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The impact of national energy structure on the concentrations, environmental behavior, and sources of polycyclic aromatic hydrocarbons in riverine and coastal sediments of the Beibu Gulf, China

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ABSTRACT

In this study, polycyclic aromatic hydrocarbons (PAHs) were measured in sediments of the Beibu Gulf in 2017 to investigate sources and a risk assessment. The results showed the total PAH concentration ($\sum_{16}$PAHs) in sediments of the Beibu Gulf in 2017 (17.6 ± 16.7 ng g^{-1}) was significantly lower than that in 2010 (47.8 ± 27.4 ng g^{-1}). The $\sum_{16}$PAHs concentrations varied spatially within the Beibu Gulf, impacted by point source pollution. The results of adsorption/desorption and water-air partitioning suggest that the environmental behavior of PAHs in the Beibu Gulf is affected by atmospheric deposition and sediment-water partitioning. A risk assessment showed that the PAHs in sediments were within a safety threshold. Three source apportionment methods show that oil spills and oil and biomass burning were the most important (>83.8%) sources of PAHs in sediments of the Beibu Gulf.

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) with high toxicity, carcinogenicity, and teratogenicity (Bansal and Kim, 2015; Wang et al., 2019). The primary sources of PAHs include natural sources (e.g., biosynthesis, grasslands, forest fires, and volcanic eruptions) and anthropogenic sources (e.g., incomplete combustion and pyrolysis of fossil fuels and other hydrocarbons) (Braendli et al., 2007; Yunker et al., 2002). The concentration of PAHs in the environment has increased significantly in response to increasing human activity; more PAHs have integrated into the biogeochemical cycle of the surface system that includes their migration, exchange, enrichment, precipitation, and transformation (Gioia et al., 2011; Liu et al., 2017).

The coastal zone is affected by land and ocean processes, forming an independent environmental system with a land-sea transition (Fei et al., 2011). While coastal environments have degraded under the influence of global climate change and sea level rise, the release of toxic substances, such as PAHs, promoted by human activities (Hu et al., 2014; Kirwan and Megonigal, 2013), is negatively impacting these environments. Previous studies have found that PAHs can accumulate in benthic organisms and have adverse effects on other organisms in aquatic environments (Han et al., 2020; Li et al., 2019; Oladi and Shokri, 2021; Witt and Trost, 1999; Yang et al., 2020; Zhang et al., 2021). The Beibu Gulf is located northwest of the South China Sea, with a tortuous coastline, and is the most important and convenient harbor in Southwest China. The Beibu Gulf is one of China's 20 major coastal hub ports, navigable to more than 100 countries and regions in the world (Chen et al., 2016). The shallow, coastal sea has a broad tidal flat, promoting locally developed seafood aquaculture, and has a well-known pearl breeding land at home and abroad. Previous study have shown that the $\sum_{15}$PAHs (total concentration of 15 PAHs) in surface sediment collected in the Qinzhou Bay, a part of the Beibu Gulf, ranged from 3.01 to 288 ng g^{-1} (mean: 95.5 ng g^{-1}) in 2010, and the $\sum_{15}$PAHs in a sediment core from Qinzhou Bay showed an increasing trend from 2009 to 2010 (Li et al., 2015). In recent years, the Chinese energy structure has shifted, and the economy in the regions adjacent to the Beibu Gulf has developed rapidly. Therefore, the environmental level of PAHs may change in response to recent energy structure developments. The environmental behavior of PAHs, such as sediment-seawater partitioning and gas-

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seawater exchange, may also change; yet, previous studies have not focused on the environmental behavior of PAHs in the Beibu Gulf.

The present study aimed to investigate: (1) the spatial changes in the concentration and composition of PAHs in surface sediments of rivers and coastal areas of the Beibu Gulf; (2) the environmental behavior of PAHs in sediment, seawater, and the atmosphere; (3) the source characteristics and contributions of PAHs by three different source apportionment methods; and (4) the ecological risk of PAHs in sediments of the Beibu Gulf.

In August 2017, a total of 60 river and coastal sediment samples were collected from four bays (Pearl Bay, Qinzhou Bay, Sanniang Bay, and Lianzhou Bay), two ports (Ports of Fangcheng and Tieshan), and five rivers (Fangcheng, Maoling, Qinjiang, Dafeng, and Nanliu rivers) in the Beibu Gulf. A polyurethane foam passive sampler (PUF-PAS) was installed near sampling site 27 (Pearl Bay, 23 December to 1 March, 7 June to 8 August, 2017) for the long-term monitoring of PAHs in the atmospheric environment, as per previous studies (Chaemfa et al., 2014; Wang et al., 2007). The total collection time was 59 days in winter and 65 days in summer. The longitude and latitude of each sampling site are shown in Table S1. Sediment samples were collected using a gravity sampler and stored in pre-cleaned glass bottles. All collected sediment samples were stored at 20 °C and transported to the laboratory for analysis.

Sixteen priority PAHs were selected in this study, including naphthalene (NAP), acenaphthylene (ACEY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANTH), fluoranthene (FLUA), pyrene (PYR), chrysene (CHR), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DiB), indeno[1,2,3-*cd*]pyrene (Ind), and benzo[*g*,*h*,*i*]perylene (BghiP). The physicochemical properties and molecular formulas of the 16 target PAHs are listed in Table S3 and Fig. S1.

Five deuterium-labeled PAHs (naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12) were used as analytical surrogates. Procurement sources and processing procedures for all chemicals and materials used in this study are summarized in Text S1 and Table S3. Sediment samples were cleaned and extracted according to previously described method (Han et al., 2020; Xu et al., 2012; Zhang et al., 2021). Briefly, 10 g of freeze-dried, homogenized sediment samples was extracted by Soxhlet extraction with dichloromethane. After purification and preconcentration, 200 ng of hexamethylbenzene was added as an internal standard for the analysis. The target PAHs were analyzed using an Agilent 7890 gas chromatograph coupled to a tandem 7000C triple quadrupole mass spectrometer system (GC–MS/MS). The detailed GC–MS/MS operational parameters for the PAHs analysis are presented in Text S2 and Table S2.

Before the extraction, five known concentrations of deuterated PAHs were added to all samples as surrogate standards to monitor analytical recovery. Blank and duplicate samples were collected at the sampling site, analysis site, and laboratory to detect possible contamination. Contamination observed during the sampling and extraction of samples was detected by adding repeated samples, experimental blanks, and program blanks. The recoveries of five deuterium-labeled PAH surrogates were 60–82% (naphthalene-D8), 71–92% (acenaphthene-D10), 73–94% (phenanthrene-D10), 75–104% (chrysene-D12), and 71–93% (perylene-D12), respectively. The relative standard deviation (RSD) between replicate samples was 14 ± 5%. The target PAHs in all blank samples were lower than the detection limit. The instrument detection limits (IDLs) and instrument quantitation limits (IQLs) were defined as three- and ten-times the signal-to-noise (S/N) ratios, respectively. The Method detection limit (MDLs) of target PAHs were 0.01–0.07 ng g^{-1} (Table S3).

The concentrations of 16 PAHs ($\sum_{16}$PAHs) in sediments of the Beibu Gulf are summarized in Fig. 1 and Table S4. All 16 PAHs were detected in sediments, and the detection frequencies of the 16 PAHs were more than 95%, indicating that PAHs were ubiquitous in surface sediments of the Beibu Gulf. The $\sum_{16}$PAHs ranged from 0.53 to 295 ng g^{-1}, with an average concentration of 29.8 ± 59.1 ng g^{-1}. As shown in Fig. S2, the relative compositions of PAHs in all samples were comparable. The 4-ring PAHs accounted for the highest proportion, with an average of 35.4 ± 9.4%. The average $\sum_{16}$PAHs were lower than those detected in 2010 and 2011 (Li et al., 2015; Yang et al., 2013) (Table S7).

In general, the $\sum_{16}$PAHs concentrations in surface sediments of the Beibu Gulf show a significant regional difference, with high concentrations in the west and low concentrations in the east. PAH concentrations were found to be higher in Qinzhou Bay, Fangcheng Port, and Pearl Bay but were lower in Sanniangwan, Lianzhou Bay, and Tieshan Port (Fig. 1). The occurrence of PAHs is closely related to local source emissions, human activities, and energy structures. With the influence of Fangcheng Port and Qinzhou industrial park in recent years, the rapid development of the port shipping industry may have directly increased PAH concentrations in these waters. The eastern part of the Beibu Gulf is adjacent to the Leizhou Peninsula, with a low level of economic development and a slow urbanization process, contributing to minimal pollution. The average $\sum_{16}$PAHs in sediments from the upstream rivers

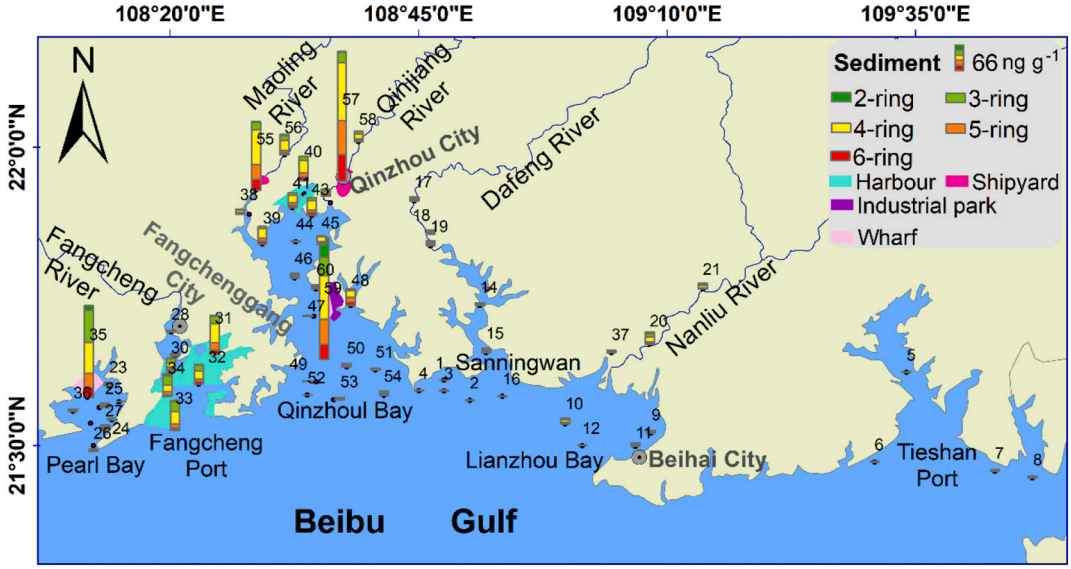

Fig. 1. Spatial distribution of PAHs in coastal sediments of the Beibu Gulf.

(59.8 ± 89.1 ng g^{-1}) of various Bay areas or ports is higher than that in downstream coastal areas (23.8 ± 49.0 ng g^{-1}) (nonparametric-test, $p < 0.05$). The river is directly affected by urban, industrial, and agricultural activities, and land-based pollutants, such as sewage from industrial parks, tail gas from urban transportation, and particulate matter from farmland straw combustion, entering the rivers through rainwater scouring and sedimentation. Terrestrial PAHs can bioaccumulate in aquatic organisms, threatening their health, and adsorb to suspended particles, migrating to the river bottom via physical settlement or biochemical reactions. Compared with the river water system, coastal seawater is continuously exchanged with offshore seawater, owing to the sea currents, diffusion and other factors, and PAHs in surface sediments of the seabed may re-suspend and enter the overlying water (Guigue et al., 2017; Wang et al., 2020). In addition, river discharge is an important pathway through which pollutants migrate to the marine environment; rivers usually store more pollutants than the marine environment.

The concentrations of PAHs in river sediment samples varied spatially in the Beibu Gulf (Fig. 2-a), and the concentrations were in the order of: Qinjiang (159 ± 135 ng g^{-1}, $n = 2$) > Maoling River (101 ± 54.5 ng g^{-1}, n = 2) > Nanliu River (15.4 ± 9.01 ng g^{-1}, $n = 3$) > Dafeng River (10.0 ± 1.36 ng g^{-1}, n = 3) (nonparametric-test, $p < 0.05$). The Qinjiang and Maoling rivers are important water sources for industrial and agricultural production and domestic use in Qinzhou City. The industrialization of Qinzhou City promotes human activities, such as the direct discharge of domestic sewage containing PAHs, industrial and agricultural activities, and urban transportation, possibly contributing to increasing PAHs concentrations in sediments of these two rivers flowing through Qinzhou City (Bi et al., 2014). Elevated $\sum_{16}$PAHs concentrations were found at sampling sites 57 and 55, reaching 295 and 156 ng g^{-1}, respectively. Potential point source pollution may increase the level of PAHs at these sites (Fig. 1). The concentrations of PAHs in sediments from the coastal zone also varied spatially (Fig. 2-b). The $\sum_{16}$PAHs concentrations were present in the order of: Fangcheng Port (41.7 ± 29.2 ng g^{-1}, $n = 7$) > Pearl Bay (31.5 ± 66.7 ng g^{-1}, n = 7) > Qinzhou Gulf (30.8 ± 60.0 ng g^{-1}, $n = 19$) > Lianzhou Bay (6.79 ± 4.22 ng g^{-1}, $n = 4$) > Sanningwan (3.01 ± 3.50 ng g^{-1}, n = 7) > Tieshan Port (2.27 ± 1.17 ng g^{-1}, n = 4) (nonparametric-test, $p < 0.05$). Fangcheng Port is a deep-water port with a highly developed port transportation industry in Guangxi. The impact of the shipping industry, aquaculture, and industrial activities in the bay enhances PAH pollution. Moreover, Fangcheng Port lies a river valley, and PAHs are more likely to deposit. The water exchange capacity of Qinzhou Bay is low, forming intertidal shoals and wide underwater deltas. The pollution of the Maoling and Qinjiang rivers flows into Qinzhou Bay, enhancing PAH pollution. In addition, Qinzhou is the key development base of the Beibu Gulf, and port development and ship transportation also enhance PAH pollution. High $\sum_{16}$PAHs concentrations occurred at sites 59 (276 ng g^{-1}) and 35 (208 ng g^{-1}). Petroleum pollution from nearby terminals may be a potential source of PAHs, and site 59 may be directly affected by the sewage discharge from enterprises in the park (Fig. 1). PAHs are transported to the marine environment via suspended solids and aerosol particles (i.e., atmospheric deposition) and accumulate in surface sediments through sedimentation. When the concentration of PAHs in sediments increases, some PAHs are partition into the water column or bioaccumulate in aquatic organisms, especially in benthos (Han et al., 2020; Li et al., 2019), threatening the marine ecological environment.

The occurrence of pollutants in the environment is often closely related to the transformation of the national energy structure, regional economic transformation, and national environmental governance. The environmental carrying capacity of the land-sea transition zone is limited, and it is sensitive to chemical pollutants, reflecting regional pollution temporal trends (Hu et al., 2016; Khuman et al., 2018). As shown in Fig. 3, PAH pollution in Qinzhou Bay in 2017 was significantly lower compared to that in 2010 (Li et al., 2015), and the average $\sum_{16}$PAHs concentration in 2017 (17.6 ± 16.7 ng g^{-1}; range: 0.86–55.3 ng g^{-1}) was about 60% lower than that in 2010 (47.8 ± 27.4 ng g^{-1}; range: 3.01–388 ng g^{-1}). The concentrations of PAHs with 3 and 4 rings (i.e., PHE, PYR, FLUA, and BbF) significantly decreased. Previous studies suggest that these PAHs are mainly released during coal combustion (Sofowote et al., 2008), providing strong, supporting evidence for economic transformation and energy reform in the Beibu Gulf Economic Zone. Since the 2010s, the transformation of China's energy strategy is accelerating, and the production structure is optimizing, reducing PAH emissions (Li et al., 2021). With the continuous improvement of laws and regulations by the Chinese government and the continued increase in environmental governance investments, the heavy industry of Chinese enterprises continues to transform and improve. China has gradually established a long-term monitoring mechanism for POPs, and its environmental awareness is improving. Various positive factors have promoted effective regional environmental

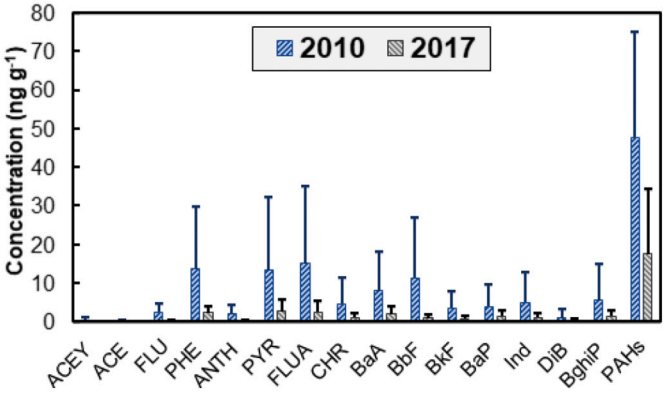

Fig. 3. Comparison of PAH concentrations in Qinzhou Bay in 2010 and 2017.

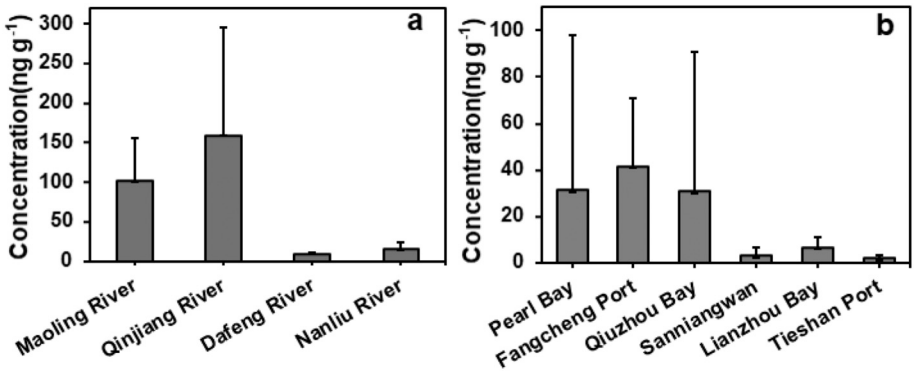

Fig. 2. Concentration of PAHs in sediments of various rivers (a) and the coastal zone (b) of the Beibu Gulf.

treatments for PAHs, as observed in Qinzhou Bay.

POPs can partition between different media, and adsorption–desorption is an important factor affecting the distribution of POPs between sediment and water. The environmental behavior of PAHs during different seasons was investigated by estimating the partition coefficients of PAHs between sediment and water. The corresponding PAH concentrations in the water of the Beibu Gulf are taken from our previous study (Han et al., 2021). K_d (L/kg) is used to describe the distribution coefficient when the concentration of a chemical substance establishes an equilibrium between sediment and water for a certain period. K_{OC} (L/kg) is the organic carbon-normalized distribution coefficient:

$$K_d = C_S/C_W \times 1000 \quad (1)$$

$$K_{OC} = K_d/TOC \quad (2)$$

where C_s and C_w are the concentrations of PAHs in the sediment (ng g^{-1}) and water (ng L^{-1}), respectively. PAHs below the detection limit in the water samples were replaced by their MDLs.

We calculated the field-derived K_{OC} regardless of PAHs establishing an equilibrium between sediments and water. Here, we use the following formula (Zhang et al., 2020) to define the adsorption–desorption coefficient for PAHs:

$$f = \text{field}K_{OC}/\text{experimental } K_{OC} \quad (3)$$

$$log\, f = log \text{ field } K_{OC} - log \text{ experimental } K_{OC} \quad (4)$$

The experimental K_{OC} was measured in the laboratory using the EPA CompTox Chemicals Dashboard (EPA, 2021, accessed May 08). The adsorption–desorption equilibrium is established for PAHs when $\log f = 0$, whereas PAHs are desorbed from and adsorb to sediment when $\log f > 0$ and $\log f < 0$, respectively. In this study, most of the Beibu Gulf area is characterized by the desorption of PAHs from sediments to water; however, adsorption is observed at some sites, especially at Qinjiang, Qinzhou Bay, and Pearl Bay, represented by sites 57, 27, and 38, respectively (Tables S8 and S9). The relationship between the average experimental K_{OC} and the average field-derived K_{OC} is shown in Fig. 4. Without considering other factors, most PAHs in sediments of the Beibu Gulf desorb from sediments to water, irrespective of the season (i.e., summer or winter). Three PAHs (ANTH, DiB, and Ind) adsorbed to sediment; ANTH adsorption only occurred during the summer, while DiB and Ind adsorption occurred in both seasons. The field-derived K_{OC} values of DiB and Ind were lower than the experimental values, possibly because they were not detected in water, and the field-derived K_{OC} values were calculated using MDLs. Unfortunately, in the calculation of adsorption desorption in winter, due to the lack of data on PAHs in winter sediments, we use the PAHs concentration in summer sediments for calculation, which may cause some uncertainty. In addition, a two-film transport model was used to estimate the air-water exchange fluxes for PAHs in the Beibu Gulf in summer and winter (Whitman, 1924), according to the method described in Text S3. The negative flux of $\sum_{15}$PAHs showed PAH partitioning from the atmospheric environment to water (winter: −12.0 ng m^{-2} d^{-1}; summer: −1.67 ng m^{-2} d^{-1}) (Fig. S4). The high flux in winter may be due to atmospheric deposition to the marine environment from northeast winds, resulting from the heating and convection of air masses in northern China. Furthermore, the temperature in winter is lower than that in summer, and PAHs are more likely to sink (Reisen and Arey, 2005). Therefore, PAHs in sediments and the atmospheric environment of the Beibu Gulf tend to partition to the water. Once PAHs continue to partition to the water environment, their concentrations increase in water (Lin et al., 2013). PAHs are further transported to distant places through currents and water exchange, threatening the marine ecological environment (Li et al., 2019; Zhang et al., 2021). Simultaneously, PAHs can easily enter aquatic organisms through bioaccumulation, causing negative ecological effects and potential health risks (Beek, 2000; Han et al., 2020; Jafarabadi et al., 2018).

Three typical source apportionment methods were used to investigate PAH source contributions in sediments from the Beibu Gulf area: diagnostic ratio, principal component analysis and multiple linear regression (PCA/MLR), and probabilistic matrix factorization (PMF). The three methods are described in detail in Text S4.

The source apportionment of PAHs using the diagnostic ratio method is based on the same molar mass and similar physicochemical properties of the compounds. As shown in Text S4, the potential sources of PAHs can be determined using different ratios (Chen et al., 2012; Yunker et al., 2002). The ratios of ANTH/(ANTH+PHE) were mostly below 0.1, and the BaA/(BaA + CHR) ranged between 0.52 and 0.79 (Fig. 5-a and b), respectively, indicating a petrogenic source of PAHs in this region (Yunker et al., 2002; Zhang et al., 2008). The ratios of FLUA/(FLUA + PYR) and Ind/(Ind + BghiP) mostly ranged from 0.40 to 0.50 and 0.20 to 0.50, respectively, suggesting the combustion of liquid fuel as the source of PAHs (Fig. 5-c). The ratios of FLUA/(FLUA+PYR) at sites 35 and 59 (high concentrations) were much greater than 0.5, indicating that the nearby wharf partly contributed to the solid fuel combustion source. Furthermore, the ratios of ANTH/PHE and FLUA/PYR were greater than 0.1 and 1, respectively, suggesting coal and wood combustion sources, whereas ANTH/PHE and FLUA/PYR ratios were less than 0.1 and 1, suggesting petrogenic sources (Chen et al., 2012; Duodu et al., 2017). The ratios of ANTH/PHE were less than 0.1 in most samples, while ratios of FLUA/PYR were mostly less than 1.0, indicating that a petrogenic source was the main contributor of PAHs in this region (Fig. 5-d). Combined with all diagnostic ratios, PAH sources in surface sediments of the Beibu Gulf are likely from petrogenic and combustion of liquid fossil fuel sources. The combustion and leakage of gasoline and diesel used in urban vehicles and coastal vessels may be an important source of PAHs in sediments. Based on previous study on PAHs in Beibu Gulf sediments, the ratios of ANTH/PHE and FLUA/PYR indicated that coal and biomass

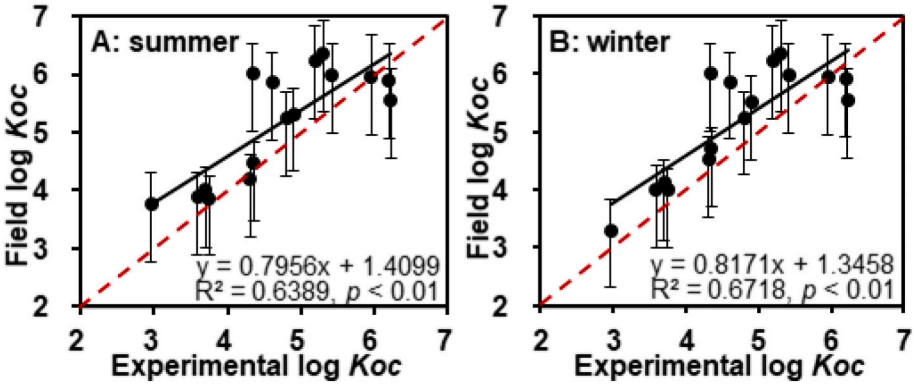

Fig. 4. Relationship between the field-derived log K_{OC} and experimental log K_{OC} for PAHs (A: summer; B: winter).

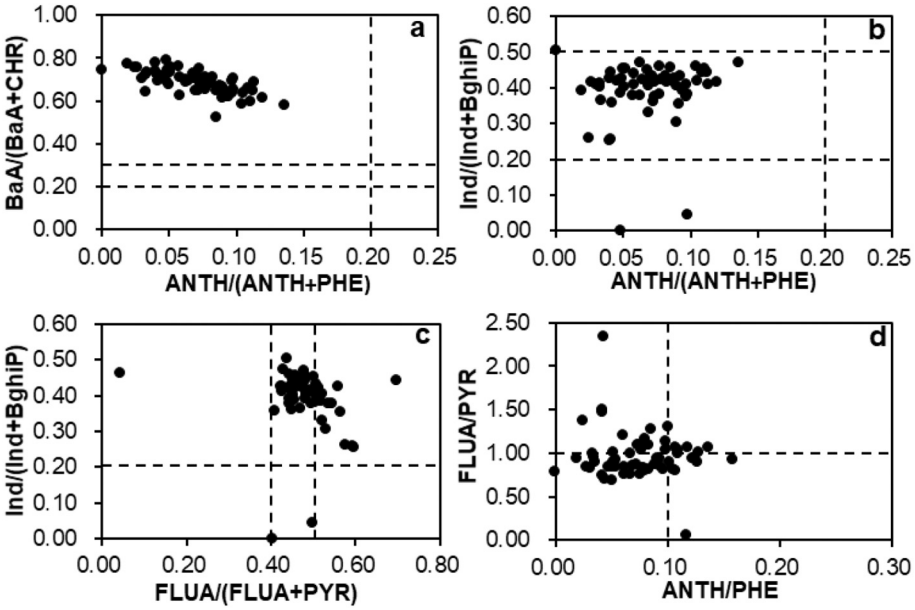

Fig. 5. Diagnostic ratios for source identification of PAHs in sediments of the Beibu Gulf.

combustion was an important source of PAHs in this area in 2010 (Li et al., 2015). However, the ratio results show that coal combustion contributes little to PAHs. As mentioned above, the change in PAH contribution sources may be closely related to changes in the local energy structure (Hu et al., 2016; Khuman et al., 2018).

The PCA results of PAH concentrations in sediments of the Beibu Gulf are shown in Fig. S3. The explained variances of the two principal components (PCs) were 78.4% and 14.6%, respectively, accounting for 91.9% of the total variability. PC1 was significantly correlated with PAHs produced by the combustion of petroleum-related products, including PYR, CHR, BkF, Ind, BGP, BaP, and other HMW-PAHs (Harrison et al., 1996; Larsen and Baker, 2003). In contrast, PC2 was mainly loaded with LMW- and MMW-PAHs, including ACE, FLU, PHE, NAP, FLUA, and ACEY, attributed to oil spill and biomass combustion sources (Ko et al., 2014; Zhang et al., 2021). Overall, PAHs in surface sediments of the Beibu Gulf coastal area mainly originated from ship navigation and fishery activities. Accidental oil spills from coastal oil extraction activities and straw combustion from nearby agricultural activities are also important PAH sources in this area. The MLR was used to evaluate the contributions of the two sources. The results showed that the contribution of oil combustion-related sources was 57.2%, while that of the oil spill and biomass combustion was 42.8% (Fig. 6). Therefore, the pollution of urban vehicle exhaust, coastal shipping industry, and fishery activities were the main contributors to PAHs in surface sediments. Meanwhile, accidental oil spills caused by industrial activities, and biomass combustion caused by agricultural activities, should not be ignored.

According to previous studies (Larsen and Baker, 2003; Lin et al., 2013; Liu et al., 2017; Ma et al., 2014; Xiong et al., 2020; Zhang et al., 2021), the EPA PMF5.0 was applied to estimate the source of PAHs in sediments of the Beibu Gulf (Text S4).

In this study, 3–8 factors were initially tested for PMF analysis and based on the uncertainty analysis, a solution of four factors with 100 seeds yielded the most stable PMF identification results (Tables S10 and S11). The ratio of the PMF predicted concentration to the measured concentration was almost uniform in the sediment ($y = 0.9998x + 0.0037$, $R^2 = 0.999$) (Fig. S6). Four sources, namely, oil spills, oil combustion-related sources, coal combustion, and biomass combustion, were preliminarily determined based on the tracer species and specific ratios of paired PAHs (Fig. 7). Specifically, the first factor contributed 16.3% to the PAHs and was dominated by NAP, characterizing petroleum. The second factor accounted for 37.7% of the $\sum_{16}$PAHs (Fig. 6). It was highly weighted in Ind, BkF, and CHR, suggesting oil combustion-related sources (Harrison et al., 1996; Larsen and Baker, 2003). The third factor represented 16.2% of the $\sum_{16}$PAHs and had a significant loading of FLUA. Research literature has cited FLUA as a good tracer for

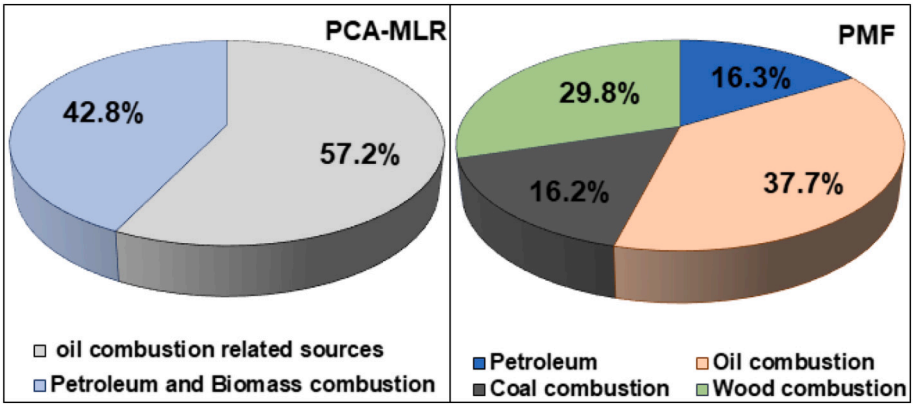

Fig. 6. Source contribution of two source apportionment methods to PAHs in sediments of the Beibu Gulf.

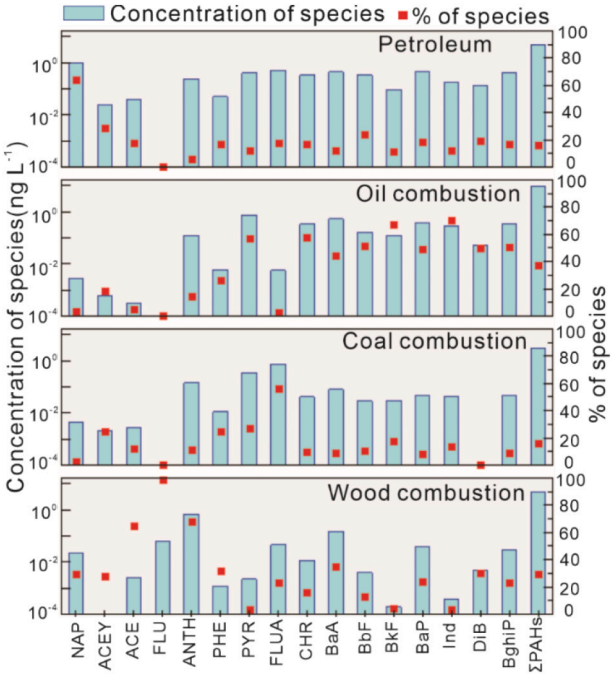

Fig. 7. Source profiles of PAHs derived from PMF modeling in the sediment of the Beibu Gulf.

coal combustion (Sofowote et al., 2008). The fourth factor accounted for 29.8% of the $\sum_{16}$PAHs, predominantly composed of FLU, PHE, and ACE that are dominant components produced via wood combustion (Chen et al., 2005; Sofowote et al., 2008). Compared with PCA/MLR, the PMF patterns of sources 1 and 4 (46.1%) were similar to those of the PCA/MLR source 2 (42.8%) oil spill and biomass combustion, and the PMF patterns of sources 2 and 3 (53.9%) were associated with the PCA/MLR oil combustion source 1 (57.2%). PCA/MLR may not fully identify specific sources (e.g., oil combustion vs. coal combustion). However, the results of PAH source apportionment using the two quantitative methods were consistent. Oil spills, biomass combustion sources, and oil-related combustion sources were the main contributors (>83.8%) of PAHs in the Beibu Gulf coastal sediments.

Overall, similar results were obtained from the three source apportionment models: the mixed sources of oil spills, oil-related combustion, and biomass combustion were the most significant contributors to PAHs in sediments of the Beibu Gulf (Fig. 6). The potential sources of PAHs in sediments of the Beibu Gulf include emissions from urban automobile exhaust, industrial pollution sources (e.g., iron and steel plants and shipyards), agricultural pollution sources (e.g., straw burning, oil spills from oil platforms along the coast of the Beibu Gulf), fishing, and other ship activities. In particular, PAH pollution caused by urban industrial and agricultural activities may be transported to coastal waters of the Beibu Gulf via rivers and accumulate in the seabed environment (i.e., sedimentation). Compared to the scenario in 2010, the sources of PAHs in the Beibu Gulf sediments appear to have changed, especially PAHs that are generated by coal combustion, which could be an important embodiment of upgrading and transformation of national energy structure and adjusting the regional economic development model. The transformation and upgrading of energy structures and the active development of renewable energy would make a positive contribution to promoting sustainable development, energy conservation, and emission reduction, which is of great significance for coping with climate change (Ibrahim et al., 1998; IPCC et al., 2011).

Sediment quality guidelines (SQGs), sediment quality criteria (SQC), and toxic equivalent quantity (TEQ) were used to evaluate the ecological risk of PAHs in Beibu Gulf sediments (Batley and Simpson, 2014; He et al., 2014; Li et al., 2014). The detailed assessment methods are presented in Text S5. SQGs provide two boundaries: the effect range low (ERL) and the effect range median (ERM) (Long et al., 1995; Long and Morgan, 1990; Macdonald et al., 1996). As shown in Tables 1 and S12, the concentrations of 16 PAHs in Beibu Gulf sediments were lower than the ERL. SQC has often been used to determine the concentrations of chemicals or contaminants in sediments and identify prioritized areas for regulation or restoration (Bellas et al., 2011; Long et al., 1995; Macdonald et al., 1996). The corresponding standard was established according to the concentration of a single PAH in organic carbon. The average standards for FLUA, ACE, and PHE were 300 μg (g organic carbon)$^{-1}$, 240 μg (g organic carbon)$^{-1}$, and 240 μg (g organic carbon)$^{-1}$, respectively (Long and Morgan, 1990; Macdonald et al., 1996). The concentrations of PAHs calculated based on the normalization of organic carbon in the sediments in this study were two orders of magnitude lower than the SQC value of EPA (Table S6). The TEQ concentration of each PAH in sediment samples is shown in Table S13; it ranged from 0.01 to 236.47 ng g^{-1}, with an average value of 32.79 ng g^{-1}. BaP and DiB were the main contributors to TEQ, accounting for 45.1% and 39.0%, respectively, having the highest potential risk of carcinogenesis.

Numerous other studies have assessed the risk of PAHs in coastal and estuarine sediments. Corresponding to these minimum values, the concentrations of PAHs that often have adverse effects on organisms are also given in these standards and references. The concentrations of each standard are given in Table 1 and compared with the PAH concentrations in this study, to determine the risk level of PAHs in sediments of the Beibu Gulf. The assessment results indicated that the PAH concentrations in the sediments of the Beibu Gulf were all within the safety thresholds; they had no toxic effect on benthos or posed only a shallow ecological risk. As mentioned above, the pollution level of PAHs in Qinzhou Bay was significantly lower than that recorded seven years ago (Fig. 3), indicating that the regional control on PAH pollution is effective in the Beibu Bay area. Therefore, concerted efforts should be made to achieve the coordinated and sustainable development of humans and nature as soon as possible.

This study investigated the occurrence, concentrations, ecological risk, and sources of PAHs in sediments of the Beibu Gulf in 2017. Compared with those in 2010, the pollution levels of PAHs in Beibu Gulf sediments have decreased significantly. Regardless of the river or coastal zone, the PAH concentrations showed spatial differences. Adsorption/desorption and water-air exchange indicated that the environmental behavior of PAHs in summer and winter is driven by partitioning from the atmospheric environment and sediment to the water environment, which undoubtedly enhances the ecological pressure of the water environment. Three different source apportionment methods showed that oil spills, biomass combustion sources, and oil-related combustion sources were the main contributors (>83.8%) of PAHs in the Beibu Gulf coastal sediments. Compared to the scenario in 2010, the reduction of coal combustion sources in this study may confirm the transformation and upgrading of China's energy institutions, and it is also an important embodiment of the adjustment of the Beibu Gulf regional economic development model. Moreover, the risk assessment showed that the concentrations of PAHs in sediments of the Beibu Gulf were within the safety threshold.

CRediT authorship contribution statement

Minwei Han and Yaru Kang: Formal analysis, Visualization, Methodology, Data analysis, Writing – Original draft; **Weiquan Wang**, **Fang Liu** and **Jiying Pei**: Investigation, Sample pretreatment; **Yinghui Wang**: Writing – Reviewing and Editing; **Ruijie Zhang** and **Kefu Yu**: Conceptualization, Methodology, Data curation, Supervision; Conceptualization, Funding Acquisition, Project Administration Resource.

Table 1
A comparison of other sediment quality guidelines for coastal and marine waters, and the concentration values in this study.

PAHs	TEL	ERL	PSDDA-SL	SQC-chronic	SQO	PAH concentrations		
						Min	Max	Mean
NAP	34.6	160	210	500	200	0.02	44.9	1.63
ACEY	5.87	44	64	–[a]	60	nd[b]	1.31	0.12
ACE	6.71	16	63	2400	50	0.01	2.63	0.25
FLU	21.2	19	64	59	50	0.04	14.2	0.84
PHE	86.7	240	320	2400	15	0.10	53.3	4.47
ANTH	46.9	85.3	130	190	10	nd	2.94	0.34
PYR	153	665	430	850	260	0.02	53.1	3.77
FLUA	113	600	630	1600	170	0.02	26.0	2.96
CHR	108	384	670	1200	140	0.01	31.6	2.03
BaA	74.8	261	450	1600	130	0.02	44.0	3.63
BbF	–	–	–	–	–	0.01	19.2	1.46
BkF	–	–	–	–	–	0.01	16.0	0.97
BaP	88.8	430	680	18,000	160	0.01	33.5	2.57
Ind	–	–	–	–	–	nd	27.6	1.62
DiB	6.22	63.4	120	12,000	60	0.01	9.14	0.68
BghiP	–	–	–	–	–	0.02	32.3	2.49
PAHs	–	–	–	–	–	0.53	295	29.8
Refs	(Macdonald et al., 1996)	(Long et al., 1995; Long and Morgan, 1990)	(USACOE, 1988)	(Lyman et al., 1987; Pavlou, 1987)	(Swain and Nijman, 1991)	This study		

[a] –: missing data.
[b] nd = not detection.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2021.112817.

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