Shandong, Hebei, and Liaoning provinces, which have experienced rapid industrialization, urbanization, and economic development in recent decades (He et al., 2018; Zhao et al., 2011; Zheng et al., 2016). The most extensive production base of BFRs in northern China is in the BR, a region that supports approximately 22% of China's population. As the largest producer of BFRs in China, Shandong Province reported the highest emissions of 21.4 kt, of which ~5.8 kt was converted to solid waste to landfill, and ~8.33 kt entered the hydrosphere through discharges into nearby rivers (Chen et al., 2020). More than 100 rivers flow into the BS, which equates to a river water input of ~$10^{11}$ t $yr^{-1}$ that carries a variety of organic pollutants, including BFRs (Wang et al., 2015).

To date, only one publication had focused on the levels of BFRs in a river of the BR (Zhen et al., 2018); however, the estimated annual inputs of pollutants were generally inaccurate as the data concentrated on a specific period but not the entire year. Hence, the actual levels of BFRs in riverine inputs to the BR have not yet been fully understanded. Accordingly, the main objectives of the present study are (1) to investigate the current pollution levels and spatiotemporal variability of BFRs in 36 human impacted rivers that drain into the BS and North Yellow Sea (NYS); (2) to explore the seasonal variations of BFRs in relation to different input patterns; and (3) to provide accurate and valuable data for the assessment of annual riverine inputs of BFRs to the BS and NYS.

## 2. Method and materials

### 2.1. Sample collection

Water samples were collected from the mouths of 36 major rivers (R1 – R36) around the BS and NYS during four seasons: December 2017 and May, August, and October 2018. These rivers were chosen based on their lengths, water-loading volumes, and polluted conditions. The samples were collected across floodgates/dams (and bridges in some cases) as close as possible to the river mouth but avoiding to collect the seawater samples (Fig. 1). A global positioning system (GPS) was used to fix the location of each sampling site. For detailed information, see Table S1 in the Supporting Information (SI). Sampling was carried out using a 10 L stainless steel bucket. Glass microfiber filters (Whatman™, GF/F, diameter of 150 mm) were used to trap suspended particles, which was followed by a self-packed XAD-2 (20 g) glass column for the dissolved phase (~20 L for each sample). All glass columns and filter samples were stored at 4 °C and −20 °C prior to chemical analysis, respectively. The water sampling procedure followed the Chinese National Standard-Technical Specifications Requirements for Monitoring of Surface Water and Waste Water (HJ/T91 2012), with small modifications.

### 2.2. Chemicals and materials

The target analytes in this study included eight PBDEs (BDE28, BDE47, BDE99, BDE100, BDE154, BDE153, BDE183, and BDE209) and seven NBFRs (PBT, PBEB, TBP-DBPE, HBB, EH-TBB, TBE, and DBDPE). Standard mixtures of PBDEs and the seven NBFRs were acquired from Wellington Laboratories (Guelph, Ontario, Canada). PCB208 (AccuStandard, New Haven, CT, USA) was used as the internal standard, and $^{13}$C-HBB (Cambridge Isotope Laboratories, Woburn, MA, USA) was used as a surrogate standard. Neutral silica gel (80–100 mesh) was Soxhlet extracted with dichloromethane (DCM) for 72 h prior to use. Anhydrous sodium sulfate was baked at 450 °C for 5 h and liquid sealed with hexane. Laboratory glassware was cleaned and oven-dried at 450 °C before use.

### 2.3. Sample preparation and chemical analysis

Before extraction, each water filter was freeze-dried to remove the remaining water, and 10 ng of $^{13}$C-HBB (concentration: 0.5 ng $\mu L^{-1}$) was spiked into the solvent as a surrogate standard. Analytes in XAD-2 and filter samples were extracted using a modified Soxhlet extractor with ~250 mL dichloromethane (DCM, Merck KGaA, Germany; purity: > 99%) for 24 h (Xie et al., 2011), and the temperature is approximately 50 °C. Extracts were evaporated to 1–2 mL while the solvent was exchanged to hexane (Merck KGaA, Germany; purity: > 99%), and then cleaned in 2.5 g silica gel columns (10% water deactivated) topped with 3 g of anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Ltd; purity: > 99%), which was baked at 450 °C for 5 h prior to use. The extracts were then eluted with 22 mL of hexane and reduced to a final volume of 100 μL with nitrogen (purity 99.999%). As an internal standard, 20 ng of PCB208 (concentration: 1 ng $\mu L^{-1}$) was added to the solvent.

An Agilent 7890 gas chromatograph (GC) coupled with a 5975C mass selective detector (MSD) was operated in the electron-capture

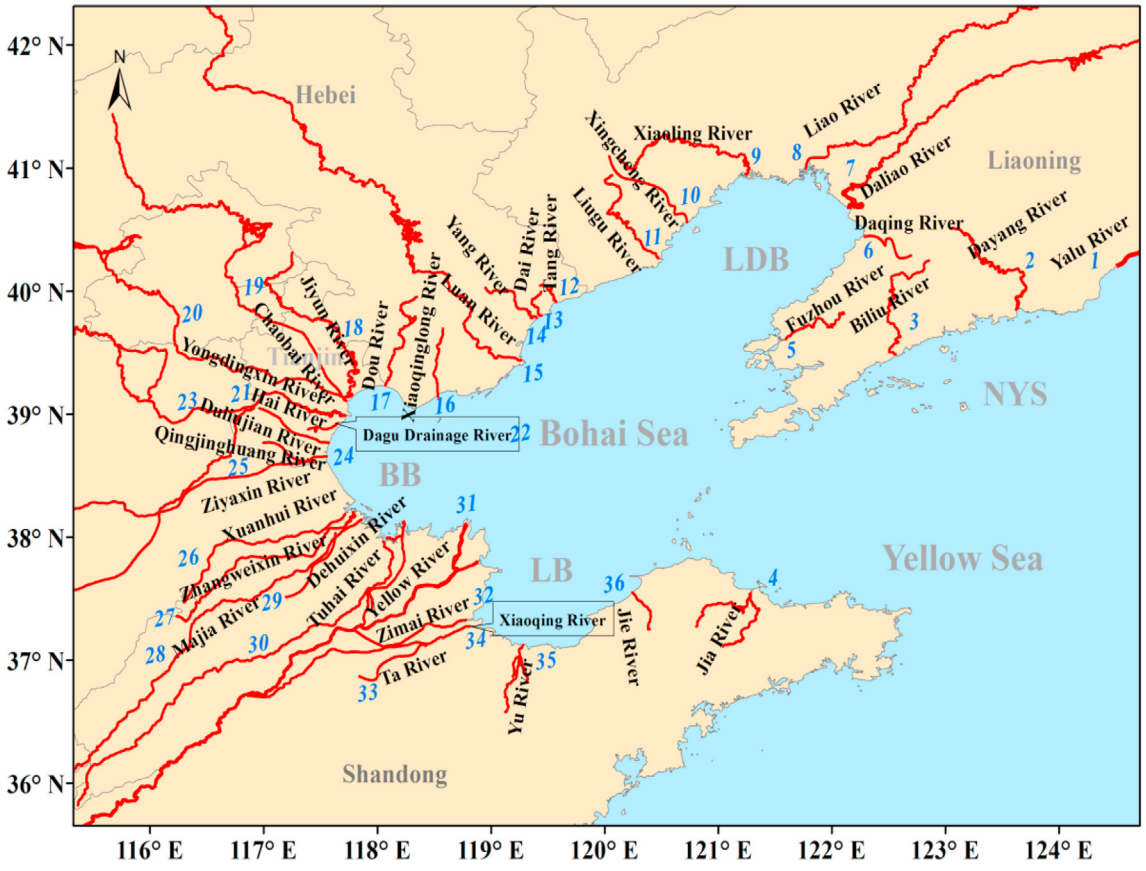


**Fig. 1.** Study area and sampled rivers around the Bohai Sea and North Yellow Sea. LDB (Liaodong Bay); BB (Bohai Bay); LB (Laizhou Bay); NYS (North Yellow Sea). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

negative-ion chemical ionization (ECNICI) mode to quantify PBDEs, NBFRs, and DPs. The applied MSD detector works in SIM mode, and the high purity helium was used as carrier gas. The capillary column was a DB-5HT typed column (15 m × 0.25 mm i.d., 0.10 μm film thickness, J&W Scientific). Split-less injection of a 1 μL sample was carried out with a 10 min solvent delay time. Details can be found in previous studies (Zhen et al., 2016, 2018).

### 2.4. Quality assurance and quality control

Glass vials, filters, silica gel, and anhydrous sodium sulfate were baked at 450 °C for 12 h prior to use, and XAD-2 columns were cleaned using a modified Soxhlet extractor with methanol, hexane/acetone (1:1), and dichloromethane, respectively, for 24 h. All columns were dried under a gentle flow of pure nitrogen (purity 99.999%). Field blanks, laboratory blanks, and replicate samples were analyzed with the field samples. The method detection limits (MDLs) were calculated based on the mean blank values plus three times the standard deviations of the blanks. If the values were below the MDL, they were considered as not detected (n.d.). The MDL ranges of PBDEs and NBFRs for the particle phase were 0.19–0.66 pg $L^{-1}$ and 0.31–76.0 pg $L^{-1}$, respectively. For the seawater dissolved phase, the MDL ranges in the dissolved phase were 0.33–2.80 pg $L^{-1}$ and 0.30–53.0 pg $L^{-1,}$ respectively. The recoveries of the target analytes ranged from 65% to 127% (mean of 96%) in the dissolved phase, and the range in the particle phase ranged from 57% to 88% (mean of 66%), with relative standard deviations of <7%.

### 2.5. Data analyses

Data analyses were performed using Microsoft Excel 2016. Correlation analysis for normal or non-normal distributed data groups was conducted using the corresponding Spearman or Pearson tests. Significant differences between different regions or seasons were analyzed using a one-way analysis of variance (ANOVA) test, followed by a least significant difference (LSD) multiple comparisons test. All statistical analyses were performed using PASW Statistics 18 (Statistical Product and Service Solutions, SPSS). The BFRs in each river around the NYS and BS were mapped using ArcGIS 10.2 (Environmental Systems Research Institute, ESRI). The following equations were used to calculate the seasonal BFR discharge fluxes (kg season$^{-1}$) and risk quotient (RQ).

$$F_R = \sum_{j=1}^{n}(C_d + C_p) \times V_r \quad (1)$$

where $C_d$ and $C_p$ (pg $L^{-1}$) are dissolved and particulate HFRs concentration in the $j$th river, respectively. $V_r$ is the runoff amount of each river ($10^8$ $m^3$) and the details have been listed in Table S1. The ecological risk of PBDEs in water was assessed using the risk quotient (RQ) on non-target organisms (Liang et al., 2019; Xiong et al., 2016).

$$\mathrm{RQ} = \frac{MEC}{PNEC} = \frac{MEC}{EC_{50}\ or\ LC_{50}/f} \quad (2)$$

where *MEC* is measured concentration of pollutants in waters (mg

$L^{-1}$); *PNEC* is the predicted no-effect concentration (mg $L^{-1}$) estimated as a quotient of toxicological relevant concentration ($EC_{50}$ or $LC_{50}$) with a security factor ($f = 1000$). At three trophic levels, the values of $EC_{50}$ or $LC_{50}$ for fish, daphnia, and algae associate with PBDEs were collected from assessment in River Aire (Cristale et al., 2013).

## 3. Results and discussion

### 3.1. Concentration and composition profiles of BFRs

Seven PBDE congeners and eight NBFRs were identified in the water samples (particle and dissolved phases) from 36 rivers around the BS. Their concentration characteristics are shown in Table S2 – S5. With the exception of PBEB, HBB, and TBE (detection rate < 10%), most BFRs were detected in estuaries, thus suggesting their ubiquitous distribution in the water environments of the BR region. As shown in Table 1, among the 144 water samples, the total BFR concentration (ΣBFRs) ranged from 12.9 pg $L^{-1}$ to 284 ng $L^{-1}$, with a median of 2.86 ng $L^{-1}$. The median PBDE concentration in samples from R1 – R36 over the four sampling seasons was 2.58 ng $L^{-1}$ (range: 12.1 pg $L^{-1}$ – 238 ng $L^{-1}$). As the predominant compound, BDE209 (range: 2.86 pg $L^{-1}$ – 238 ng $L^{-1}$; median: 2.47 ng $L^{-1}$) accounted for approximately 99.6% of the PBDE congeners, and was followed by BDE99 (median: 1.12 pg $L^{-1}$), BDE47 (median: 0.82 pg $L^{-1}$), and BDE183 (median: 0.74 pg $L^{-1}$). BDE99 and BDE47 can be produced by the debromination of BDE209, and can be bioaccumulated in organisms, presenting potential long-term environmental concerns (Yan et al., 2018). The findings suggest that although penta-BDE and octa-BDE were not widely applied in China, their still can be widely detected in the environment, and also indicate that the production and application of deca-BDE (mainly composed of BDE209) continues in China despite having been listed as a POP in 2018 (UNEP 2018).

Concentrations of NBFRs ranged from <MDL to 46.4 ng $L^{-1}$ (median: 130 pg $L^{-1}$), with DBDPE (range: <MDL – 46.4 ng $L^{-1}$, median: 129 pg $L^{-1}$) as the predominant compound (99.7% of the total NBFRs). The median DBDPE concentration (129 pg $L^{-1}$) was considerably lower than the median BDE209 concentration (2470 pg $L^{-1}$). According to a previous study in the BS, DBDPE exhibited higher concentrations in seawater samples in comparison to BDE209, which indicate that there are additional sources of DBDPE in the BS besides the common source of river discharge (Liu et al., 2020). In the present study, PBT was also detected in 84% of water samples, with a median concentration of 0.53 pg $L^{-1}$. Most studies have focused on BFR concentrations in estuarine sediments or organisms (Gui et al., 2018; Hu et al., 2019; Simond et al., 2017; Zhang et al., 2019), and no results have been reported on the occurrence of BFRs in such a wide range of estuarine environments. Our findings revealed that the highest BFR concentrations were found in the Xiaoqing River (up to 284 ng $L^{-1}$), which is close to the largest manufacturing base of BFRs in China. Generally, contamination of the BRs is of a moderate to high level in comparison to global levels. For example, the PBDE concentrations in water samples from the Yellow River (406 pg $L^{-1}$ – 7.89 ng $L^{-1}$) (Pei et al., 2018), Beijiang River (<MDL – 232 pg $L^{-1}$) (Xiong et al., 2016), Pearl River Estuary in China (344 pg $L^{-1}$ – 68 ng $L^{-1}$) (Guan et al., 2009), and San Francisco Estuary in the USA (3–513 pg $L^{-1}$) (Oros et al., 2005), and Chenab River, Pakistan (48 pg $L^{-1}$ -73.4 ng $L^{-1}$) (Mahmood et al., 2015) were lower than those reported in the current study (12.1 pg $L^{-1}$ – 238 ng $L^{-1}$). The latter were comparable to those previously reported for the Svitava River in the Czech Republic (<MDL – 335 ng $L^{-1}$) (Jarova et al., 2016), the Guanlan River in China (8.20 ng $L^{-1}$ – 186 ng $L^{-1}$) (Liang et al., 2019) and the River Aire in UK (17 ng $L^{-1}$ – 295 ng $L^{-1}$) (Cristale et al., 2013). While the concentrations of PBDEs from this study were lower than those reported in Diep River, Cape Town, South Africa (320 ng $L^{-1}$ - 485 ng $L^{-1}$) (Daso et al., 2013).

### 3.2. Variations of BFRs between 2013 and 2018

To explore the source signatures, rivers were categorized into three groups according to their surrounding environmental characteristics: i) "BFR-production rivers" included the Tahe River (R33), Xiaoqing River (R34), and Yuhe River (R35); ii) rural and remote rivers included the Yalu River (R1), Dayang River (R2), Biliu River (R3), and Fuzhou River (R5); and iii) urban rivers included the Jiyun River (R18), Haihe River (R21), and Dagu Drainage River (R22), of which the latter passes through Tianjin City. To compare the changes in BFR pollution over time, the BFR concentrations in the samples collected from 27 rivers in August 2013 (unpublished data) and from the current study were analyzed. Generally, BFR concentrations in 2018 were significantly lower than those in 2013 (Fig. 2). The median concentrations of BDE209 and DBDPE in the particle phase in August 2013 were 509 pg $L^{-1}$ (50.4 pg $L^{-1}$ – 38 ng $L^{-1}$) and 318 pg $L^{-1}$ (11.8 pg $L^{-1}$ – 14.4 ng $L^{-1}$), respectively;

**Table 1**
Concentration of BFRs in river estuaries of the study area during four sampling seasons (particle phase + dissolved phase; unit: pg $L^{-1}$).

| Compounds | December 2017 | | May 2018 | | August 2018 | | October 2018 | | Median of all |
|---|---|---|---|---|---|---|---|---|---|
| | Range | Median | Range | Median | Range | Median | Range | Median | |
| BDE28 | <MDL-2.82 | 0.3 | <MDL-3.58 | 0.08 | <MDL-181 | <MDL | <MDL-13.4 | <MDL | <MDL |
| BDE47 | <MDL-66.8 | 0.813 | <MDL-31.8 | 0.784 | <MDL-118 | 0.914 | <MDL-26.7 | 0.571 | 0.818 |
| BDE100 | <MDL-7.62 | <MDL | <MDL-0.94 | <MDL | <MDL-22.1 | <MDL | <MDL-2.90 | <MDL | <MDL |
| BDE99 | <MDL-73 | 1.19 | <MDL-10.4 | 0.805 | <MDL-230 | 1.75 | <MDL-23.6 | 1.1 | 1.12 |
| BDE154 | <MDL-14.8 | 0.26 | <MDL-2.74 | 0.199 | <MDL-57.6 | <MDL | <MDL-5.23 | 0.126 | 0.171 |
| BDE153 | <MDL-55.2 | 0.484 | <MDL-7.03 | <MDL | <MDL-230 | <MDL | <MDL-197 | 0.28 | <MDL |
| BDE183 | <MDL-13.8 | 1.389 | <MDL-12.6 | <MDL | <MDL-33.5 | 0.59 | <MDL-11.3 | 1.21 | 0.737 |
| BDE209 | 4020–238,000 | 5580 | 50.1–13200 | 4120 | 14.2–8920 | 144 | 2.86–19900 | 68.6 | 2470 |
| **PBDEs** | 4030–238,000 | 5590 | 96.9–13200 | 4130 | 14.6–8920 | 175 | 12.1–20100 | 73 | 2580 |
| PBT | <MDL-12.2 | 0.819 | <MDL-7.79 | 0.37 | <MDL-5.72 | 0.454 | <MDL-34.5 | 0.454 | 0.53 |
| PBEB | <MDL-2.59 | <MDL | <MDL-6.29 | <MDL | <MDL-1.73 | <MDL | <MDL-20.7 | <MDL | <MDL |
| DPTE | <MDL-2.03 | 0.293 | <MDL-1.01 | 0.17 | <MDL-0.514 | <MDL | <MDL-50.8 | <MDL | <MDL |
| HBB | <MDL-47.2 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL |
| TBB | <MDL-2.91 | <MDL | <MDL-5.48 | <MDL | <MDL-3.91 | <MDL | <MDL-7.33 | <MDL | <MDL |
| TBE(BTBPE) | <MDL-16.9 | <MDL | <MDL-22.8 | <MDL | <MDL | <MDL | <MDL-13.0 | <MDL | <MDL |
| DBDPE | 32.5–46400 | 120 | <MDL-5080 | 112 | <MDL-9870 | 112 | <MDL-16100 | 251 | 129 |
| **NBFRs** | 32.5–46400 | 121 | <MDL-5080 | 114 | <MDL-9880 | 115 | 0.252–16200 | 252 | 130 |
| **ΣBFRs** | 4210–284,000 | 5840 | 196–18300 | 4240 | 16.5–17100 | 322 | 12.9–36300 | 327 | 2860 |

however, in August 2018, these values decreased to 109 pg $L^{-1}$ (14.2 pg $L^{-1}$ – 7.15 ng $L^{-1}$) and 85 pg $L^{-1}$ (<MDL – 9.87 ng $L^{-1}$), respectively. As shown in Fig. 2, BFR concentrations decreased by > 90% in most rivers flowing into BB, especially those passing through the Tianjin City. This illustrates the excellent effects of pollution control policy and environmental project that was implemented by Tianjin municipal government commenced in September 2013. However, BFR concentrations did not decrease between 2013 and 2018 in other rivers around the BS, and actually increased in the Yalu River (R1), Dayang River (R2), and Fuzhou River (R5). The upstream region of R1 is mountainous and forested, while the downstream region is predominantly rural with a low population, abundant fishery resources, and a tourism industry. Domestic sewage and industrial wastewater from Dandong City and the surrounding towns in the lower reach of R1 are discharged into the river. The concentrations of BDE209 (571 pg $L^{-1}$) and DBDPE (519 pg $L^{-1}$) in samples from R1 in August 2018 were more than 10 times higher than those in August 2013. Other rural rivers in this study, such as R2 and R5, also presented increasing BFR concentrations between 2013 and 2018. These findings imply an increased use and non-point source emission of BFR pollution in some remote aquatic environments in the study region. This may relate to improved living standards in the less developed areas, which could have increased the use of BFR-containing domestic furniture or/and electrical appliances. The DBDPE concentrations in 2018 were higher than those in 2013 in R8, R18, R22, and R34. The BDE209 concentrations in R34 were comparable in both years. Therefore, it can be concluded that BDE209 did not exhibit a decreasing trend in the Xiaoqing River, and even DBDPE increased by 82.5% between 2013 and 2018 in this river. Hence, our results imply that deca-BDE production is still the major source of BFR pollution in the BS environment.

### 3.3. Spatial trends in BFR levels

Compared to BDE209 and DBDPE concentrations, the other compounds showed extremely low levels in the water samples, and were mainly partitioned into the particle phase (>99%) due to their low water solubility and high $K_{ow}$ values. The following discussion focuses on BDE209 and DBDPE in suspended particle matter (SPM). Fig. 2 (A – D) displays the spatial distributions of BDE209 and DBDPE in the sampled rivers around the BS during the four sampling seasons. Table S6 and Fig. S1 present the mean BFR concentration in each season. The samples could be divided into four areas according to their geological locations: the NYS, LDB, BB, and LB. The NYS and LDB are adjacent to Liaoning Province, and rivers run through many important large- or medium-sized industrial cities in northeast China. Bohai Bay receives a large amount of industrial wastewater and domestic sewage from the Beijing-Tianjin-Hebei megalopolis. Laizhou Bay is close to Shandong Province, where bromine production capacity accounts for 80%–90% of the national production (Gong et al., 2017). The most famous chemical industrial base - Weifang Binhai Economic Development Zone, is located along the south coast of the LB (Pan et al., 2011), which mainstay industries is brominated chemical production and a large number of BFR-manufacturing plants of are scattered in this region (Jin et al., 2008), such as Shandong Brother Sci. & Tech. Co., LTD, Shandong Haiwang Chemical Co., LTD, and Shandong Haihua Group Co., LTD, which bromine production capacity are in the forefront of China. It was studied that there were approximately 200 million tons of terrigenous sewage discharged into the LB every year (Pan et al., 2011). The general tendency of BFRs in the four regions was ranked as: LB > BB > NYS > LDB (Fig. 3 and S1).

The Jiahe River (R4, mean: 3.62 ± 4.04 ng $L^{-1}$) is strongly affected by BFR pollution in Shandong Province. As the river belonging to the NYS, inputs from the Jiahe River aggravate pollution levels in the NYS. The Daliao River (R7, mean: 3.82 ± 5.01 ng $L^{-1}$) receives sewage from eight prefecture-level cities in Liaoning Province, and had the highest BFR concentrations of all the rivers flowing into LDB. The Luanhe River (R15, mean concentration: 5.75 ± 5.82 ng $L^{-1}$) has a water depth of <20 m and was found to be the most polluted river among the 19 rivers in the BB region. The Luanhe River is the most important water source for Tianjin, Tangshan, and Chengde City; however, this basin has experienced rapid industrialization and urbanization in recent decades. The Xiaoqing River (R34, mean concentration: 88.9 ± 131 ng $L^{-1}$) was found to be the most polluted river in LB and the entire BR region, thus suggesting the direct influence of nearby production of BFRs. Regional differences in the total BFR, BDE209, and DBDPE concentrations were analyzed using LSD multiple comparisons test. The test excluded R33, R34, and R35 as these were heavily affected by the original production of deca-BDE. Although the BFR concentrations varied across the regions, their variation ranges were similar (Table S6). BDE209 and DBDPE were no significant difference between any two regions excepted for R33, R34, and R35 (a >0.05) (Table S7), thus exhibiting relatively uniform patterns of usage in Liaoning Province, Beijing-Tianjin-Hebei megalopolis, and Shandong Province.

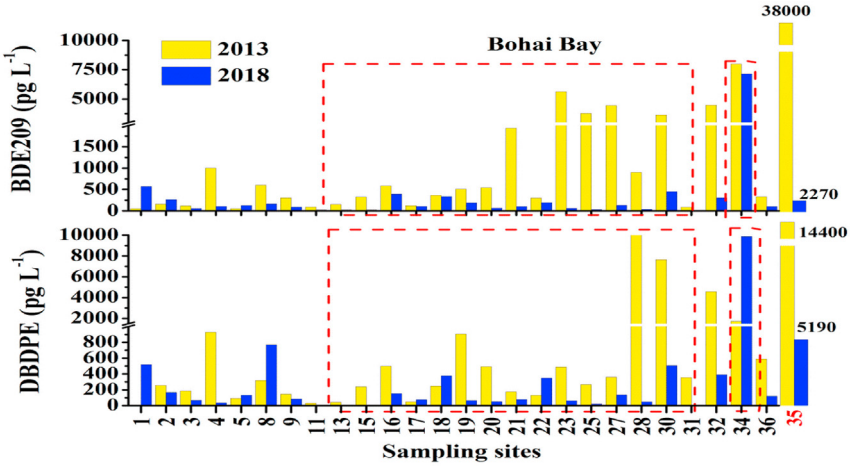


**Fig. 2.** Spatial variations of two BFRs in 27 rivers during August 2013 and August 2019.

With the exception of R33, R34, and R35, which are heavily affected by neighboring manufacturing activities, the elevated levels of BFRs observed in BB were associated with the high population density (PD) of the Beijing-Tianjin-Hebei megacities. The results showed that R4, R7, R15, and R34 were the most polluted rivers in the NYS, LDB, BB, and LB, with mean concentrations of 3.62 ± 4.04 ng $L^{-1}$, 3.82 ± 5.01 ng $L^{-1}$, 5.75 ± 5.82 ng $L^{-1}$, and 88.9 ± 131 ng $L^{-1}$, respectively (Table S6). Population density and gross domestic product (GDP) have been considered as important influential factors on the distribution of BFRs (Li et al., 2020; Su et al., 2017). In the cities where R4, R7, R15, and R34 pass through, the PD in 2018 was 518 people $km^{-2}$, 432 people $km^{-2}$, 587 people $km^{-2}$, and 591 people $km^{-2}$, respectively, and the corresponding GDP in 2018 reached 783, 135, 695, and 616 billion RMB (http://tjj.ln.gov.cn; http://www.tangshan.gov.cn; http://www.stats-sd.gov.cn). These PD and GDP values were the highest or second highest compared to those for other rivers in each region. Therefore, in accordance with the finding that high values of these two indices imply intensive anthropogenic activities, this would, to some extent, have resulted in high levels of BFR pollution in these river basins. The correlation between the total BFR concentration and urban PD of each river was calculated. A strong correlation was found for the LDB area ($P < 0.05$, $R^2 = 0.723$) (Table S8; Fig. S2), whereas no significant correlations were observed in the NYS, BB, and LB areas. However, high BFR concentrations (R15 in BB: 5.75 ng $L^{-1}$; R33, R34, and R35, mean: 36 ng $L^{-1}$) co-existed with relatively high PDs (e.g., Tangshan City: 587 people $km^{-2}$; Weifang City: 591 people $km^{-2}$). Overall, it can be concluded that the populous regions corresponded to high BFR concentrations.

### 3.4. Seasonal variation in BFRs

The seasonal variations of BDE209 and DBDPE in the particle phases are also presented in Fig. 3. The BFR concentrations in December (range: 4.21–284 ng $L^{-1}$; median: 5.84 ng $L^{-1}$) and May (range: 106 pg $L^{-1}$ – 14.9 ng $L^{-1}$; median: 4.22 ng $L^{-1}$) were significantly higher than those in August (range: 14.2 pg $L^{-1}$ – 12.3 ng $L^{-1}$; median: 262 pg $L^{-1}$) and October (range: 11.3 pg $L^{-1}$ – 35.9 ng $L^{-1}$; median: 321 pg $L^{-1}$). For individual target compounds, BDE209 showed a distinguishable variation between the dry season and wet season (Table S6). However, no significant variation in DBDPE was observed between the four seasons using a one-way ANOVA ($a = 0.537$). The BDE209 concentrations in rural and urban rivers in December and May were one or two orders of magnitude higher than those in August and October. However, the seasonal variation in BFR-production rivers was different; BDE209 levels were indistinguishable between May and October in R33, R34, and R35. Although BDE209 concentrations reduced considerably in August, they were still higher than those of rural/remote and urban rivers over the same period. There was no obvious seasonal variation of DBDPE concentrations in urban, rural/remote, and BFR-production rivers. In most rural/remote and urban rivers, the DBDPE concentrations in October were higher than those of BDE209. This was inconsistent with the trend observed in BFR-production rivers, where BDE209 was the major pollutant in all seasons, which suggests its continuous production and mass residues in the LB area.

As shown in Fig. 3, BDE209 was the major compound in the particle phase of river water samples (median: 2.47 ng $L^{-1}$), and had a much higher concentration than the second dominant compound DBDPE (median: 121 pg $L^{-1}$). The BDE209 concentration was 2–3 orders of magnitude lower during the wet season in comparison to the dry season, which suggests a dominant process of dilution during the wet season due to substantial overland flow after rainfall events (Gdara et al., 2018). In addition, biodegradation and photodegradation might be stronger in summer due to the higher activity of microorganisms and increased sunlight (Han et al., 2020). Phytoplankton blooms, which are common in freshwater ecosystems, can not only affect water quality but also influence the biogeochemical processing of pollutants in aquatic environments (Gunnarsson et al., 1995; Yang et al., 2020). An increasing abundance of algae is an important source of particulate organic carbon (POC) in SPM (Yang et al., 2020). Fig. S3 presents a seasonal comparison of the SPM levels in various water bodies. This shows that the total SPM content was much higher in summer than in spring, autumn, and winter, thus implying an extensive biomass along with algae blooms. Enhanced biodegradation, which might be attributed to the increased metabolic capacity of the bacterial community, can lower the concentration of hydrophobic organic chemicals in rivers (Shi et al., 2017). However, unlike the profound seasonal variations of BDE209, no obvious seasonal variation was observed for DBDPE. This result strongly suggests that extra DBDPE may have been discharged into the rivers from rainfall/runoff in summer, which could have added to relatively high concentrations despite the dilution effect. Rainfall can not only dilute pollutant concentrations in river water, but may also lead to additional DBDPE inputs from atmospheric particulates during the wet season. A previous study reported that atmospheric deposition played a primary role in DBDPE inputs to the BS (Liu et al., 2020). Table S9 summarizes the mean monthly rainfall of 2018 at seven coastal sites in the BR region. Fig. S4 shows that August was the rainiest month, with a high frequency of rainfall under the influence of the East Asian monsoon. Precipitation during the wet season (July, August, and September) accounted for ~70% of the total rainfall in 2018. Furthermore, high SPM concentrations in August indicate heavy rainfall (Fig. S4). Majority of the particles entering rivers were accompanied by rainfall/runoff, or were resuspended from the river bottom, which further increased the concentrations of hydrophobic organic pollutants. There are many studies have been reported that atmospheric deposition played an important role in transferring organic pollutants from air to soils, waters and sediments (Huang et al., 2014; Li et al., 2010; Wang et al., 2013). Hence, wet deposition was an important pathway for DBDPE to enter the rivers of the study area. As shown in Fig. 4, the percentages of DBDPE increased further in autumn, except for the river near production source in LB, thus indicating that the effect of time lag on the accumulation of DBDPE lasted from the wet season to the beginning of the dry season. The results showed that DBDPE was not detected in some rivers in August (e.g., R13 and R15), but then increased sharply (R13: 1.8 ng $L^{-1}$, R15: 13.8 ng $L^{-1}$) in October. This implies the input of extra DBDPE into some rivers via untreated sewage or hidden sewage outfalls, and the continued contribution of point-source emissions. Owing to their similar physicochemical properties and environmental behavior, the variation of the DBDPE/BDE209 ratio in different seasons (Table S10) may indicate unequal emission sources in various aquatic environments. Among the three rivers most affected by production sources (R33, R34, and R35), which belong to Weifang City, the DBDPE/BDE209 ratio was always < 1 in all seasons. This result suggests the enhanced production and mass residues of BDE209, although DBDPE has been widely used worldwide.

### 3.5. BFR fluxes and water discharge of coastal rivers

Riverine runoff is a vital mode for transporting anthropogenic pollutants from terrestrial sources to adjacent oceans. The annual runoff (cubic meters) of each of the 36 rivers (Table S1) was used to estimate the corresponding fluxes of BFRs to the BS and NYS. The fractions of runoff during the wet, normal, and dry seasons were estimated as 0.7, 0.2, and 0.1, respectively, according to the rainfall

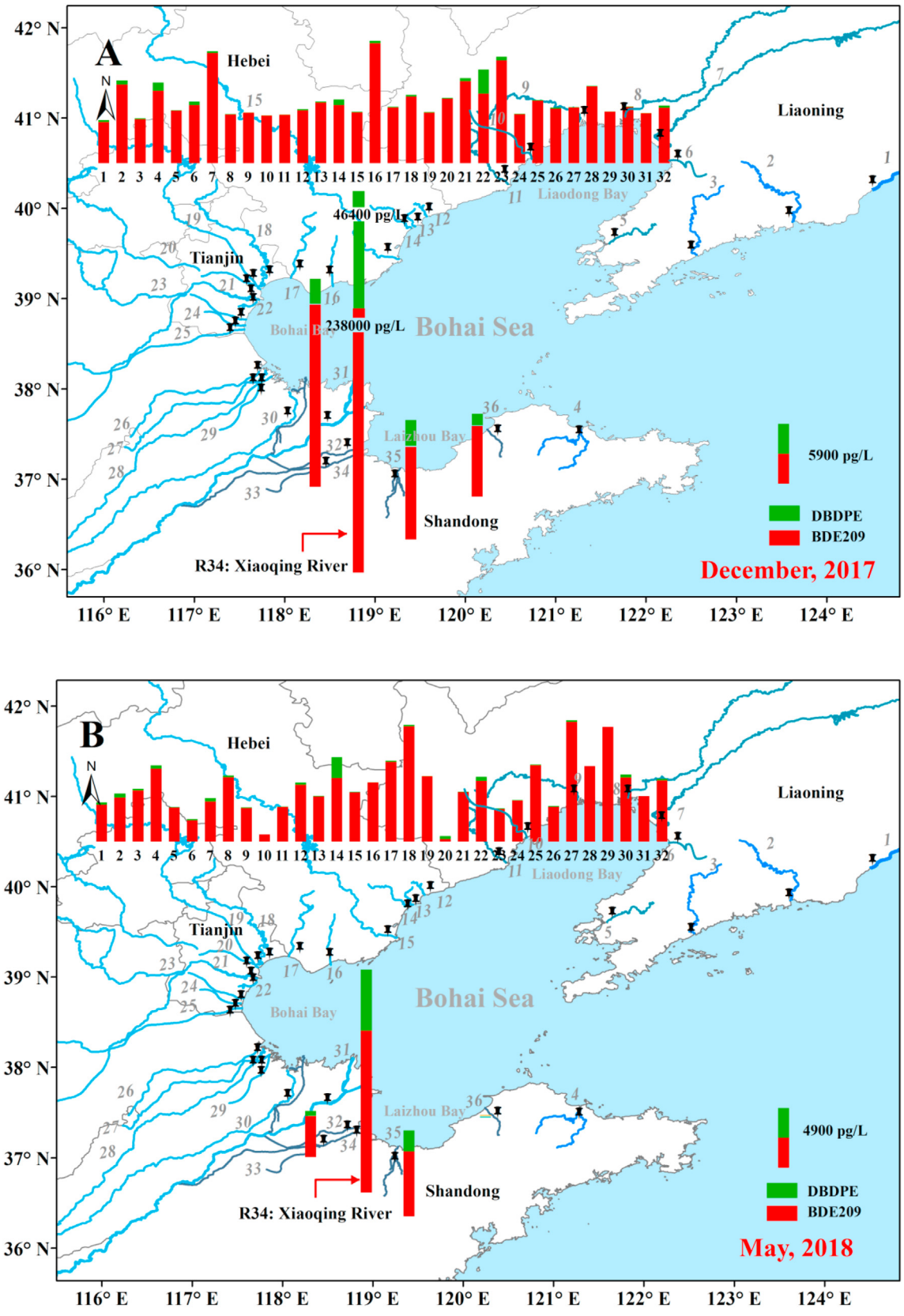


**Fig. 3.** Sampling stations of 36 rivers and spatial distributions of BDE209 and DBDPE in December 2017 (A), May 2018 (B), August 2018 (C), and October 2018 (D).

fractions in these periods (Liang et al., 2018; Wang et al., 2015). The annual discharges of BDE209 and DBDPE were estimated to be ~95.9 kg $yr^{-1}$ and ~26.8 kg $yr^{-1}$ to the BS, respectively, and ~24.1 kg $yr^{-1}$ and ~8.38 kg $yr^{-1}$ to the NYS, respectively (Table S11).

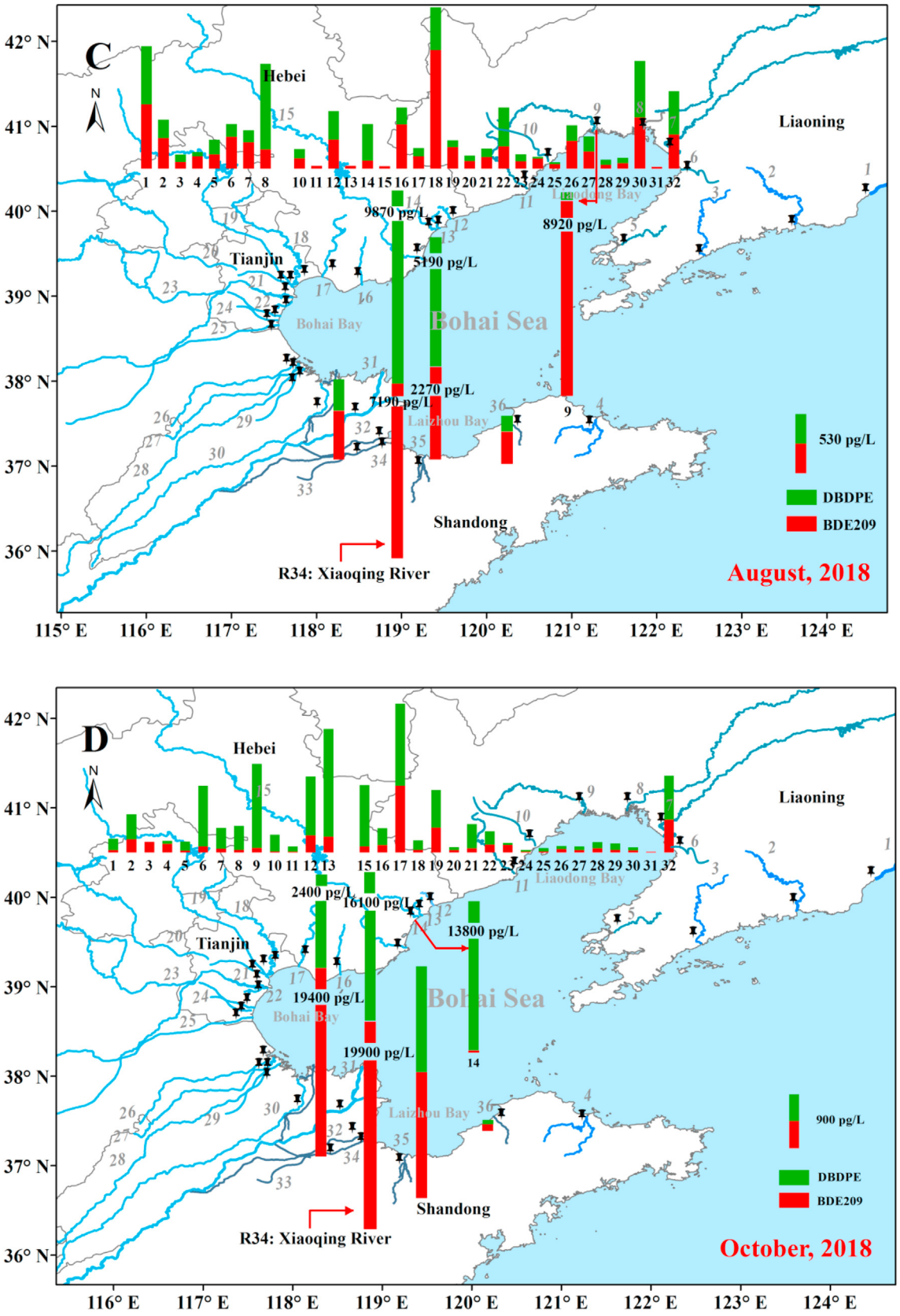


**Fig. 3.** (*continued*).

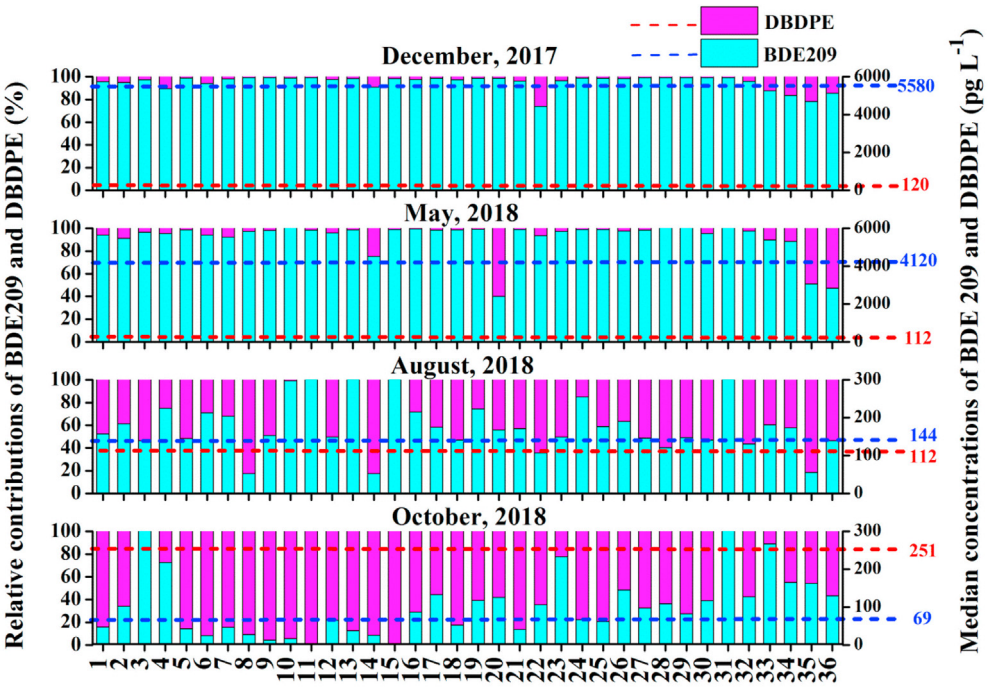


**Fig. 4.** Relative contributions (%) and median values (pg $L^{-1}$) of BDE209 and DBDPE in four sampling seasons.

With respect to individual estuaries, five riverine outlets (the Yalu, Daliao, Liaohe, Luanhe, and Yellow rivers) discharged considerably more BFRs in comparison to the other rivers in the NYS, LDB, and BB areas (Fig. S5). This may be attributed to the high river runoff in these five estuaries, although the mean BFR concentrations did not exhibit the same variability as the inputs. Influenced by mass production, the Xiaoqing River (R34) contributed the highest BFR fluxes (BDE209: 28.2 kg $yr^{-1}$; DBDPE: 12 kg $yr^{-1}$) among the 36 rivers. These BFR fluxes were higher than those in 2013 (BDE209: 7.02 kg $yr^{-1}$; DBDPE: 1.52 kg $yr^{-1}$); hence, there was an overall increasing temporal trend since 2013. The correlations between the riverine inputs of BDE209 ($P < 0.01$, $R^2 = 0.543$) and the volume of water discharged from each river were relatively linear, whereas those for DBDPE were non-correlation (Fig. S6). These results indicate that the levels of BDE209 in the rivers of the BR may have reached a quasi-steady state in recent years, and that precipitation has become a controlling factor in the transport of these contaminants to the BS and NYS. As the most popular NBFR in current China (Wang et al., 2018), the fluxes of DBDPE were not only influenced by seasonal river flows, but also by unsteady production, use, and discharge.

### 3.6. Ecological risk assessment of PBDEs in rivers

The ecotoxicity of BFR pollutants in water was assessed using the RQ (Eq. (2)) for living organisms (Liang et al., 2019). As the ecological screening assessment of DBDPE has not yet been accurately reported by Environment Canada, and the other NBFRs were at a low detection rate or low concentration, the ecotoxicity of BDE 28, BDE47, BDE99, BDE100, BDE153, BDE183 and BDE209 (mean values > 3.5 pg $L^{-1}$, detection rates > 50%) at three trophic levels (green algae, daphnia, and fish) were investigated in each sampled river during the four seasons using the EC50/LC 50 data from Cristale et al. (2013) and Xiong et al. (2016) (Table S12). The results revealed that there was no PBDE-associated risk posed to surrounding organisms and ecosystems, except from BDE209. According to the results for BDE209, low ($1.0 < RQ < 10$) potential for adverse effects associated to BDE209 were observed along the most rivers in winter. However, for the sampling point in the Xiaoqing River, significant ($10 < RQ < 100$) potential for adverse effects were the same for these three aquatic organisms, with RQs value of 52.3 for fish, 49.6 for Daphnia, and 45.7 for algae, respectively. In May, the most rivers in LDB presented no risk for adverse effects, while low risk was observed at the sampling rivers situated near BB and LB. The risk assessment indicated no risk for potential effects to aquatic organisms associated to the sampling seasons in August and October expected the Xiaoqing River, indicating that deca-BDE occur in Xiaoqing River at constant contamination especially in winter. A detailed and refined assessment of the potential risk of DBDPE to aquatic life in the study region should be undertaken soon.

## 4. Conclusion

BFRs were investigated in 36 river mouths at different seasons around the Bohai Sea and Northern Yellow Sea, and BDE209 and DBDPE were two dominant species. BDE209 concentrations were evidently higher in the dry season than in the wet season, thus indicating a significantly dilution effect of precipitation. Enhanced biodegradation during the summer may have been one reason for the lower concentrations of hydrophobic organic pollutants in the sampled rivers. The DBDPE concentration was comparable in summer and winter, which suggests that wet deposition was an important pathway for DBDPE to enter water bodies. The results of the correlation between riverine inputs and water flow indicated that BDE209 might have reached a quasi-steady state in the rivers of the BR region; however, the fluxes of DBDPE were not only controlled by the volume of river discharge but also by unsteady production, use, and discharge. Deca-BDE contamination in the 36 sampled rivers was found to pose a low risk to aquatic organisms in winter excepted for Xiaoqing River, which pose significant ($10 < RQ < 100$) potential for adverse effects for these three aquatic

organisms. This could lead to the bioaccumulation of this compound in fishes that is ultimately exported to the market.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This study was supported by the National Natural Science Foundation of China (NSFC)-Shandong Joint Fund (No. U1806207) and NSFC (No. 41773138), key deployment project of the Centre for Ocean Mega-Science, Chinese Academy of Sciences (COMS2019J08) and by the seed project of Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences (No. YIC Y855011024).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117093.

## Contribution of the authors

Lin LIU: Conceptualization; Investigation; Methodology; Writing – original draft. Xiaomei ZHEN: Investigation; Methodology, Xinming WANG: Funding acquisition; Project administration; Resources; Supervision; Writing – review & editing, Daochang ZHANG: Investigation, Linting SUN: Investigation, Jianhui Tang: Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Writing – review & editing.

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