Occurrence, Distribution, Sources And Bioaccumulation of Polycyclic Aromatic Hydrocarbons (PAHs) of Multi Environmental Media In Estuaries And Coast of The Beibu Gulf, China: A Health Risk Assessment Through Seafood Consumption

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Abstract

The coastal zone is the crucial transitional zone between the ocean and the land. Under the influence of global climate change and human activities, the coastal zone is suffering from huge environmental pressure. It is necessary to pay close attention to the pollution of PAHs to coastal ecological environment and the risk to human health. Taking the Beibu Gulf coastal zone as an example, we investigated the pollution status of PAHs in various environmental media. Results showed the total concentration of 16 PAHs (Σ_{16}PAHs) in winter were significantly higher than that in summer. Compared with the coastal area, the pollution of PAHs in the estuarine area is more serious: the Σ_{16}PAHs in estuarine waters (summer: 71.4 ± 9.58 ng/L; winter: 96.8 ± 24.7 ng/L) > coastal waters (summer: 50.4 ± 9.65 ng/L; winter: 91.7 ± 18.9 ng/L); estuarine sediment (146 ± 116 ng/g) > coastal zone (76.9 ± 108 ng/g). The source apportionment results indicated that spilled oil, biomass and coal burning were the main sources of PAHs in water, whereas the primary sources were spilled oil, fossil fuel burning and vehicle emissions in sedment. Shellfish showed the highest average PAHs concentration, followed by fish, shrimp, and crabs. The calculated bioaccumulation factor indicates that the seafood has a low bioaccumulation capacity for PAHs in the ambient environment. Human health risk assessment shows that accidental ingestion of PAHs through the consumption of seafood generally does not pose a health risk, but children should properly control the intake of shellfishes.

Introduction

PAHs are persistent organic pollutants (POPs) widely distributed in environmental media. Because of their strong carcinogenicity, potential teratogenicity, and mutagenic, they have attracted wide attention (Samanta et al. 2002, Zhu et al. 2017). PAHs are mostly present in environmental media in a low content and mixed state, and enter human bodies, water bodies and ecosystems at relatively low doses. Although its toxicity is difficult to expose in the short term, in the long run it greatly threatens human health and ecological safety (Keenan et al. 2010).

The oceans exchange material and energy with land, sediments, and marine organisms in various forms, including migration of pollutants. Various pollutants generated and emitted by human industrial and agricultural activities, including the combustion of petroleum and its by-products, crop straw, wood and so on, are the main anthropogenic sources of PAHs in the environment (Wen et al. 2009, Yu et al. 2015). With increasing human activities, the concentration of PAHs in the environment has increased significantly. A large number of land-based PAHs continuously enter the marine ecosystem through rainwater, sewage discharge, river runoff and atmospheric transmission, exacerbating the pressure on the marine environment. After PAHs in terrestrial and atmospheric environments enter the water body, part of them are dissolved in seawater, and part of them are adsorbed on the particulate matter and settle into the marine sediment with the particulate matter. The secondary release of PAHs in marine sediments poses a huge risk to marine organism (Nikolaou et al. 2009). The highly lipid soluble characteristics of PAHs also cause marine organisms to accumulate more PAHs in the seawater and sediments by bioaccumulation (Cortazar et al. 2008, Han et al. 2019). This has exacerbated the threat of PAHs to the

marine ecosystem to a certain extent, and also increased the health risks of human consumption of seafood. The mouth of the river is the intermediate zone between land and ocean, and is also one of the important carriers for land-based PAHs to enter the ocean. Previous studies have also studied PAHs in the transition zone between ocean and land (Liu et al. 2014, Niu et al. 2019). However, there are few studies on PAHs in the aquatic ecosystems in the Beibu Gulf of Guangxi. It is of great ecological significance and ecological value to study the distribution characteristics of PAHs in this area.

Located in the southwest of China, Guangxi is the hub and frontier of ‘Chinese open cooperation with Southeast Asia (Huang 2014). It has rich ecological resources and an important strategic position. Beibu Gulf is ’Chinese national strategic development area, known as the last piece of China's net sea. It is rich in natural resources and extensive coastal mudflats, and is an excellent place for the development of marine aquaculture (Chen et al. 2016). There are more than 40 sea areas available for fishing, with more than 500 kinds of fish. The quality of shrimps, crabs and shellfish is also well-known at home and abroad. It is ’Chinese most biodiversity bay area and an important golden fishing ground (Lu 2016). However, with the continuous deepening of reforms in Guangxi, economic development has tended to become seaside. Industrialization, the development of aquaculture and tourism, and increasingly polluted estuarine waters have put increasing pressure on the ecosystem of the Beibu Gulf (Chen et al. 2016). Previous studies have shown that the PAHs concentration in the columnar sediments of the Beibu Gulf appeared an increasing trend after 2009 (Li et al. 2015). As a semi-closed bay, Beibu Gulf has weak ocean currents, slow exchange of water, and poor diffusion of pollutants in seawater. This will inevitably lead to the accumulation of terrestrial PAHs in the sea area. It is urgent to assess the possible pollution caused by PAHs in the Beibu Gulf ecosystem in recent years. Therefore, the purpose of this study is to (1) investigate systematically the PAHs levels in the waters, sediments and marine organisms in the Beibu Gulf of Guangxi, (2) analyze the temporal and spatial differences of PAHs in different waters in the Beibu Gulf, (3) compare the bioaccumulation of PAHs by various marine organisms, and (4) conduct a comprehensive ecological risk assessment of marine organisms in the Beibu Gulf of Guangxi and render some guiding suggestions.

Materials And Methods

2.1 Study area and sampling

Beibu Gulf is a natural semi-closed shallow water bay located in the northwestern part of the South China Sea (SCS). Its has a total length of about 1629 km with an area of about 1.28×10^5 km^2. The Beibu Gulf estuarine waters include Nanliu River, Qinjiang River, Maoling River, and Dafengjiang River. Its total river length is about 979 km, the total drainage area is about 1.69 million km^2, and its annual runoff is about 1.70×10^{11} m^3 (Fan et al. 2015). There are many harbors along the coast, including Pearl Bay, Fangcheng port, Qinzhou bay, Sanniang Bay and Lianzhou Bay. Among them, the Pearl River estuary is narrow and belongs to a typical funnel-shaped shallow bay, with few industrial and municipal sewage outlets and strong water exchange inside and outside the Bay, so the water quality has been excellent. Qinzhou bay

has the freshwater inflow of Qinjiang River and Maoling River, with blue crabs, groupers, prawns, and big oysters as the four famous products of Qinzhou bay, and has a large oyster breeding base. Sanniang bay faces the sea on three sides, and the beach waters are vast. Its dynamic seawater conditions are good, which is conducive to the migration of terrestrial materials and the reproduction of the marine organism. Sanniang bay is also a habitat for Chinese endangered animal, the humpback dolphin (Sousa Chinensis) (Gong et al. 2019).

A total of 54 water samples, 23 sediment samples in the surface layer and 48 marine organism samples (including 15 fishes, 16 crabs, 6 shrimps, and 11 shellfishes) were collected in this study. The 54 water samples including 27 summer water samples and 27 winter water samples, were collected at 27 sampling points in the aquatic ecosystem of Beibu Gulf, Guangxi in August and December 2017, respectively. There are 15 sampling points in the upper reaches of the river, the abrupt change points of hydrological characteristics and the estuary, and 12 sampling points in the coastal area (Fig. S1). All the 23 sediment and 48 marine organism samples were collected from the aquatic ecosystem of Beibu Gulf, Guangxi in August 2017 (Fig S1). The water samples were collected into cleaned and rinsed brown glass bottles, put in iceboxes, and transferred to the refrigerator at -4 ° C as soon as possible for storage until analysis. The 23 sediment samples were collected by the bucket dredge in the form of grid layout method, immediately after sampling. All the 48 marine organism samples were collected by local and our own divers. Because sampling is difficult and there is no fixed habitat for biological samples, we did not record the collection location of biological samples in detail. However, we divide them into Fangcheng, Qinzhou and Beihai according to different areas for processing and analysis. All sediment and organism samples were collected and put into polyethylene sealed bags in insulated ice box. They were brought back to the laboratory as soon as possible and frozen it at -20 ° C until analysis.

2.2 Analytical procedures

Sixteen target PAHs and 5 deuterated-labeled PAHs purchased from O2si, Charleston, United States. The physicochemical properties and molecular formula of the 16 target PAHs are listed in Table S3 and Fig S2. Five deuterated-labeled PAHs (NAP-D8, ACE-D10, PHE-D10, CHR-D12, Pery-D12) were used as analytical surrogates. The purchasing sources of all the chemicals and materials used in this study are summarized in Text S1 and Table S3.

The PAHs in the water samples were extracted by liquid-liquid extraction (Hou et al. 2018) with the detailed extraction process in Text S2. Sediment and organism samples were freeze-dried for 72 hours and then ground to homogenization. The methods of extracting the target PAHs in the sediment and organism were developed based on the previous methods (Han et al. 2019, Xu et al. 2012). 20 g sediment sample and 1 g organism sample were loaded into pre-treated filter paper for Soxhlet extraction for 48 h, respectively. Dichloromethane was used as the extraction solution for the sediment, and a mixed solvent of 1: 1 volume ratio of acetone and dichloromethane was used as the extraction solution for the organism sample. Five deuterated-labeled analytical surrogates were added to the extraction solution in advance during Soxhlet extraction. 20g copper flakes were also added to the extract for desulfurization treatment. After the extraction, all the extracts were concentrated by a rotary evaporator, and solvent-

exchanged into a volume of 4 mL hexane. About 0.5 mL of the organism extract was dried at 80°C for lipid content measuring. Then all the extracts were concentrated to 1 mL by blowing down under gentle nitrogen separated. ENVI™-Florisil cartridges (500 mg, 3 mL, Supleco, Bellefonte, PA, USA) were used for cleanup and fractionations. The first fraction was eluted with 10 mL mixture of hexane and dichloromethane (8:2, V/V), which included PAHs and was further purified with a 10 mm i.d silica gel column. The column has an inner diameter of 7 mm, and filled with 3 cm 3% deactivated alumina, 3 cm 3% deactivated silica gel, and 1 cm anhydrous sodium sulfate from bottom to top. The column was eluted with 15 mL of hexane and dichloromethane (1:1, V/V) mixed solution. The eluent was concentrated to 0.5 mL with nitrogen purge by nitrogen purge added with 200 ng of hexamethylbenzene as an internal standard before instrumental analysis.

Qualitative and quantitative analysis of PAHs in the extract was performed using an Agilent 7890B gas chromatography tandem 7000C triple quadrupole mass spectrometer (GC-MS/MS) in an electron impact ionization (EI) mode. An Agilent HP-5MS low loss quartz elastic capillary column (30m, 0.25mm i.d., 0.25 μm film thickness) was used to separate target PAHs. The m/z parameters used in the 16 PAHs quantification were summarized in Table S2. The column oven temperature program: Hold at 80°C for 2 minutes, heat up to 180°C at 15°C/min and hold for 20 minutes, heat up 260°C at 5°C/min and hold 2 mins, heat up to 300°C at 3°C/min. EI ion source is a source temperature of 230°C and the data acquisition was performed in the multiple reaction monitoring (MRM) mode.

2.3 Quality assurance and quality control

The experimental process strictly follows the relevant standards, setting experimental blanks, filed blanks, spiked surrogate recoveries, replicate samples and GC–MS/MS detection limits to ensure method quality control. The average recoveries of the five deuterium-labeled PAH were (63 ± 14)%, (70.5 ± 12)%, (74 ± 13)%, (91 ± 17)% and (101 ± 16)% for NAP-D8, ACE-D10, PHE-D10, CHR-D12 and Pery-D12, respectively. The standard deviation of replicate samples was within 5%, and the target compounds in the blank samples were not detected or lower than the instrumental detection limits (IDLs). The final reported concentrations were not adjusted according to the surrogate recoveries. The method detection limits (MDLs) were calculated as three times the IDLs, the IDLs values were defined as 3 times the signal-to-noise (S/N) ratio of the lowest standards. The MDLs of PAHs measured in water, sediment and organism samples were 0.07 ng/L – 0.32 ng/L, 0.01–0.04 ng/g and 0.14–0.64 ng/g, respectively.

2.4 Bioaccumulation factors of PAHs

As shown in Text S3, the BWAFs (bio-water accumulation factors) were calculated based on the wet weight concentration of PAHs in marine organisms (*Cm*) divided by the concentration of PAHs in water (C_W), the BSAFs (bio-sediment accumulation factors) were calculated on an organic carbon and lipid normalized basis (Burkhard 2003, Moermond et al. 2005).

$$BWAF = \frac{C_m}{C_W} \times 1000 \qquad (1)$$

$$BWAF = \frac{C_{bio}/f_{lip}}{C_S/f_{oc}} \times 1000 \quad (2)$$

Where the C_{bio} is the concentration in biota, the f_{lip} is the lipid fraction in biota, the Cs is the concentration of PAHs in the sediment, the foc is the total organic carbon (TOC) fraction in sediment. The detailed determination method of TOC is shown in Text S5, the lipid conent of organism were shown in Table S1.

2.5 Risks assessment of PAHs

Calculation of toxic equivalency quotients (TEQ). The TEQ concentrations of 16 target PAHs in marine organisms samples were calculated by Eq. (3) as follow:

$$\mathrm{TEQ} = \sum \mathrm{C} \times \mathrm{TEF_{BaP}} \quad \text{Eq. (3)}$$

Where C is the concentration (wet weight, ww) of individual PAH, the toxicity equivalent factor (TEF) was used to calculate the TEQ of individual PAH relative to BaP (Nisbet &LaGoy 1992).

Cancer risk assessment. The following formula was used to assess the risk of excessive cancer caused by exposure to PAHs in the seafood diet:

$$\text{Excess cancer risk} = \sum_{j=1}^{n} Q^* \times \mathrm{TEQ} \times \mathrm{IR}_j \times \mathrm{ED}_j/(\mathrm{BW}_j \times \mathrm{AT}) \quad (4)$$

$$\text{Excess cancer risk} = \sum Q^* \times \mathrm{TEQ} \times \mathrm{IR}_j \times \mathrm{ED}_j/(\mathrm{BW}_j \times \mathrm{AT}_j) \quad (5)$$

Where the Q* is the cancer potency of BaP (7.3 mg kg^{-1} $day^{-1})^{-1}$ (EPA 2017), TEQ is the toxic equivalency quotients, AT is the average carcinogenic life, generally taken as 70 years, AT*j* is the average time (year) for sub-group *j*, ED_j is the exposure time (year) for age group *j*.

2.6 Data analysis

The Shapiro–Wilk was used to test the normality of grouped data. When the data were normal distribution, the statistical significance of the differences among the groups was tested by independent sample t-test (IBM SPSS statistics 24.0); otherwise, a non-parametric test was used. The *p*-value of < 0.05 was regarded as signifificant, while $p < 0.01$ was considered extremely signifificant.

Result And Discussion

3.1 Pollution status of PAHs in Beibu Gulf

Water. One member in our research group reported the distribution and source of PAHs in the surface waters of Nanliu River and Lianzhou Bay, but failed to study the overall situation of PAHs in Beibu Gulf (Wang et al. 2019). To further understand the concentration characteristics of PAHs in Beibu Gulf, we combined these data for unified analysis in this study. Nine PAHs were detected in water samples in

different regions in winter and summer, including all low molecular weight PAHs (LMW-PAHs, 2- and 3-ring) and two 4-ring PAHs (PYR and FLUA) detected in all water samples, the detection rate of BaP was 11.1% and 22.2% in summer and winter water samples, respectively. The Σ_{16}PAHs showed different temporal and spatial distribution (Fig. 1-a and Fig. 1-b). The average Σ_{16}PAHs were significantly higher in estuarine waters (mean: 71.4 ± 9.58 ng/L ; rang: 57.9–90.8 ng/L) than in the coastal waters (mean: 50.4 ± 9.65 ng/L (range: 29.7–68.7 ng/L) (t-test, $p < 0.01$) in summer, while they were slightly higher in estuarine waters (mean: 96.8 ± 24.7 ng/L) than coastal waters (mean: 91.7 ± 18.9 ng/L) (*t*-test, $p > 0.05$) (Fig. 2). Estuarine water through the city was directly affected by urban human activities. PAHs point source pollution caused by factories and agricultural activities along the river aggravates PAHs pollution, and the diffusion ability of the water body in estuary is weak, making PAHs pollution difficult to spread. Compared with the rivers, even if the rivers finally flowed into the sea, the tidal current promoted the water exchange between the seawater and diluted the concentration of PAHs to a certain extent, resulting in the Σ_{16}PAHs in the coastal seawater were significantly lower than that in the seagoing rivers. However, in the dry season (winter), the rainfall is greatly reduced, and the current in Beibu Gulf is relatively slow. Due to the lack of timely water exchange with inshore seawater, it is difficult to dilute the PAHs in inshore seawater, which reduces the PAHs concentration difference between the estuarine and the coastal seawater.

In this study, the Σ_{16}PAHs were significantly higher in winter than in summer, and this seasonal difference seems to be not limited by the region (*t*-test, $p < 0.01$) (Fig. 2). Previous studies have also reported similar seasonal differences (Lv et al. 2014, Zhang et al. 2016). This difference is often caused by a variety of comprehensive factors. Firstly, rainfall determines the dilution degree of PAHs in water body and affects the concentration of PAHs in water body. The concentration of PAHs in the Beibu Gulf was low because of the abundant precipitation in summer. This is well confirmed by the difference in salinity: estuarine waters (0.98 ± 2.00‰) and coastal waters (10.6 ± 8.1‰) in summer were much lower than that in winter (18.1 ± 6.7‰ and 32.7 ± 2.7‰). Meanwhile, some PAHs were degraded by strong solar radiation in summer (Jia et al. 2015). Previous studies have found that PAHs photolysis rapidly under irradiation follows the apparent first-order kinetics, photoionization to yield the PAHs radical cation and a hydrated electron, resulting in PAH-destroying reactions involving water (Chen et al. 2001, Chen et al. 2011, XiaoWu &Shao 2017, Zepp &Schlotzhauer 1979). The strong sunshine in summer can not only promote the photodegradation of PAHs, the higher temperature can also promote the reproduction and growth of microorganisms and some PAH-degrading bacteria, making the concentration of PAHs appear low (Gibson et al. 1975). In addition, the increase in PAHs emissions due to heating in northern cities in winter was transmitted to the south through the northeast monsoon, increasing the PAHs' concentration in winter in the south of China (Kong &Miao 2014). PAHs' concentrations were also affected by fishing activities. The closed fishing season in Beibu Gulf is from May to August, which reduces the PAHs produced by fishing activities. On the contrary, the pollution caused by frequent fishing activities in winter may increase the concentration of PAHs.

Sediment. The spatial distribution of PAHs in the Beibu Gulf sediments were shown in Fig. 1-c. All the 16 PAHs were detected in the sediments, with the detection rates of ranging from 82.6–100%. Like surface seawater, the Σ_{16}PAHs were significantly higher in the estuarine sediments (range: 19.6–359 ng/g, mean: 146 ± 116 ng/g) than coastal sediments (range: 2.39–297 ng/g, mean: 76.9 ± 108 ng/g).

Estuary. The Σ_{16}PAHs in surface sediments showed significantly regional differences, with the order of Qin River (210 ± 104 ng/g, n = 4) > Maoling River (175 ± 111 ng/g, n = 3) > Nanliu River (83.6 ± 28.3 ng/g, n = 2) > Dafeng River (34.0 ± 14.4 ng/g, n = 2) (*nonparametric*-test, $p = 0.057$). The highest Σ_{16}PAHs appeared in the upper reaches of the Qin River (359 ng/g), which may be due to the sampling point being close to a local shipyard. Building ships usually generates sandblasted and polished dust, oil pollution, and domestic sewage. The PAHs produced by these pollutions would be adsorbed on the particulate matter after entering the water body, and finally settle into the sediment to produce the high Σ_{16}PAHs. A high value in the upper reaches of the Maoling River (320 ng/g), which may be caused by the docking points of ships nearby.

Coast. The Σ_{16}PAHs in the coastal surface sediments also showed obvious regional differences (Fig. 1-c). Except for ANTH, CHR, BbF, BkF, and DiB, the remaining PAHs were detected in all coastal sediment samples. The Σ_{16}PAHs in different coastal zone were in the following rank orders: Fangcheng Port (227.9 ± 33.7 ng/g, n = 2) > Qinzhou Bay (167.9 ± 129 ng/g, n = 2) > Lianzhou Bay (30.3 ± 17.7 ng/g, n = 3) > Pearl Bay (14.6 ± 3.10 ng/g, n = 2) > Sanninag Bay (3.50 ± 1.50 ng/g, n = 3) (one-way analysis of variance, $p = 0.042$). Fangcheng Port is a valley-type harbor, sediments are easy to silt, and there are thermal power plants on the east side of the bay. As the largest commercial port along the coast of Guangxi, Fangcheng Port's pillar industry is mainly port transportation. The petroleum burning and leakage may also be a potential source of contribution to PAHs. Qinzhou Bay has weak water exchange capacity and slow water flow in the bay mouth area, which is the confluence of Maoling River and Qinjiang River. The intertidal shoals and broad underwater delta formed by the interaction of river sediment transport and tidal current inevitably provide conditions for the deposition of a large number of pollutants. Meanwhile, Qinzhou port is the key development base of Beibu Gulf, and the oil pollution caused by port development and ship transportation can not be ignored. The Σ_{16}PAHs at sampling site 13C in the middle of Qinzhou Bay may be affected by the pollutants from the nearby Petrochemical Industrial Park. The Σ_{16}PAHs in Pearl Bay and Sanniang Bay were much lower than Fangcheng Port and Qinzhou Bay. The mouth of Pearl Bay is narrow and belongs to a typical funnel-shaped shallow bay, and the water exchange between inside and outside of the bay is strong. The Σ_{16}PAHs in the water were relatively lower than those in Fangcheng Port and Qinzhou Gulf and were not easily adsorbed in sediments.

Marine organisms. All 16 PAHs were detected in different types of marine organisms. The Σ_{16}PAHs in organisms ranged from 15.3 to 559 ng/g, of which the Σ_{16}PAHs ranged from 19.0 to 225 ng/g in fishes, 15.3 to 41.5 ng/g in crabs, 25.4 to 76.9 ng/g in shrimps, and 23.8 to 559 ng/g in shellfish. The obvious order of the Σ_{16}PAHs in the four marine organisms were as follows: Shellfish (183 ± 165 ng/g) > Fish (73.7 ± 57.2 ng/g) > Carb (42.7 ± 19.2 ng/g) > Shrimp (30.4 ± 8.3 ng/g) (nonparametric test, $p < 0.001$)

(Fig. 1-d). The Σ_{16}PAHs were significantly lower in our study than edible fishes in Poyang Lake, Daqing Lake, and Ramsar site, China (Jyethi &Khillare 2019, Wang et al. 2015b, Zhao et al. 2014) and coastal areas of Bangladesh (Habibullah-Al-Mamun et al. 2019). Previous studies have shown that the levels of PAHs in organisms were related to the pollution status of the living environment and biological species. It was negatively correlated with the trophic level of organisms (Wan et al. 2007). Benthic organisms had a lower trophic level than other marine organisms, and their ability to accumulate PAHs was higher than that of swimming organisms (Fig. 1-d). Shellfishes exhibit unexpectedly high PAH tissue burden, even in moderately contaminated areas (Knutzen &Sortland 1982, Meador et al. 1995).

3.2 Composition of PAHs in Beibu Gulf

Water. The proportion of 2-ring PAHs was significantly higher in winter (coastal: 72% ± 4%; estuary: 74% ± 2%) than in summer (coastal: 37% ± 14%; estuary: 41% ± 9%), whereas the proportion of 3-ring PAHs was higher in summer (coastal: 57% ± 12%; estuary: 53% ± 9%) than that in winter (coastal: 25% ± 4%; estuary: 23% ± 2%) (Fig. 2). The difference may be related to the physicochemical properties of the compounds and temperature. 2-ring PAHs are more volatile than 3-ring PAHs, and the temperature is high in summer. More 2-ring PAHs evaporate from water to the atmosphere, resulting in a relatively low proportion in summer. For the individual PAHs, it was found that the concentrations of different PAH congeners in estuarine waters were significantly positively correlated with that in coastal waters (summer: $R^2 = 0.9844$, $p = 0.000$; winter: $R^2 = 0.9996$, $p = 0.000$). The PAHs' compositions in estuaries and coastal waters were similar in the same season, indicating that PAHs in the two areas were homologous, and rivers had a significant impact on coastal pollution. The logarithm of the average concentration of different PAH congeners in the water samples shows a significant positive correlation with the logarithms tof heir water solubilities but a significant negative correlation with the logarithms of their octanol-water partition coefficients (K_{OW}) (Fig. 3). The greater the solubility and the greater the polarity, the higher the concentration of PAHs in water. Affected by the dilution of seawater, the Σ_{16}PAHs in the Maoling River, Qin River, and Dafeng River shows a gradual decrease along the direction of entering the sea. In summer, the Σ_{16}PAHs appeared: Nanliujiang > Maolingjiang > Qinjiang > Dafengjiang (Fig S1-A), while the ranks were Dafengjiang > Nanliujiang > Qinjiang > Maolingjiang in winter, and the concentration in Dafengjiang (155 ng/L) was significantly higher than other rivers (Fig S1-B). By estimating the flux of PAHs into the sea (Text S4), we found that the annual flux of PAHs from these four rivers is 826 kg, and the rainy season (700 kg) accounts for more than 85% of the total (Table S6). The Nanliu River has the highest PAHs flux (459 kg) into the sea, accounting for about 55.6% of the total, followed by the Qinjiang (21.1%), Maoling Rivers (15.2%), and the Dafeng River (8.1%). It can be seen that although the Dafeng River has the heaviest degree of PAH pollution in winter, its river runoff was relatively small and the PAH flux into the sea was low, so the impact on the Beibu Gulf was the least. The Nanliu River was the largest river in Guangxi alone that flows into the sea. Its runoff was relatively large, and the flux of PAH into the sea was relatively high, which may have the greatest impact on the Beibu Gulf.

Sediment. The compositions of PAHs in the coastal sediments and the estuarine sediment were similar, and they were mainly 3-, 4- and 5-ring PAHs, accounting for more than 80% of the Σ_{16}PAHs. Compared

with previous studies on the occurrence level of PAHs in the sediments of Beibu Gulf (Li et al. 2015, Yang et al. 2013), the Σ_{16}PAHs in this study were higher than that in 2005, but lower than that in 2011. The high concentration of NAP in 2011 may be due to the impact of accidental oil spill. On the whole, the Σ_{16}PAHs has an obvious increasing trend, especially the HWM-PAHs, which may be related to the local economic development level. Fossil fuels, automobile exhaust and other oil combustion related pollution sources may be the main contributors to the increase of PAHs concentration. Terrestrial PAHs enter the marine environment in many ways and are ubiquitous in the marine water and sediment environment (Han et al. 2019). The distribution coefficient (K_P) was generally used to evaluate the distribution of PAHs between sediment and water in the aquatic environment. The results showed that the Kp values of 16 PAHs ranged from 0.89 to 147, and the partition coefficients increased with the increase of molecular weight. Therefore, HMW-PAHs are more easily enriched in sediments, which is consistent with previous studies (Liu et al. 2012, Zhang et al. 2013).

Marine organisms. For the marine organisms, the proportion of 2-ring PAHs in crabs (55%) and shrimps (63%) were significantly higher than that of fishes (29%) and shellfishes (13%), while the proportion of 3- and 4-ring PAHs in fishes (57% and 11%) and shellfishes (67% and 15%) were higher than that of crabs (38% and 4%) and shrimps (35% and 2%) (Fig. 1-d). This distribution feature may be closely related to habitat and biological characteristics.

3.3 Bioaccumulation of PAHs

Generally speaking, organisms ingest various nutrients and refractory organic compounds from surrounding environmental media (atmosphere, water, soil, sediment, etc.) and food, including various pollutants (Ding et al. 2020, Ding et al. 2019, Han et al. 2019, Pan et al. 2017, Zhang et al. 2018a, Zhang et al. 2019, Zhang et al. 2018b). When the environmental pollutants reach a certain level, it would threaten the survival of organisms. Therefore, bioaccumulation factors (BAFs, in L kg^{-1}) were used to evaluate the accumulation ability of the marine organisms for PAHs in this study (Text S3). In brief, the bio-water accumulation factors (BWAFs) were calculated based on the wet weight concentration of PAHs in marine organisms divided by the concentration of PAHs in water, the bio-sediment accumulation factors (BSAFs) were calculated on an organic carbon and lipid normalized basis (Burkhard 2003, Moermond et al. 2005). The results are presented in Table S9 and Table S10. For all marine organism samples, the average Log *BWAFs* were 1.82 to 3.00, while the Log *BSAFs* ranged from − 0.07 to 2.73. As shown in Fig. 4-A and Fig S4-A, the possibility of the accumulation of PAHs by marine organisms in the Beibu Gulf through bio-water accumulation is extremely small, only the Log *BWAFs* of BaP (1.63–3.93) was considered potential bioaccumulation or bioaccumulative in some marine organisms. The others are lower than the potential accumulation, and the Log *BWAFs* of DiB was the lowest (1.22 ± 0.54). In addition, it seems that the average Log *BWAFs* of all marine organisms for 4-ring PAHs were much higher than that of others (Fig. 4-A). Statistical data show that, for the 16 individual PAHs *BWAFs*, difference between marine organisms were very small but significant (shellfishes > fishes > crabs and shrimps) (*nonparametric*-test, $p < 0.01$). The *BSWFs* were affected by a variety of ecological characteristics, including biomagnification, sediment ingestion, elimination and metabolic transformation (Burkhard

2003, Lamoureux &Brownawell 1999, Van Hoof et al. 2001), so there is no unified standard for *BSWFs*. As shown in Fig. 4-B and Fig. S4-B, the four marine organisms in this study may be more likely to accumulate more LMW-PAHs from sediments into the body through bio-sediment accumulation. As mentioned above, the occurrence of PAHs in sediments were mainly MMW- and HMW-PAHs, but in marine organisms it was mainly LMW- and MMW-PAHs. Therefore, the values of Log *BSWFs* of 2- and 3-ring PAHs were much higher than others. Statistics show that, for the 16 individual PAHs *BSAFs*, difference between marine organisms were significant (shellfishes > fishes > shrimps > crabs (*nonparametric*-test, $p < 0.01$). These difference of *BWAFs*/*BSAFs* may be related to the feeding habits and trophic levels of marine organisms, previous studies have found that in the tropical marine food web, persistent organic pollutants are diluted rather than amplified (Ding et al. 2020). In this study, marine organisms including mollusks (oysters), mainly filter and feed on microalgae and organic debris in the ocean, the majority fishes (*Tilapia mossambica*, *Rhabdosargus sarba*, and *Trachinotus ovatus*) are omnivorous, mainly feeding on plant food, algae and benthic invertebrates, and the crabs and shrimps are carnivorous, are carnivorous, mainly feeding on benthic invertebrates. The trophic level of herbivorous marine organisms is generally lower than that of carnivorous marine organisms. The lower the trophic level, the higher the PAHs accumulation capacity of marine organisms.

Previous studies have reported the correlation between Kow and BAFs, for hydrophobic organic compounds, the BAFs is usually a function of the Kow (Ding et al. 2020, Han et al. 2019, Wang &Kelly 2018). The functional relationship between PAHs Log *BWAFs*/Log *BSAFs* and Kow were affected by different biological species, metabolic levels and living habits (Lamoureux &Brownawell 1999, Moermond et al. 2005). The *BWAFs* values are usually positively correlated with Log Kow values (Han et al. 2019, Meylan et al. 1999). Pearson correlation coefficient showed that the log Kow were positively correlated with Log *BWAFs* ($r^2 = 0.51$, $p < 0.01$) and negatively correlated with Log *BSAFs* ($r^2 = 0.88$, $p < 0.01$) (Fig. 5). In fact, log Kow were negatively correlated with PAHs log *BSAFs* of various marine organisms, but not all of them were positively correlated with PAHs log *BWAFs* of various species (Fig. 6 and Fig. S5). The lower BAF of some PAHs maybe because the estimated *BWAFs* using MDLs were much lower than their actual value, and the true concentration of these PAHs in surrounding waters may be much lower than their MDLs.

3.4 Source apportionment

Previous studies have confirmed that isomer ratio can be used as a cardinal indicator to reveal the source of PAHs (Kavouras et al. 2001, Sofowote et al. 2008, Zhang et al. 2021). As shown in Table S12, four diagnostic ratios of ANTH/(ANTH + PHE), FLUA/(FLUA + PYR), Ind/(Ind + BghiP), BaA/(BaA + CHR), ANTH/PHE and FLUA/PTR were used to speculate possible PAHs sources in sediments and water of Beibu Gulf. The results confirmed that pyrogenic origins from coal and biomass combustion could be the dominant contributors of PAHs in water, while the main sources of PAHs in sediment are produced from incomplete combustion of coal and wood sources.

Cluster analysis was carried out on the standardized concentration matrix to explore the structure of concentration data and reveal the source of PAHs. According to the previous study (Kavouras et al. 2001,

Xu et al. 2021), the distance between-groups and Euclidean Distance are used as the cluster method and measurement interval, respectively. Figure 7 depicts the Hierarchical Cluster Analysis (HCA) results presented in the form of a dendrogram. The PAHs were classified two distinguished clusters in summer water (Fig. 7-A). The first category can be subdivided into two sub categories. The first sub category were composed of ACEY, ACE, ANTH, PYR, FLUA, and BaP, indicating as a mix sources of spilled oil and biomass burning (Ko et al. 2014, Xu et al. 2021), the second sub category consisted of FLU and PHE, which could be good indicator of coal combustion (Larsen &Baker 2003). The second category composed of NAP, which is noted to characterize petroleum. As in summer, PAHs in winter water also were divided into two main groups (Fig. 7-B). The first group composed of FLUA, ACE, FLU, PYR, ANTH, ACEY, and BaP. These compounds indicate numerous sources including petroleum, coal and wood combustion. The second group consisted of PHE and NAP, indicating coal combustion is an important source of PAHs in winter. As shown in Fig. 7-C, the 16 individual PAHs were divided into two major groups in sediment. The first major group was divided into two subgroups. One subgroup were composed of ACEY, ACE, ANTH and DiB, suggesting petroleum and vehicle emissions sources (Ko et al. 2014, Wang et al. 2015a), another were consisted of FLU, CHR, BbF, BkF, BghiP and NAP, indicating fossil fuel combustion and vehicle sources (Kavouras et al. 2001, Wang et al. 2015a). The second major group also can be subdivided into two subgroups. The first subgroup contained BaA, BaP, FLUA and PYR, indicating as a mix sources of and coal burning and vehicular emission (Larsen &Baker 2003, Wang et al. 2015a). The second subgroup consisted of PHE and Ind, which is noted to characterize coal burning and vehicular emission (Larsen &Baker 2003, Sofowote et al. 2008). Briefly, this source identification indicates that spilled oil, fossil fuel burning and vehicle emissions are the main sources of sediment PAHs in Beibu Gulf. Therefore, spilled oil, biomass and coal burning had the largest influence on PAH pollutants in water, while spilled oil, fossil fuel burning and vehicle emissions were the main sources in sediment.

3.5 Risks assessment

3.5.1 Calculation of toxic equivalency quotients (TEQ)

Benzo[a] pyrene (BaP), as a strong carcinogen in PAHs, is harmful to organisms and human health. Among the maximum acceptable concentrations of BaP in aquatic products proposed by EU, drinking water was 200 ng/L, fish, carbs, shrimps and shellfish were 2–10 ng/g, while the national standard of China does not exceed 5 ng/g (Commission 2011, Zelinkova &Wenzl 2015). In this study, BAP was detected in all organisms. Their concentrations in shellfish ranged from 0.36 to 2.13 ng/g ww. BaP in a few shellfish samples in Fangcheng exceeded the European Union (EU) standard but were lower than the national standard of China. The concentration of BaP in other marine organisms were far lower than the maximum levels of EU. The results demonstrated no human health risk caused by BaP in the organism from the Beibu Gulf. For a comprehensive understanding of the possible risk of PAHs in the sea area, we combined several classic methods to assess the risk of PAHs in the sea area. The average TEQ of Σ_{16}PAHs in marine organism samples is much lower than the national standard of China and EU standard. Shellfish had the highest TEQ (694–2267 pg g^{-1}) than the other marine organisms, and the rankings were Shellfishes (1774 pg/g) > Fishes (446 pg/g) > Carbs (172 pg/g) and Shrimps (80 pg/g) (*t*-

test, $p < 0.01$) (Table. S13). For the individual PAH, even though BaP and DiB had very low concentrations (3% and 1%) in Σ_{16}PAHs, they had high TEQ values (70% and 20%), so they were the major contributors to the total TEQ of the Σ_{16}PAHs. The TEQ of PAHs may reflect toxicity more than its concentration (Ding et al. 2012). In conclusion, the results of the TEQ demonstrated PAHs did not pose a health risk to humans via seafood consumption in the Beibu Gulf.

3.5.2 Cancer risk assessment

The results of excess cancer risk are presented in Table. S14 and Table 1. The excess cancer risk of different organisms were shellfish ($2.07\times10^{-6} - 1.84\times10^{-4}$) > fish ($1.35\times10^{-6} - 5.91\times10^{-5}$) > shrimp ($2.38\times10^{-8} - 3.77\times10^{-6}$) > carb ($2.08\times10^{-8} - 1.85\times10^{-5}$). According to the US Environmental Protection Agency, excess cancer risk of less than 1×10^{-6} was considered negligible, and greater than 1×10^{-4} was listed as the priority control risk level (EPA 2017, Williams et al. 2013). Therefore, compared with other marine organisms, shellfish may have a higher edible risk, especially for children aged 2–5 years. This risk should be taken seriously: children should appropriately reduce their consumption of shellfish. The excess cancer risk resulting from lifetime exposure to the PAHs were calculated by Eq. (4). The exposure time taken as 70 years referred to a previous study (Williams et al. 2013). The excess cancer risks induced by dietary intake of the Σ_{16}PAHs via seafood consumption for a lifetime are shown in Table 1. The excess lifetime cancer risks were 2.94×10^{-5} for males and 3.06×10^{-5} for females, respectively. This value is much lower than the high incremental lifetime cancer risk in the coastal areas of Bangladesh ($5.6\times10^{-5} - 3.4\times10^{-4}$) (Habibullah-Al-Mamun et al. 2019), comparable to that in southeastern Louisiana, US ($1.2\times10^{-5} - 3.8\times10^{-5}$) and Korea ($1.8\times10^{-5} - 9.8\times10^{-5}$) (Jeong et al. 2010, Wickliffe et al. 2018), but slightly higher than that of Mexico ($4.3\times10^{-6} - 1.3\times10^{-5}$) (Rotkin-Ellman et al. 2012).

Table 1
Excess cancer risk induced by exposure to Σ_{16}PAHs via seafood ingestion for different age groups.

Age groups	Gender	Fish	carb	shrimp	shellfish	Total
2–5	Male	5.89×10^{-5}	1.85×10^{-6}	2.06×10^{-6}	1.80×10^{-4}	2.43×10^{-4}
	Female	5.91×10^{-5}	1.19×10^{-6}	$1.32\times10-^{6}$	1.14×10^{-4}	1.75×10^{-4}
6–18	Male	1.43×10^{-5}	1.55×10^{-6}	3.77×10^{-6}	1.49×10^{-5}	3.46×10^{-5}
	Female	1.46×10^{-5}	3.89×10^{-7}	4.51×10^{-7}	3.93×10^{-5}	5.48×10^{-5}
> 18	Male	1.35×10^{-6}	2.08×10^{-8}	2.38×10^{-8}	2.07×10^{-6}	3.46×10^{-6}
	Female	1.36×10^{-6}	2.19×10^{-8}	2.63×10^{-8}	2.28×10^{-6}	3.68×10^{-6}
Lifetime	Male	9.72×10^{-6}	4.73×10^{-7}	9.54×10^{-7}	1.82×10^{-5}	2.94×10^{-5}
	Female	9.83×10^{-6}	2.03×10^{-7}	2.34×10^{-7}	2.03×10^{-5}	3.06×10^{-5}

In general, the concentration of PAHs in marine organisms in the Beibu Gulf is safe. The health risk and cancer risk caused by accidental daily intake of PAHs by human consumption of seafood is very low. However, it is worth noting that excess consumption of shellfish could cause health problems and cancer risk, especially for children. It is suggested that children should control the consumption of shellfish properly.

Conclusion

Results of this study demonstrated that PAHs are widely distributed in different environmental media in the aquatic ecosystem of the Beibu Gulf. The concentration of PAHs in the water had significant spatial and temporal differences: the Σ_{16}PAHs were significantly higher in winter than in summer, and significantly higher in estuaries than in coast. PAHs' concentrations in different marine organisms were significantly different. The source apportionment results indicated that spilled oil, biomass and coal burning were the main sources of PAHs in water, whereas the primary sources were spilled oil, fossil fuel burning and vehicle emissions in sedment. In general, 16 PAHs were not accumulated in marine organisms through bio-water accumulation. The ecological risk assessment shows that PAHs in the Beibu Gulf have no ecological risk or very low ecological risk. Human consumption of seafood does not pose a health risk, but 2–5 years old children should properly control shellfish intake.

Declarations

Author contribution

Minwei Han: Investigation, Visualization, Methodology, Data analysis, Writing-Original draft preparation; Fang Liu: Visualization, Editing, Sample pretreatment; Yaru Kang: Editing, Sample pretreatment; Ruijie Zhang: Conceptualization, Methodology, Data curation, Validation, Writing-Reviewing and Editing; Kefu Yu: Conceptualization, Funding Acquisition, Resource, Supervision; Yinghui Wang: Project Administration, Writing-Reviewing and Editing; Ruixuan Wang: Sample pretreatment, Writing-Reviewing and Editing

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Data availability All data generated or analysed during this study are included in this published article.

Ethics approval and consent to participate Not applicable. (The article does not address ethical issues.)

Consent for publication Not applicable. (Personal privacy and data are not included in the manuscript.)

Conflict of interest The authors declare no competing interests.

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Figures

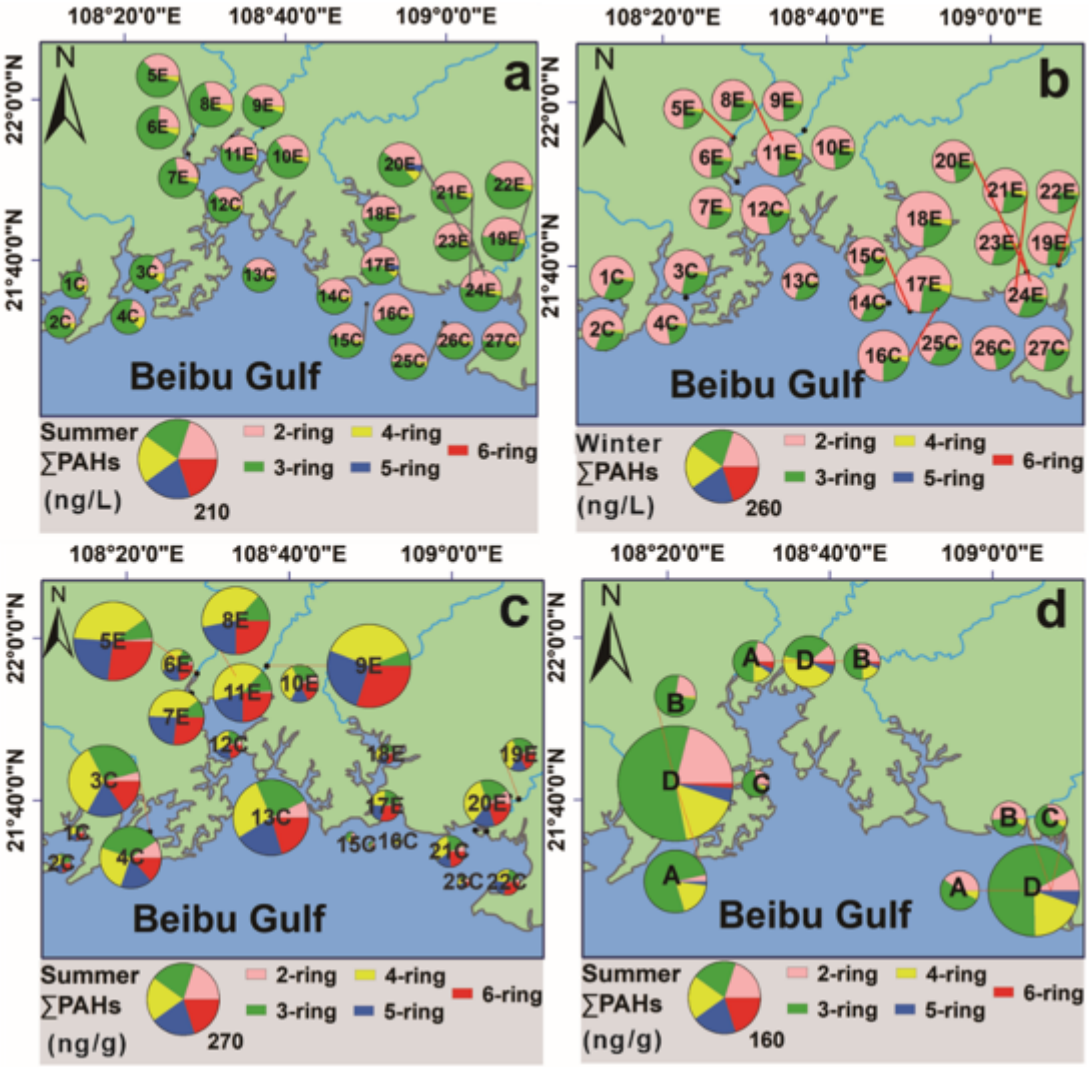

Figure 1

Concentration distribution of PAHs in different environmental media (a, b: Water; c: Sediment, E and C represent Estuary and coastal, respectively; d:Organism, A=Fish, B= Carb, C= Shrimp, D= Shellfish) in Beibu Gulf.

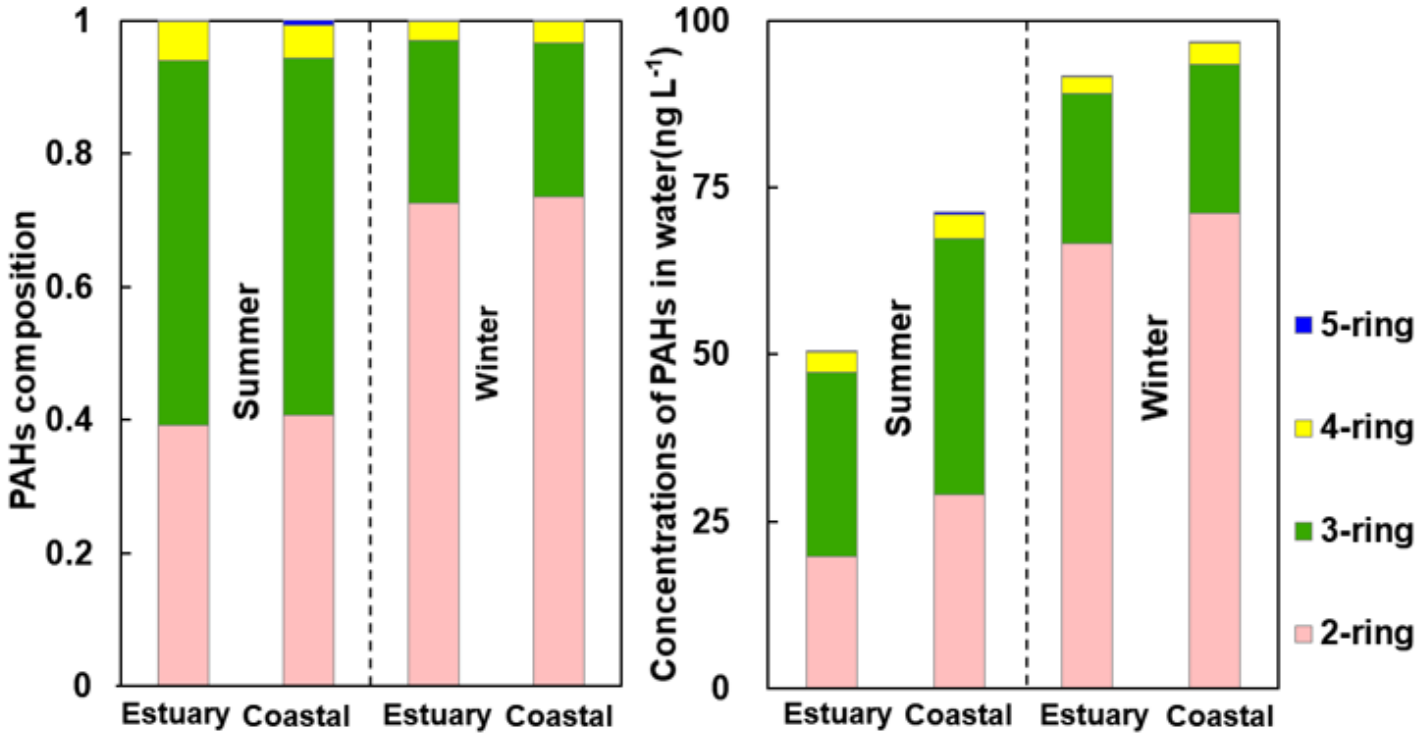

Figure 2

Composition and concentration of dissolved phase PAHs in different regions.

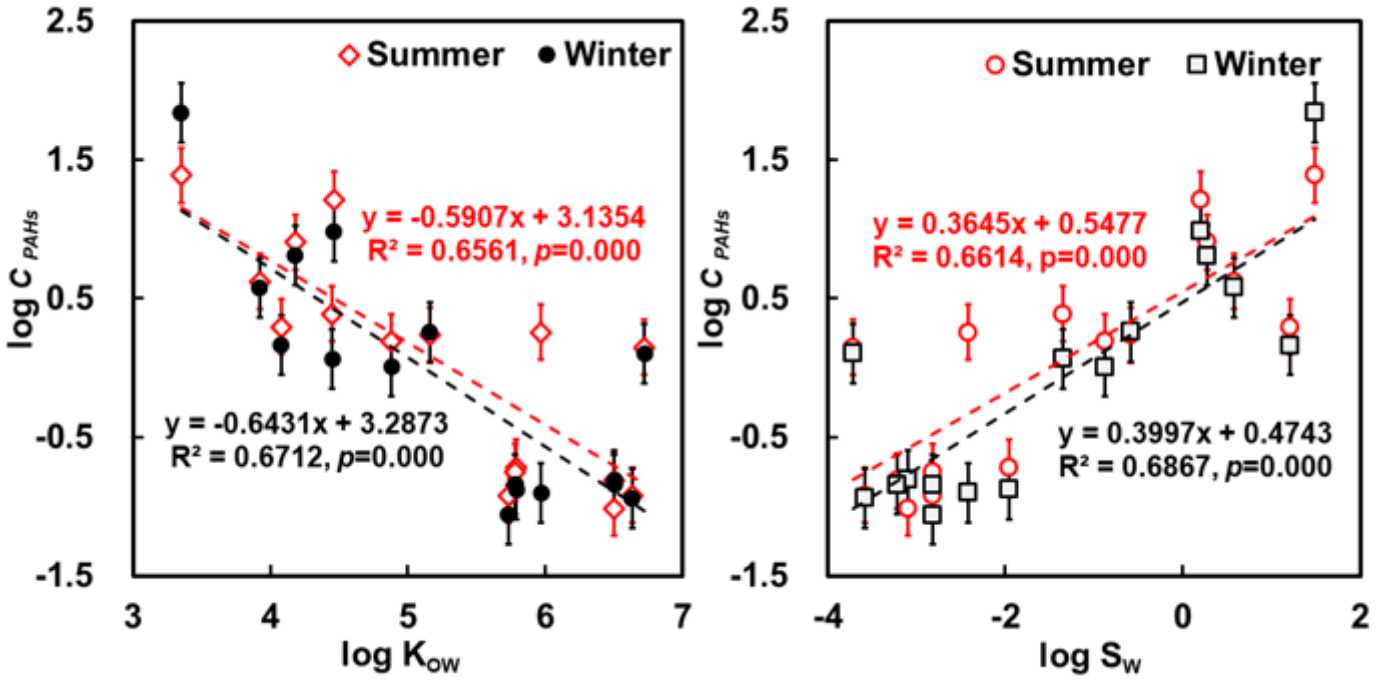

Figure 3

Correlation between the average concentration of PAHs monomer compounds in the Beibu Gulf waters and their Kow and water solubility (SW).

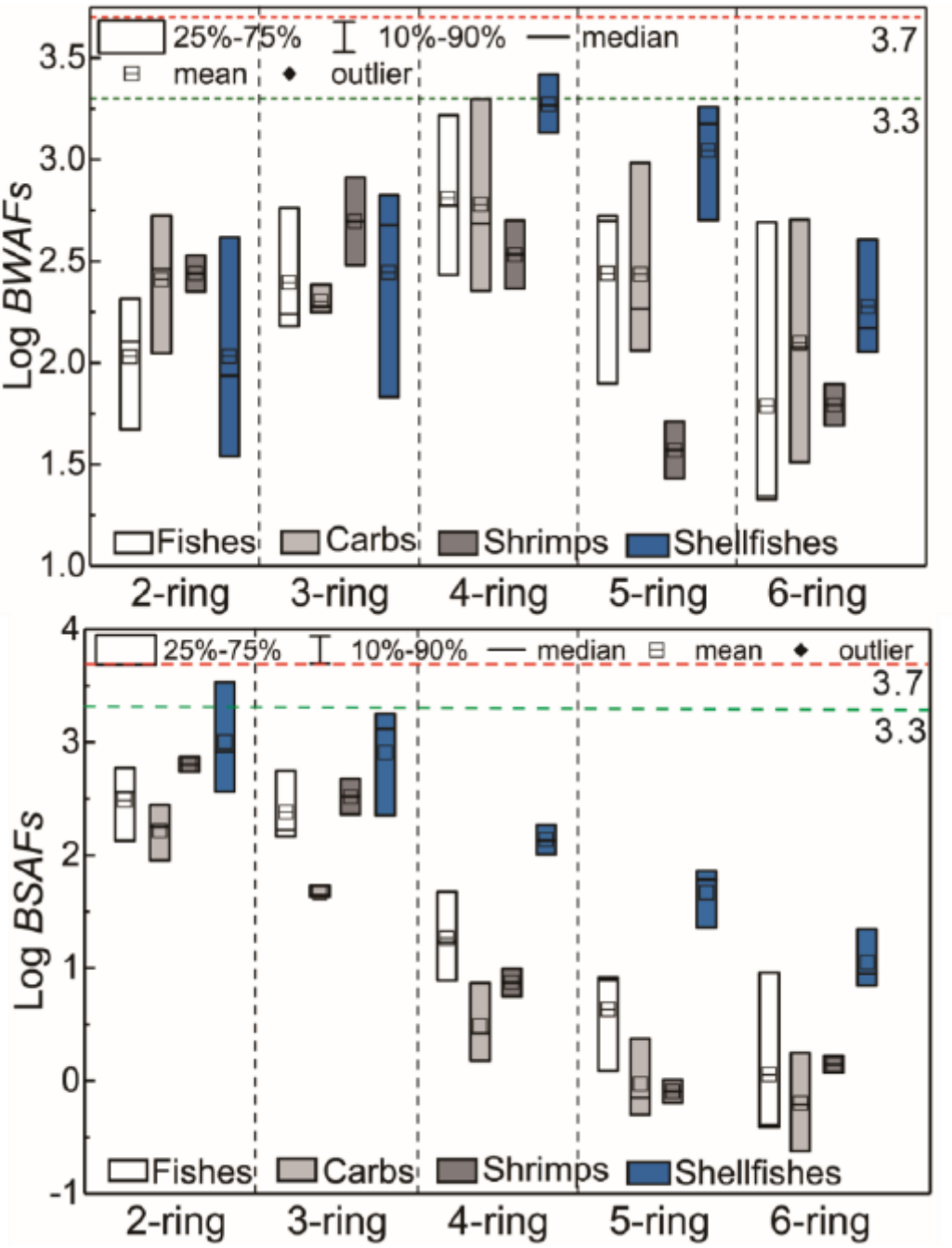

Figure 4

The Log BWAFs and Log BSAFs of PAHs in various marine organisms in Beibu Gulf.

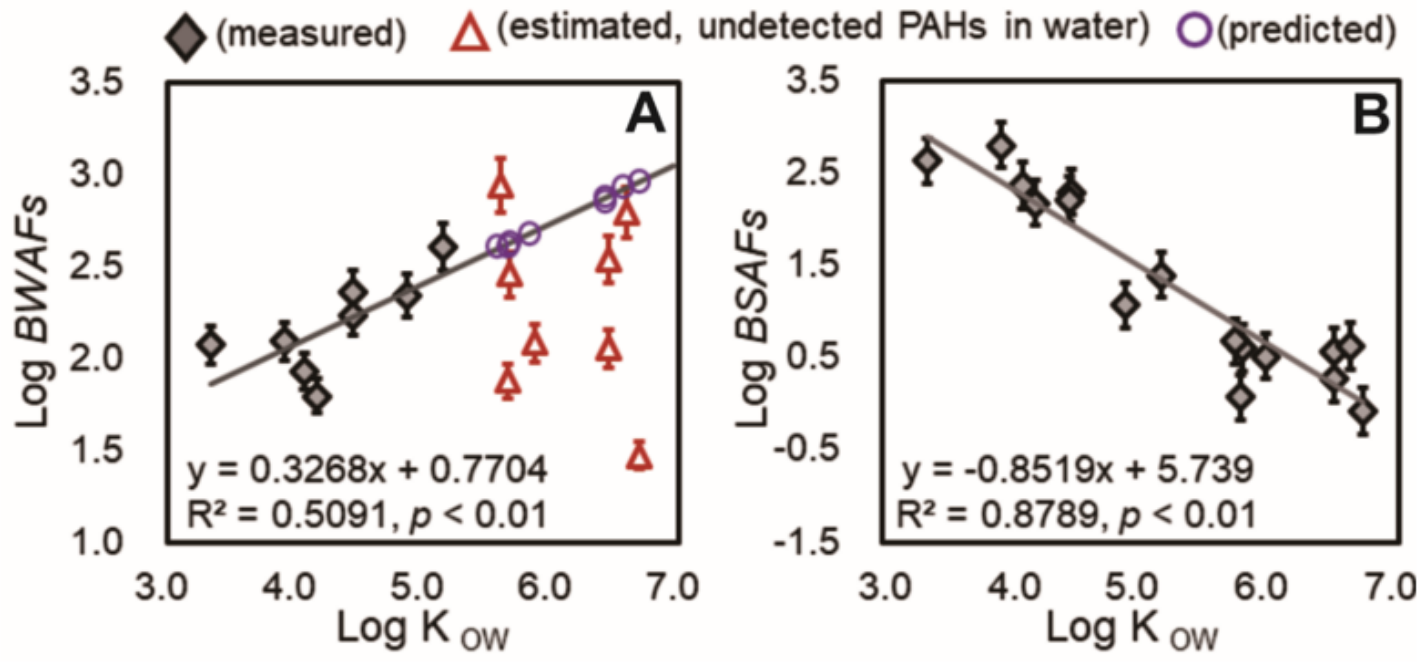

Figure 5

Relationship between the log BAFs (A: Water; B: Sediment) of detected PAHs in the marine organisms and their log KOW. The predicted log BAFs of some PAHs were predicted based on the regression equation shown in the plot.

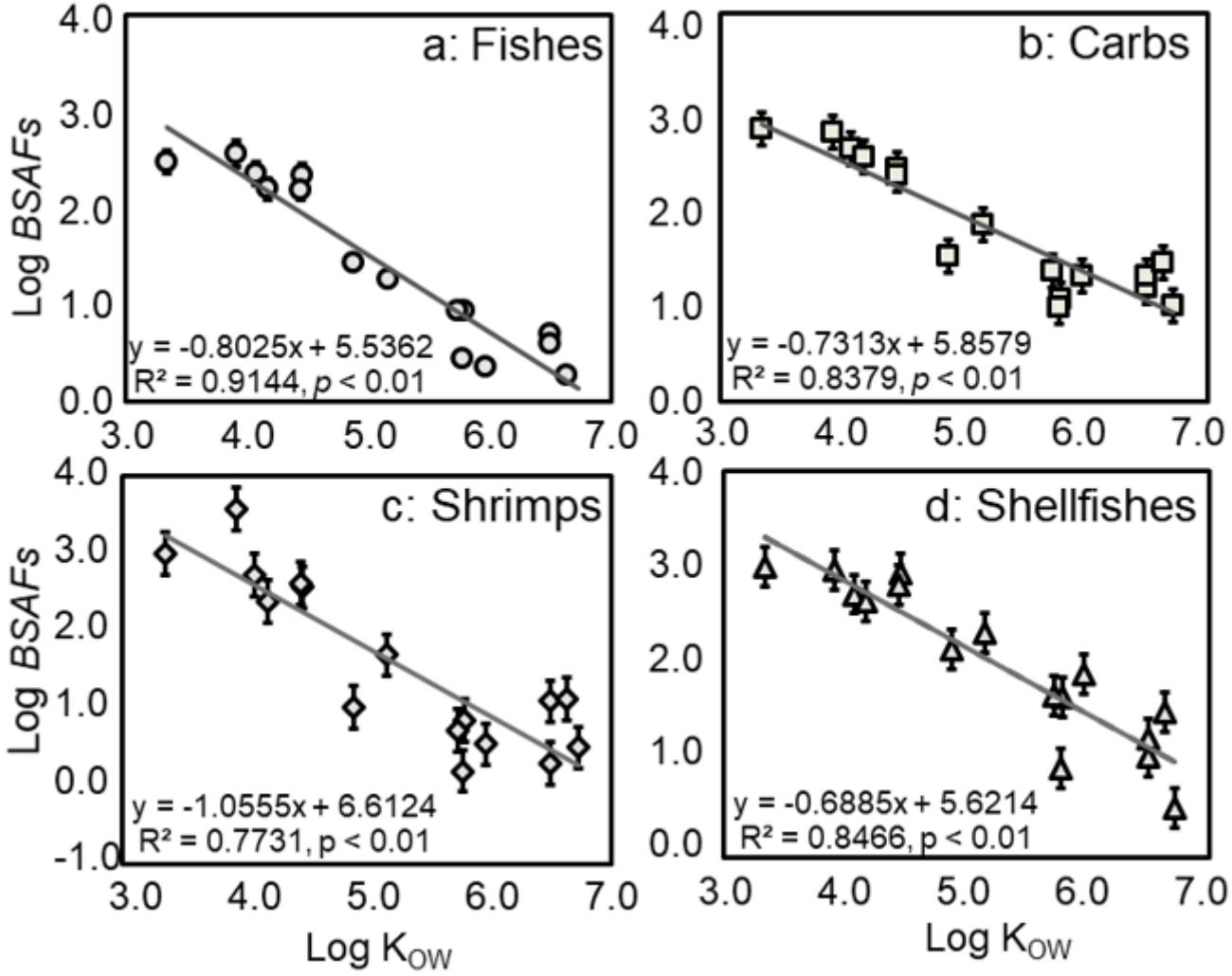

Figure 6

Relationship between the Log BSAFs of detected PAHs in the various marine organisms and their Log KOW.

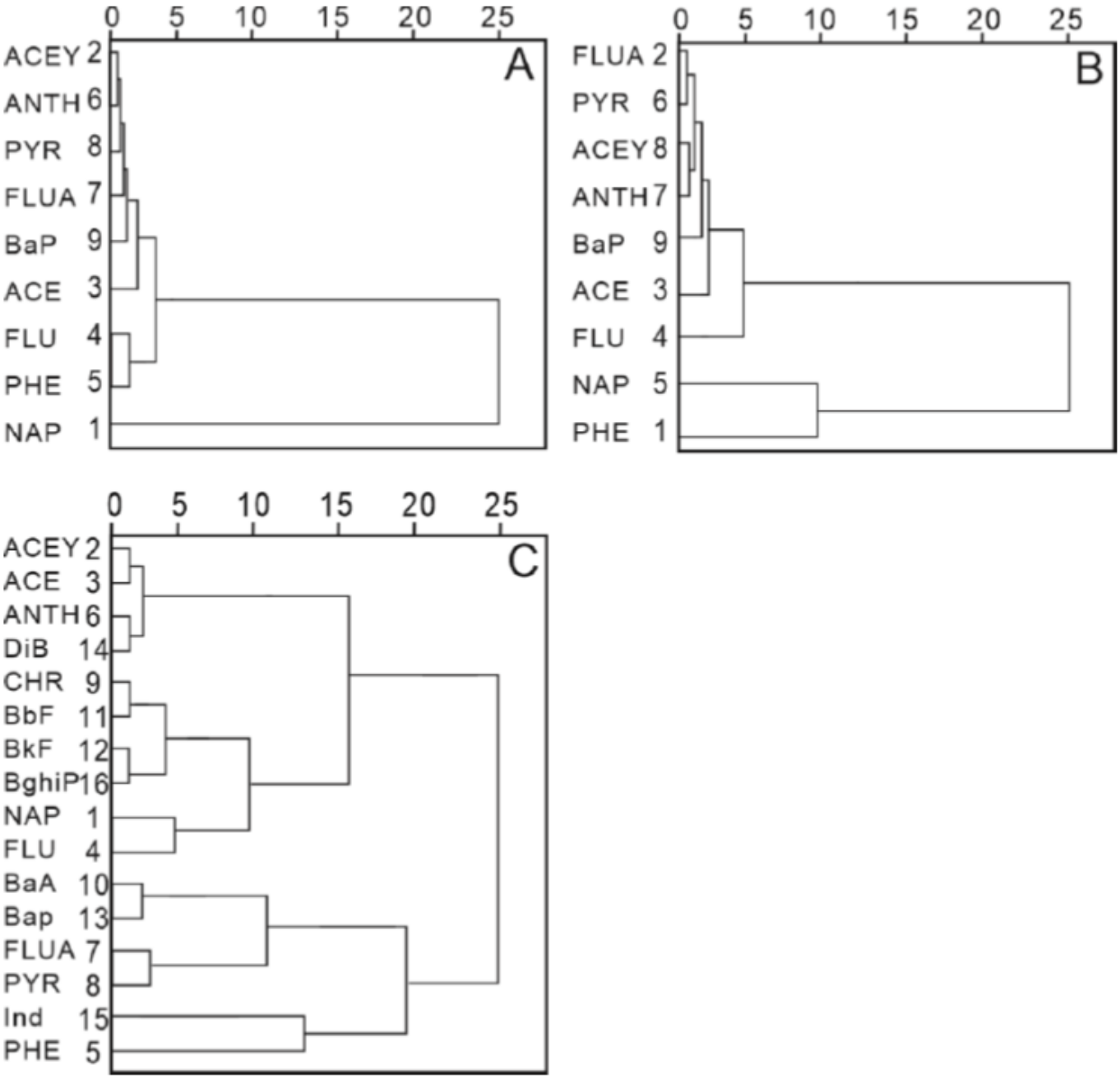

Figure 7

A dendrogram of Hierarchical Cluster Analysis of Σ16PAHs in water (A: summer; B: winter) and sediment (C: sediment) of Beibu Gulf.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- 05Supplementarymaterials.docx