



Occurrence, distribution, sources, and bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in multi environmental media in estuaries and the coast of the Beibu Gulf, China: a health risk assessment through seafood consumption

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Abstract

The coastal zone is a crucial transitional area between land and ocean, which is facing enormous pressure due to global climate change and anthropogenic activities. It is essential to pay close attention to the pollution caused by polycyclic aromatic hydrocarbons (PAHs) in the coastal environment and their effect on human health. The pollution status of PAHs was investigated in the Beibu Gulf, taking into consideration various environmental media. The results showed that the total concentration of 16 PAHs ($\Sigma_{16}\text{PAHs}$) was significantly higher in winter than in summer. Compared to the coastal area, the status of PAHs in the estuarine areas was found to be more severe in summer, while the regional difference was insignificant in winter. In summer, the $\Sigma_{16}\text{PAHs}$ in estuarine waters (71.4 ± 9.58 ng/L) > coastal waters (50.4 ± 9.65 ng/L); estuarine sediment (146 ± 116 ng/g) > coastal zone (76.9 ± 108 ng/g). The source apportionment indicated that spilled oil, biomass, and coal burning were the primary sources of PAHs in the water. The predominant sources of pollution in the sediments were spilled oil, fossil fuel burning, and vehicle emissions. With regard to the status of PAHs in marine organisms in the coastal area of the Beibu Gulf, the highest average concentration of PAHs was indicated in shellfishes (183 ± 165 ng/g), followed by fishes (73.7 ± 57.2 ng/g), shrimps (42.7 ± 19.2 ng/g), and crabs (42.7 ± 19.2 ng/g) in Beibu Gulf coastal area. The calculated bioaccumulation factor indicates a low bioaccumulation capacity of PAHs in various seafood considering the ambient environment. The human health risk assessment considering multiple age groups indicates minimal health risk on accidental ingestion of PAHs through seafood. However, it is suggested that the intake of shellfish in children be controlled.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Coastal zone · Pollution status · Source apportionment · Bioaccumulation factors · Risk assessment

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants (POPs) that are widely distributed in environmental media. PAHs have received much attention due to their carcinogenic, mutagenic, and potentially teratogenicity properties (Samanta et al. 2002; Zhu et al. 2017). PAHs are mostly present in environmental media in low concentrations and a mixed state. They, therefore, enter human bodies, water bodies, and ecosystems in relatively low doses. Although the short-term toxicity is difficult to ascertain, PAHs greatly threaten human health and ecological safety in the long run (Keenan et al. 2010).

The oceans exchange material and energy with land, sediments, and marine organisms in various forms, including

through the migration of pollutants. Various pollutants generated and released by anthropogenic activities, including industrial and agricultural activities, the combustion of petroleum and its by-products, crop straw, and wood, are the key sources of PAHs in the environment (Wen et al. 2009; Yu et al. 2015). With increasing anthropogenic activities, the concentration of PAHs in the environment has risen significantly. A large number of land-based PAHs continuously enter the marine ecosystem through rainwater, sewage discharge, river runoff, and atmospheric transmission, thereby exacerbating the pressure on the marine environment. When PAHs in terrestrial and atmospheric environments enter water bodies, a part of it is dissolved, and a part of it is absorbed by particulate matter, which subsequently settles on the marine sediments. The consequent secondary release of PAHs in the marine sediment poses an enormous risk to marine organisms (Nikolaou et al. 2009). PAHs are highly lipid-soluble, which leads to the accumulation of more PAHs in the seawater and sediments through bioaccumulation by marine organisms (Cortazar et al. 2008; Han et al. 2019). This has aggravated the threat of PAHs to the marine ecosystem and to human health via the consumption of seafood. The mouth of a river is the intermediate zone between land and ocean and is one of the most important carriers of land-based PAHs into the sea. Although previous studies have studied PAHs in the transition zone between ocean and land, there is limited research on the status of PAHs in the aquatic ecosystem of the Beibu Gulf of Guangxi, China (Liu et al. 2014; Niu et al. 2019). It is therefore of great ecological significance to study the distribution characteristics of PAHs in this region.

Located in the southwest region of China, Guangxi, is at the frontier of the country's open cooperation with Southeast Asia and is very important from a strategic standpoint (Huang 2014). The Beibu Gulf is significant in terms of China's national development strategy. Rich in ecological resources, the Beibu Gulf has extensive coastal mudflats and is an excellent area for the development of marine aquaculture (Chen et al. 2016). It is China's most biodiverse bay area and important fishing ground, with more than 40 areas available for fishing and harboring more than 500 varieties of fish (Lu 2016). The quality of shrimps, crabs, and shellfishes is well-known locally and abroad. However, with the continually deepening reforms in Guangxi, economic development has become increasingly dependent on the sea. Industrialization, the development of aquaculture and tourism, and the consequent pollution to the estuarine waters have put enormous pressure on the ecosystem of the Beibu Gulf (Chen et al. 2016). Previous studies have shown an increasing trend in PAH concentration in the columnar sediments of the Beibu Gulf post-2009 (Li et al. 2015). As a semi-closed bay, the Beibu Gulf has weak ocean currents slow exchange of water, resulting in poor diffusion of pollutants. This will

inevitably lead to the accumulation of terrestrial PAHs in the sea area. It is therefore urgent to assess the level of pollution caused by PAHs in the ecosystem of the Beibu Gulf in recent years. The purpose of the study is to (1) investigate the PAH levels in the water, sediments, and marine organisms in the Beibu Gulf of Guangxi; systematically (2) analyze the temporal and spatial differences of PAHs in the different waters of 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 provide recommendations.

Materials and methods

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 km². 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 km², and its annual runoff is about 1.70×10^{11} m³ (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 $-4\text{ }^{\circ}\text{C}$ 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 residents and our own divers through fishing and diving. 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 tinfoil sealed bags in insulated ice box. They were brought back to the laboratory as soon as possible and frozen it at $-20\text{ }^{\circ}\text{C}$ until analysis.

Analytical procedures

Sixteen target PAHs and 5 deuterated-labeled PAHs purchased from O2si, Charleston, USA. 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 h 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). A total of 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. Exactly 20 g 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 $80\text{ }^{\circ}\text{C}$ 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 (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used to separate target PAHs. The m/z parameters used in the 16 PAHs quantification are summarized in Table S2. The column oven temperature program: hold at $80\text{ }^{\circ}\text{C}$ for 2 min, heat up to $180\text{ }^{\circ}\text{C}$ at $15\text{ }^{\circ}\text{C}/\text{min}$ and hold for 20 min, heat up $260\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$ and hold 2 min, and heat up to $300\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C}/\text{min}$. EI ion source is a source temperature of $230\text{ }^{\circ}\text{C}$, and the data acquisition was performed in the multiple reaction monitoring (MRM) mode.

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 $(63 \pm 14)\%$, $(70.5 \pm 12)\%$, $(74 \pm 13)\%$, $(91 \pm 17)\%$, and $(101 \pm 16)\%$ 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 IDL 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 0.07–0.32 ng/L, 0.01–0.04 ng/g, and 0.14–0.64 ng/g, respectively.

Bioaccumulation factors of PAHs

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

$$\text{BWAf} = \frac{C_{\text{bio}}}{C_w} \times 1000 \quad (1)$$

$$\text{BSAF} = \frac{C_{\text{bio}}/f_{\text{lip}}}{C_s/f_{\text{oc}}} \times 1000 \quad (2)$$

where the C_{bio} is the concentration of PAHs in biota, C_w is the concentration of PAHs in water, the f_{lip} is the lipid fraction in biota, the C_s is the concentration of PAHs in the sediment, and the f_{oc} is the total organic carbon (TOC) fraction in sediment. The detailed determination method of TOC is shown in Text S5; the lipid content of organism is shown in Table S1.

Risk assessment of PAHs

Calculation of TEQ

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

$$\text{TEQ} = \sum C \times \text{TEF}_{\text{BaP}} \quad (3)$$

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 Benzo [a] pyrene (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:

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

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

where the Q^* is the cancer potency of BaP ($7.3 \text{ mg kg}^{-1} \text{ day}^{-1}$)⁻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 ; and BW_j and IR_j is the body weight and seafood intake rate (g/day) for age group j , respectively (Guo et al. 2010). Their true values for the various groups are presented in Table S14.

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 significant, while $p < 0.01$ was considered extremely significant.

Result and discussion

Pollution status of PAHs in Beibu Gulf

Water

The study initially reported the distribution and source of PAHs in the surface waters of Nanliu River and Lianzhou Bay but failed to study the overall state of PAHs in the Beibu Gulf (Wang et al. 2019). To further understand the concentration characteristics of PAHs in the gulf, the existing data was combined for unified analysis. Nine PAHs, including low molecular weight PAHs (LMW-PAHs, 2- and 3-ring) and two 4-ring PAHs (PYR and FLUA), were detected in the water samples of different regions in winter and summer. The detection rate of (BaP) was 11.1% and 22.2% in the summer and winter water samples, respectively. The Σ_{16} PAHs showed different temporal and spatial distributions (Fig. 1a and b). The average concentration of Σ_{16} PAHs were significantly higher in estuarine waters (mean: $71.4 \pm 9.58 \text{ ng/L}$; range: 57.9–90.8 ng/L) than in the coastal waters (mean: $50.4 \pm 9.65 \text{ ng/L}$; range: 29.7–68.7 ng/L) (t -test, $p < 0.01$) in summer. No significant difference was observed between estuarine waters (mean: $96.8 \pm 24.7 \text{ ng/L}$) and coastal waters (mean: $91.7 \pm 18.9 \text{ ng/L}$) during winter (Fig. 2). The estuarine water was found to be directly affected by urban anthropogenic activities, further aggravated by point source pollution from factories and agricultural activities. The weak diffusion ability of the estuarine water makes the PAHs difficult to spread. Compared to rivers, the tidal currents in estuaries promote water exchange and dilute the concentration of PAHs to a certain extent. This resulted in significantly lower Σ_{16} PAHs in the coastal seawater than in the seagoing rivers. However, in the dry season (winter), because the rainfall is greatly reduced, the current in the Beibu Gulf is relatively slow. Due to the lack of timely water exchange with inshore seawater, there is a minimal dilution of PAHs, thereby reducing the PAHs concentration difference between estuarine and coastal seawater.

The Σ_{16} PAHs was significantly higher in winter than in summer. This difference does not seem to be impacted by the region (t -test, $p < 0.01$) (Fig. 2), as previous studies have indicated (Lv et al. 2014; Zhang et al. 2016). This is often caused by several factors. Firstly, rainfall determines the degree of dilution and subsequent concentration of PAHs in the waterbodies. The concentration of PAHs in the Beibu Gulf was low due to abundant precipitation in the summer.

Fig. 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

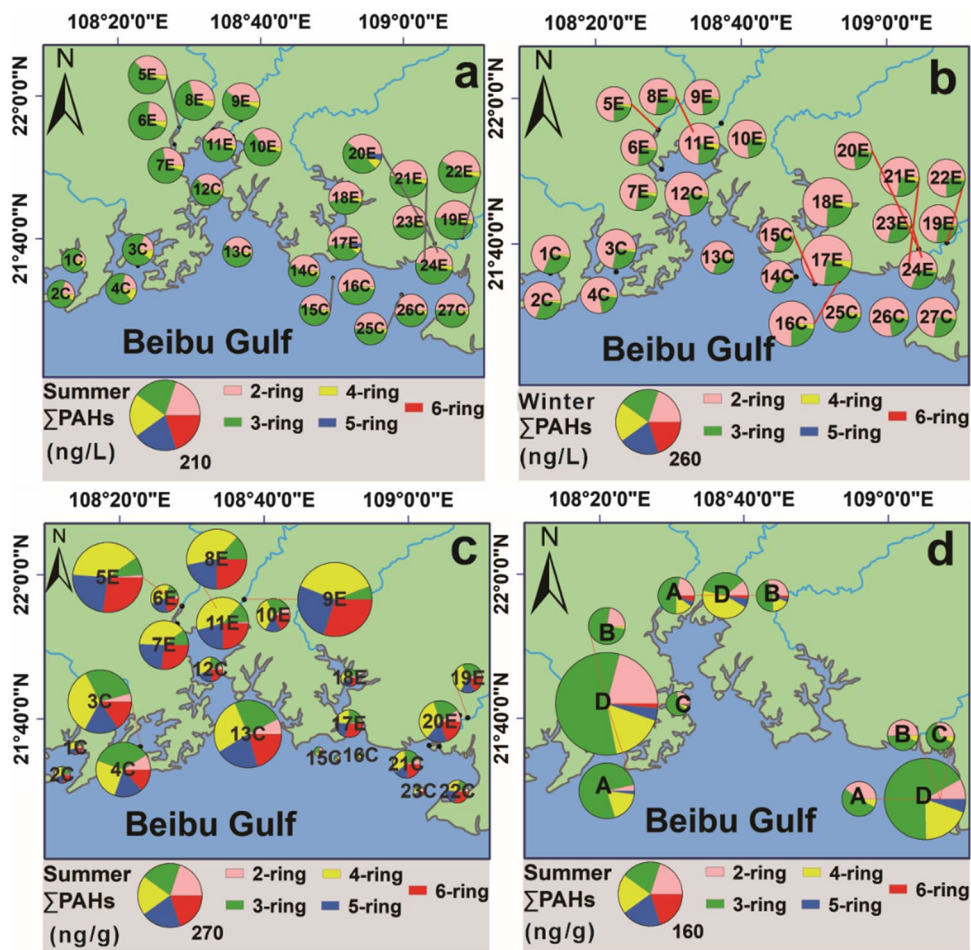
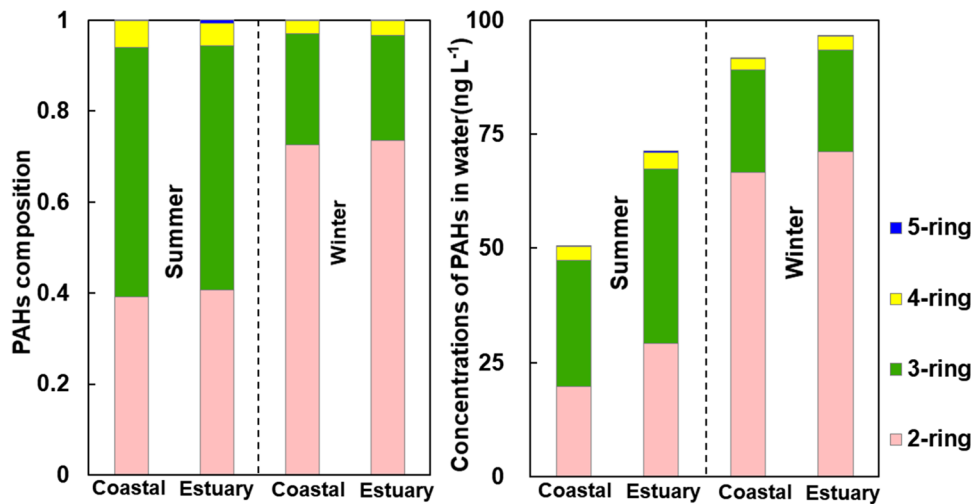


Fig. 2 Composition and concentration of dissolved phase PAHs in different regions



This is confirmed by the difference in salinity, where the salinity in estuarine waters ($1.2 \pm 2.0\text{‰}$) and coastal waters ($10.0 \pm 9.4\text{‰}$) in summer were much lower than that in winter ($12.1 \pm 9.29\text{‰}$ and $25.0 \pm 10.0\text{‰}$) (Table S4 and Table S5). Certain PAHs were also subject to degradation by strong solar radiation in summer (Jia et al. 2015). Previous

studies have indicated that PAHs photolyze rapidly under irradiation by following pseudo-first-order kinetics, where photoionization yields the PAH radical cation and a hydrated electron which is followed by PAH-destroying reactions involving water (Chen et al. 2001, 2011; Wu and Shao 2017; Zepp and Schlotzhauer 1979). The strong sunlight

in the summer not only promotes the photodegradation of PAHs, but the higher temperature also stimulates the reproduction and growth of microorganisms and PAH-degrading bacteria, thereby rendering the concentration of PAHs low (Gibson et al. 1975). In addition, the increase in emission of PAHs in the northern cities due to increasing temperature is transferred to the south through the northeast monsoon during winter. This increases the concentration of PAHs in the winter months in southern China (Kong and Miao 2014). The concentration of PAHs was also found to be affected by fishing activities. Fishing in the Beibu Gulf is suspended from May to August, which reduces the release of PAHs by fishing activities. On the contrary, pollution by frequent fishing activities in the winter months may lead to an increase.

Sediment

The spatial distribution of PAHs in the sediments of the Beibu Gulf is presented in Fig. 1c. All 16 PAHs were detected in the sediments, the detection rate ranging from 82.6 to 100%. Similar to surface seawater, Σ_{16} PAHs were significantly higher in the estuarine sediments (range: 19.6–359 ng/g, mean: 146 ± 116 ng/g) than the coastal sediments (range: 2.39–297 ng/g, mean: 76.9 ± 108 ng/g) (non-parametric test, $p < 0.01$).

Estuary

The Σ_{16} PAHs in surface sediments showed significant regional differences, in 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 was detected in the upper reaches of the Qin River (359 ng/g). This may be due to the proximity of the sampling point to a local shipyard, which generates and releases sandblasted and polished dust, oil, and domestic sewage. The PAHs produced are adsorbed by particulate matter in the water bodies, which settle on the sediments, resulting in high Σ_{16} PAHs. The upper reaches of the Maoling River may record high concentrations of PAHs (320 ng/g) due to the proximity to the docking areas.

Coast

The Σ_{16} PAHs in the coastal surface sediments also showed clear regional differences (Fig. 1c). Barring ANTH, CHR, BbF, BkF, and DiB, the remaining PAHs were detected in all the coastal sediment samples. The Σ_{16} PAHs in the coastal zone was detected in the following order: 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 where sediments are easy to silt. Thermal power plants are present on the east side of the bay. As the largest commercial port on the coast of Guangxi, port transportation is Fangcheng Port's primary industry. The resultant burning of petroleum and leakage may potentially be an additional source of PAHs. The Qinzhou Bay has weak water exchange capacity and slow water flow at the mouth of the bay—the confluence of the Maoling and Qinjiang River. The intertidal shoals and broad underwater delta formed by the interaction of river sediments transport and inevitably provide ideal conditions for the deposition of a large number of pollutants. 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 a key development base of the Beibu Gulf, where the oil pollution caused by port development and ship transportation cannot be ignored. The Σ_{16} PAHs at the sampling site 13C in the middle of Qinzhou Bay may be affected by pollutants released from the neighboring petrochemical industrial park. The Σ_{16} PAHs in Pearl Bay and Sanniang Bay were found to be much lower than in Fangcheng Port and Qinzhou Bay. Pearl Bay is a typical funnel-shaped shallow bay with a narrow mouth, where the water exchange between the inner and outer parts of the bay is strong. The Σ_{16} PAHs were found to be relatively lower and not easily absorbed by the sediments when compared with Fangcheng Port and Qinzhou Gulf.

Marine organisms

All 16 PAHs were detected in various marine organisms. The Σ_{16} PAHs in organisms ranged from 15.3 to 559 ng/g. The concentrations 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 shellfishes. The order of the Σ_{16} PAHs in the four marine organisms were found to be as follows: shellfishes (183 ± 165 ng/g) > fishes (73.7 ± 57.2 ng/g) > crabs (42.7 ± 19.2 ng/g) > shrimps (30.4 ± 8.3 ng/g) (nonparametric test, $p < 0.01$) (Fig. 1d). The Σ_{16} PAHs were significantly lower in this study as compared to previous studies conducted in Poyang Lake, Daqing Lake, and Ramsar site, China, and the coastal areas of Bangladesh (Habibullah-Al-Mamun et al. 2019; Jyethi and Khillare 2019; Wang et al. 2015b; Zhao et al. 2014). Previous studies have shown that the levels of PAHs in organisms were associated with the pollution status of the living environment and the biological species while having a negative correlation with the trophic level of the organisms (Wan et al. 2007). Benthic organisms were found to have lower trophic levels than

other marine organisms, with a higher ability to accumulate PAHs (Fig. 1d). Shellfishes exhibited an unexpectedly high PAH tissue burden, even in moderately contaminated areas (Knutzen and Sortland 1982; Meador et al. 1995). However, the concentration of PAHs in fishes was found to be higher than that in crabs, which may be closely related to their habitat. As mentioned earlier (Figs. 1 and 2), 2-ring and 3-ring PAHs were dominant in the water bodies. Fishes inhabit the water environment throughout the year and can thus accumulate further low molecular weight PAHs, especially 2-ring and 3-ring PAHs, through bioaccumulation. In contrast, crabs inhabit sediment beaches, mangroves, or marshes in the intertidal zone and are therefore exposed to fewer PAHs. In addition, these areas are usually dominated by high molecular weight PAHs that are often present in low concentrations.

Composition of PAHs in Beibu Gulf

Water

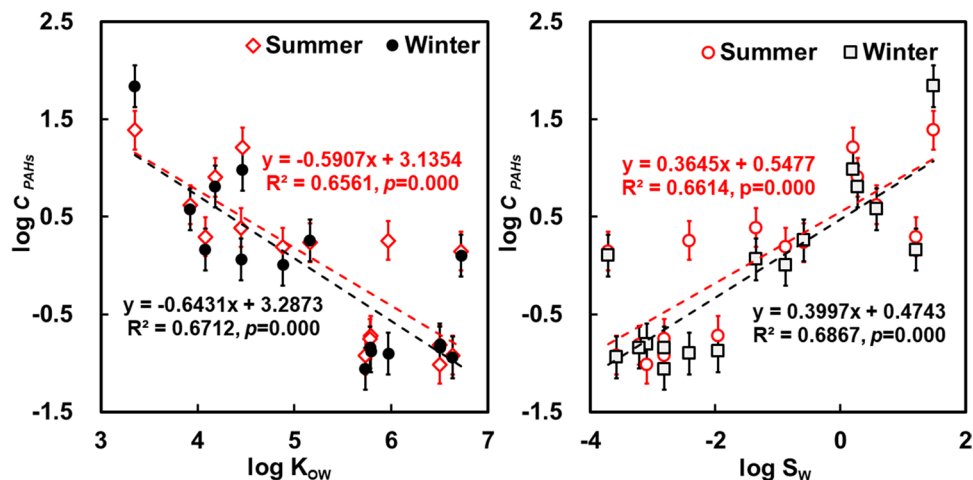
The proportion of 2-ring PAHs was found to be significantly higher in winter (coastal: $72\% \pm 4\%$; estuary: $74\% \pm 2\%$) than in summer (coastal: $37\% \pm 14\%$; estuary: $41\% \pm 9\%$), whereas the proportion of 3-ring PAHs was higher in summer (coastal: $57\% \pm 12\%$; estuary: $53\% \pm 9\%$) than that in winter (coastal: $25\% \pm 4\%$; estuary: $23\% \pm 2\%$) (Fig. 2). This difference may be associated with the physicochemical properties of the compounds and the temperature. Two-ring PAHs are more volatile than 3-ring PAHs. This leads to greater evaporation of 2-ring PAHs, resulting in relatively low concentrations in the summer months. In terms of individual PAHs, the concentration of various PAH congeners in estuarine waters exhibited a significant positive correlation than in coastal waters (summer: $R^2 = 0.9844$, $p = 0.000$; winter: $R^2 = 0.9996$, $p = 0.000$). The composition of PAHs in estuaries and coastal waters was

similar seasonally, indicating that PAHs in the two areas are homologous. The logarithms of the average concentration of the different PAH congeners in the water samples show a significant positive correlation with the logarithms of water solubility but a significant negative correlation with the logarithms of their octanol–water partition coefficients (K_{OW}) (Fig. 3). The greater the solubility and polarity, the higher the concentration of PAHs in water. The Σ_{16} PAHs in the Maoling River, Qin River, and Dafeng River show a gradual decrease as they enter the sea due to the dilution of seawater. In summer, the order of Σ_{16} PAHs was found to be as follows: Nanlijiang > Maolingjiang > Qinjiang > Dafengjiang (Fig. S1-A), while the ranking in winter was Dafengjiang > Nanlijiang > Qinjiang > Maolingjiang. The concentration in Dafengjiang (155 ng/L) was significantly higher than in other rivers (Fig. S1-B). By estimating the flux of PAHs into the sea (Text S4), it was found that the annual flux of PAHs from the four rivers is 826 kg, where the rainy season (700 kg) accounts for more than 85% of the total flux (Table S6). The Nanliu River has the highest flux (459 kg), accounting for roughly 55.6% of the total, followed by the Qinjiang (21.1%), Maoling (15.2%), and the Dafeng River (8.1%). It was observed that although the Dafeng River has the heaviest degree of PAH pollution in winter, its river runoff and PAH flux were relatively low, thereby having the least impact on the Beibu Gulf. The Nanliu River is the largest river in Guangxi alone that flows into the sea. Its runoff and thereby the flux of PAH into the sea was relatively high, which may have the greatest impact on the Beibu Gulf.

Sediment

The composition of PAHs in the coastal and estuarine sediments was found to be similar, with primarily 3-, 4-, and 5-ring PAHs accounting for more than 80% of the Σ_{16} PAHs. Compared to previous studies, this study indicated the Σ_{16} PAHs in the sediments of the Beibu Gulf to be higher

Fig. 3 Correlation between the average concentration of PAH monomer compounds in the Beibu Gulf waters and their K_{OW} and water solubility (S_w)



than in 2005 but lower than in 2011 (Li et al. 2015; Yang et al. 2013). The high concentration in 2011 may be associated with an accidental oil spill. Overall, an increasing trend in Σ_{16} PAHs has been observed, especially that of the HWM-PAHs, which may be attributed to increased local economic development. Fossil fuels, vehicle emissions, and other oil combustion-related pollution sources may be the key contributors to the observed increase. Terrestrial PAHs enter the marine environment in several ways and are ubiquitous to marine water and sediments (Han et al. 2019). The distribution coefficient (K_p) was used to evaluate the distribution of PAHs between sediments and the water in the aquatic environment. The results showed that the K_p values of the 16 PAHs ranged from 0.89 to 147; the partition coefficient increased with the molecular weight. Therefore, HMW-PAHs are readily assimilated in sediments, which is consistent with previous studies (Liu et al. 2012; Zhang et al. 2013).

Marine organisms

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

Bioaccumulation of PAHs

Organisms ingest several nutrients and refractory organic compounds, including various pollutants from surrounding environmental media (atmosphere, water, soil, sediment, etc.) (Ding et al. 2020, 2019; Han et al. 2019; Pan et al. 2017; Zhang et al. 2018a, 2019, 2018b). Elevated levels of pollution beyond a certain threshold threaten the survival of these organisms. Taking this into consideration, bioaccumulation factors (BAFs, in $L\ kg^{-1}$) were used to evaluate the accumulation ability of marine organisms (Text S3). 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 average log BWAFs of the marine organisms ranged from 1.82 to 3.00, while the log BSAFs ranged from -0.07 to 2.73. As indicated in Figs. 4A and S4-A, the possibility of accumulation of PAHs in the Beibu Gulf through bio-water accumulation is extremely low. Only the log BWAFs of BaP (1.63–3.93) were considered to be potentially bioaccumulative in certain marine organisms. The others were

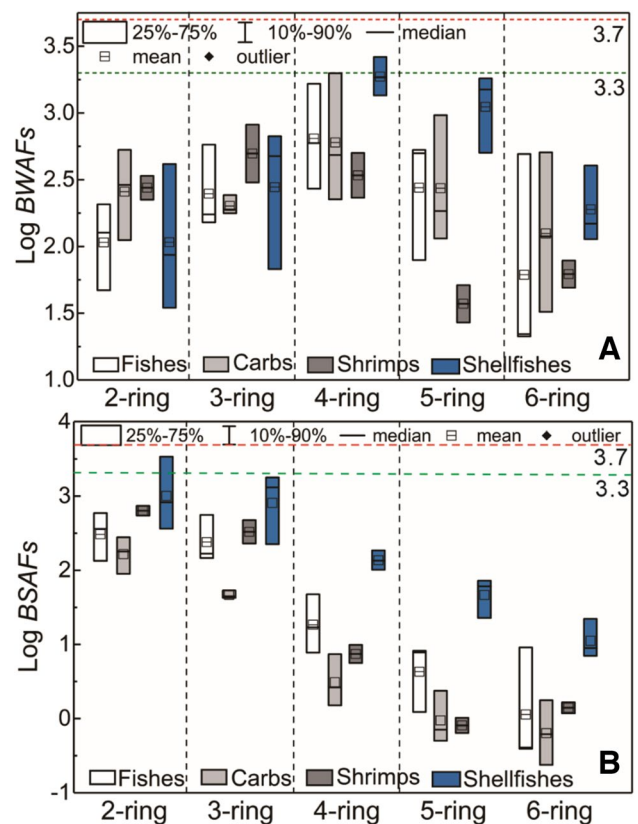


Fig. 4 The log BWAFs and log BSAFs of PAHs in various marine organisms in Beibu Gulf

lower than the potential accumulation, with the log BWAFs of DiB recorded as the lowest (1.22 ± 0.54). In addition, it was observed that the average log BWAFs for 4-ring PAHs were much higher than that of the other PAHs (Fig. 4A). The statistical data reveals a significant difference in the BWAFs of the 16 individual PAHs in the marine organisms (shellfishes > fishes > crabs and shrimps) (*nonparametric-test*, $p < 0.01$). The BSAFs were found to be affected by a variety of factors, including biomagnification, sediment ingestion, elimination, and metabolic transformation (Burkhard 2003; Lamoureux and Brownawell 1999; Van Hoof et al. 2001). As presented in Figs. 4B and S4-B, the four marine organisms considered in this study may be more likely to accumulate LMW-PAHs through bio-sediment accumulation. As mentioned earlier, the PAHs in sediments are primarily comprised of MMW- and HMW-PAHs. However, largely LMW- and MMW-PAHs were recorded in marine organisms. Therefore, the values of log BSAFs of 2- and 3-ring PAHs were much higher than others. Statistics show significant differences in the BSAFs of the 16 individual PAHs (shellfishes > fishes > shrimps > crabs) (*nonparametric-test*, $p < 0.01$). These differences in BWAFs/BSAFs may be associated with the feeding habits and trophic levels of marine organisms. This is supported by previous studies

where diluted POPs have been indicated in the tropical marine food web (Ding et al. 2020). Marine organisms, including mollusks (oysters), filter and feed on microalgae and organic marine debris, while the majority of fishes (*Tilapia mossambica*, *Rhabdosargus sarba*, and *Trachinotus ovatus*) are omnivorous, primarily feeding on plants, algae, and benthic invertebrates. On the other hand, crabs and shrimp are carnivorous, largely feeding on benthic invertebrates. The trophic level of herbivorous marine organisms is generally lower than that of carnivorous organisms. The lower the trophic level, the higher the PAHs accumulation capacity in marine organisms.

Previous studies have reported a high correlation between K_{OW} values and BAFs for hydrophobic organic compounds, where the BAFs are typically a function of the K_{OW} (Ding et al. 2020; Han et al. 2019; Wang and Kelly 2018). The functional relationship between PAHs log $BWAFs$ /log $BSAFs$ and K_{OW} depends on the species, metabolic levels, and habitat (Lamoureux and Brownawell 1999; Moermond et al. 2005). The $BWAFs$ values are usually positively correlated with log K_{OW} values (Han et al. 2019; Meylan et al. 1999). The Pearson's correlation coefficient indicated a positive correlation between log K_{OW} and log $BWAFs$ ($r^2=0.51$, $p<0.01$) and a negative correlation with log $BSAFs$ ($r^2=0.88$, $p<0.01$) (Fig. 5). In fact, log K_{OW} exhibited a negative correlation with the log $BSAFs$ of PAHs in various marine organisms. However, not all of them were positively correlated with the log $BWAFs$ of PAHs (Figs. 6 and S5). The lower BAF value of certain PAHs may be because the estimated $BWAFs$ using MDLs were much lower than their actual value. The true concentration of these PAHs in the surrounding water may be much lower than their MDLs.

Source apportionment

Previous studies have confirmed that the isomer ratio can be utilized as a cardinal indicator to determine the sources of PAHs (Kavouras et al. 2001; Sofowote et al. 2008; Zhang

et al. 2021). As presented 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 the sediments and water of the Beibu Gulf. The results confirmed pyrogenic origins from coal and biomass combustion to be the dominant contributors of PAHs in water, while the main sources of PAHs in sediments were determined to be from incomplete combustion of coal and wood sources.

A cluster analysis was carried out on the standardized concentration matrix to explore the structure of the concentration data and to determine the source of PAHs. Previous studies have used the distance between groups and Euclidean distance for the cluster method and measurement interval, respectively (Kavouras et al. 2001; Xu et al. 2021). Figure 7 shows the results of the hierarchical cluster analysis (HCA), presented in the form of a dendrogram. The PAHs in the water during the summer have been classified into two categories (Fig. 7A). The first category was further divided into two subcategories. The first subcategory comprised of ACEY, ACE, ANTH, PYR, FLUA, and BaP, indicating a combination of sources, like spilled oil and biomass burning (Ko et al. 2014; Xu et al. 2021). The second subcategory, comprised of FLU and PHE, are potentially good indicators of coal combustion (Larsen and Baker 2003). The second category is comprised of NAP, indicating petroleum as a source. Similarly, the PAHs detected during the winter were also divided into two groups (Fig. 7B). The first group comprised FLUA, ACE, FLU, PYR, ANTH, ACEY, and BaP. The sources for these PAHs include petroleum, coal, and wood combustion. The second group consisted of PHE and NAP, indicating coal combustion as an important source during the winter months. As presented in Fig. 7C, the 16 individual PAHs indicated in the sediments were divided into two major groups, which were further subdivided into two subgroups. The first subgroup comprised of the PAHs ACEY, ACE, ANTH, and DiB, indicating petroleum and vehicle emissions as potential sources (Ko et al. 2014; Wang

Fig. 5 Relationship between the log BAFs (A water; B sediment) of detected PAHs in the marine organisms and their log K_{OW} . The predicted log BAFs of some PAHs were predicted based on the regression equation shown in the plot

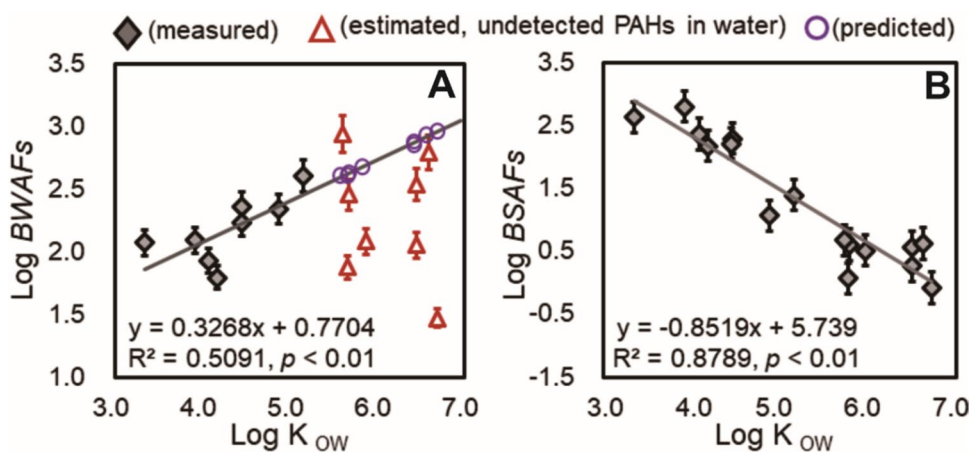


Fig. 6 Relationship between the log *BSAFs* of detected PAHs in the various marine organisms (**a** fishes, **b** carbs, **c** shrimps, **d** shellfishes) and their log *K_{OW}*

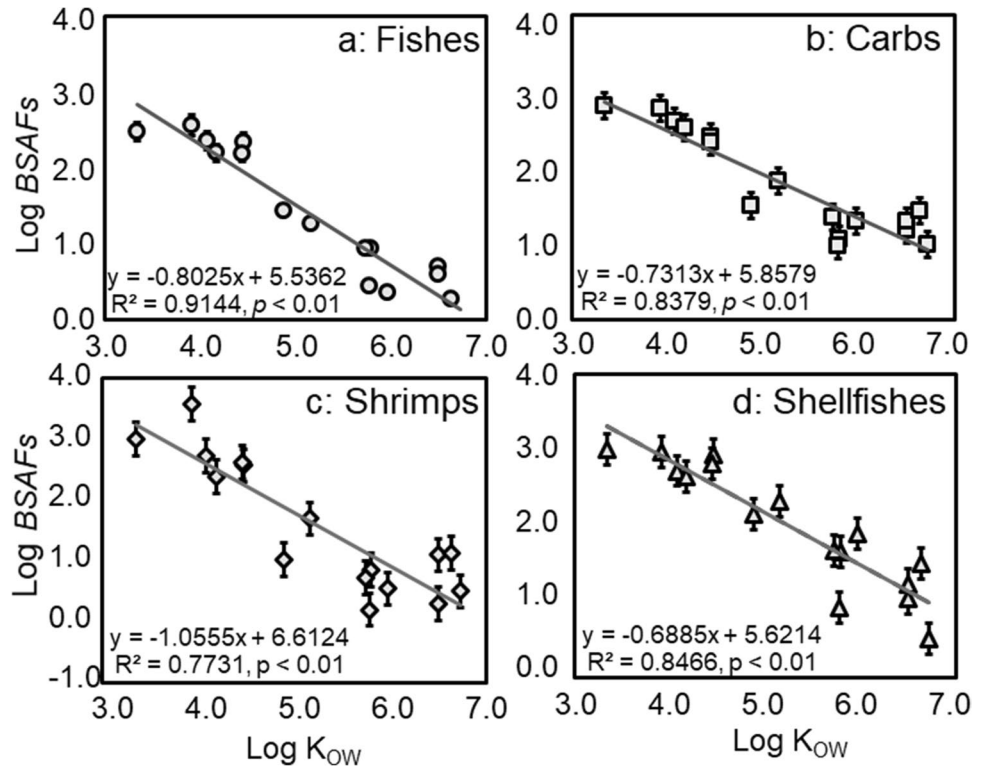
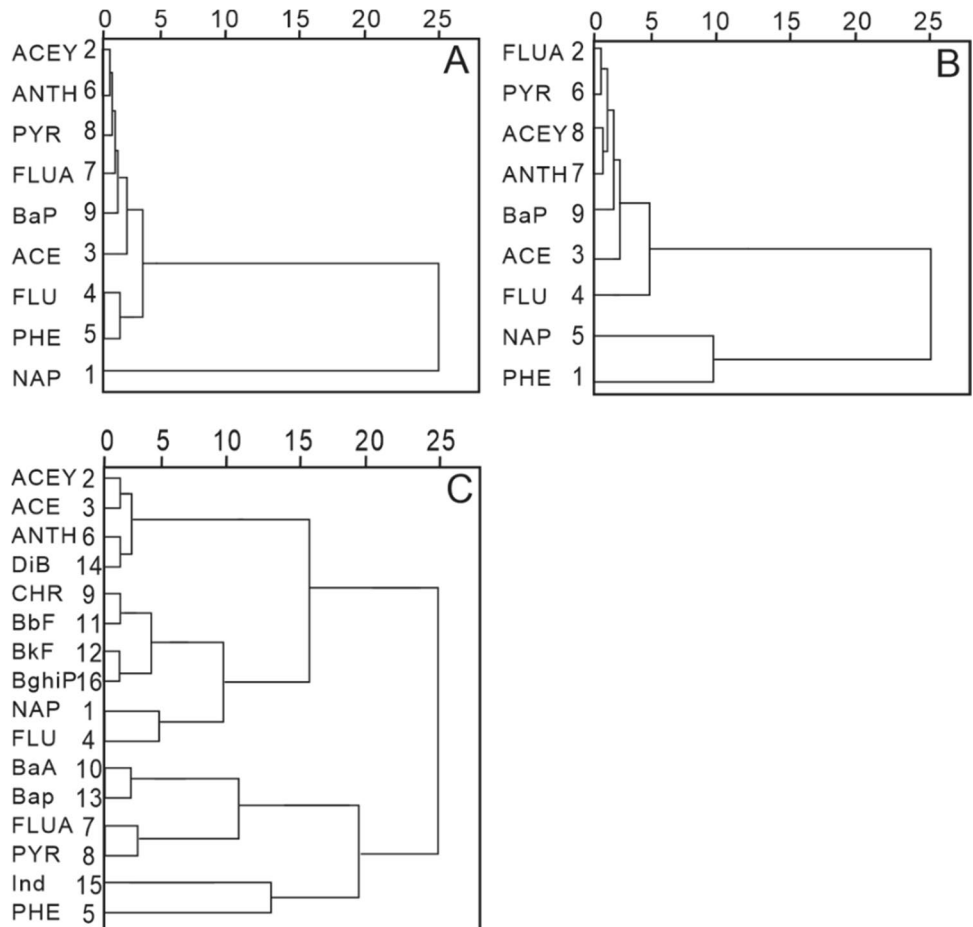


Fig. 7 A dendrogram of hierarchical cluster analysis of $\Sigma 16$ PAHs in water (**A** summer; **B** winter) and sediment (**C** sediment) of Beibu Gulf



et al. 2015a). The second subgroup comprises FLU, CHR, BbF, BkF, BghiP, and NAP, indicating fossil fuel combustion and vehicle emission as potential sources (Kavouras et al. 2001; Wang et al. 2015a). The second major group was also subdivided into two subgroups. The first subgroup contained BaA, BaP, FLUA, and PYR, indicating combined sources of coal burning and vehicular emission (Larsen and Baker 2003; Wang et al. 2015a). The second subgroup consisted of PHE and Ind, indicating coal burning and vehicular emission as potential sources (Larsen and Baker 2003; Sofowote et al. 2008). This source identification indicates that spilled oil, fossil fuel burning, and vehicle emissions are the primary sources of sediment PAHs in the Beibu Gulf. Therefore, spilled oil, biomass, and coal burning are noted to have the greatest influence on PAH pollution in water, while spilled oil, burning of fossil fuels, and vehicle emissions were found to be the main sources of pollutants in sediments.

Risks assessment

Calculation of toxic equivalency quotients

Benzo [a]pyrene (BaP), a known PAH, is a powerful human carcinogen, detrimental to both organisms and human health. The maximum permissible concentration of BaP allowed by the European Union (EU) in drinking water and in fishes, crabs, shrimps, and shellfishes is 200 ng/L and 2–10 ng/g, respectively. The national standard in China, however, does not exceed 5 ng/g (Commission 2011; Zelinkova and Wenzl 2015). In this study, BaP was detected in all the sampled organisms, the concentration in shellfish ranging from 0.36 to 2.13 ng/g ww. The concentration of BaP in a few shellfish samples in Fangcheng exceeded the EU standard but was lower than the Chinese national standard. The concentration of BaP in other marine organisms was far lower than the threshold set by the EU. The results, therefore, demonstrated no human health risk by BaP in the organisms sampled from the Beibu Gulf. Several methods were combined for a comprehensive understanding of the possible risks of PAHs in the sea area. The average TEQ of Σ_{16} PAHs in marine organisms is significantly lower

than the Chinese and the EU standard. Shellfish showed the highest TEQ (694–2267 pg g⁻¹) among the sampled marine organisms. The ranking of TEQ values in the marine organisms is as follows: shellfish (1774 pg/g) > fishes (446 pg/g) > crabs (172 pg/g) and shrimp (80 pg/g) (*t*-test, *p* < 0.01) (Table S13). For the individual PAHs, although BaP and DiB were found in low concentrations (3% and 1%), they were found to have high TEQ values (70% and 20%). The TEQ of PAHs may reflect toxicity more than the concentration (Ding et al. 2012). In conclusion, the results of the TEQ demonstrated that PAHs do not pose a health risk to human health via seafood consumption.

Cancer risk assessment

The results of the excess cancer risk are presented in Tables S15 and 1. The excess cancer risk of different organisms ranked in the order of shellfishes (2.07×10^{-6} – 1.84×10^{-4}) > fishes (1.35×10^{-6} – 5.91×10^{-5}) > shrimps (2.38×10^{-8} – 3.77×10^{-6}) > crabs (2.08×10^{-8} – 1.85×10^{-5}). According to the US Environmental Protection Agency, excess cancer risk of less than 1×10^{-6} is considered negligible, and greater than 1×10^{-4} is considered a priority control risk level (EPA 2017; Williams et al. 2013). Thus, compared to other marine organisms, shellfish may pose a higher risk, especially for children aged 2–5 years. Consumption of shellfish should therefore be appropriately monitored for this age group, because their excessive cancer risk has obviously exceeded the priority control risk level (Table 1). The excess cancer risk resulting from a lifetime exposure to the PAHs was calculated using Eq. (4). The exposure time of 70 years was considered by referring to previous study (Williams et al. 2013). The excess cancer risks induced by lifetime ingestion of the Σ_{16} PAHs via seafood consumption are presented in Table 1. The excess lifetime cancer risks were found to be 2.94×10^{-5} for males and 3.06×10^{-5} for females. This value is much lower than the high incremental lifetime cancer risk in the coastal areas of Bangladesh (5.6×10^{-5} – 3.4×10^{-4}), comparable to that in southeastern Louisiana, USA (1.2×10^{-5} – 3.8×10^{-5}) and Korea (1.8×10^{-5} – 9.8×10^{-5}), but slightly higher than that

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

Age groups	Gender	Fish	Crab	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}	1.32×10^{-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}

of Mexico (4.3×10^{-6} – 1.3×10^{-5}) (Habibullah-Al-Mamun et al. 2019; Jeong et al. 2010; Rotkin-Ellman et al. 2012; Wickliffe et al. 2018).

According to the results of the study, the concentration of PAHs in marine organisms in the Beibu Gulf is deemed safe. The health risks and cancer risks by accidental daily intake of PAHs through consumption of seafood are very low. However, it is worth noting the health issues and cancer risks associated with excess consumption of shellfishes, especially in children. It is suggested that the consumption of shellfishes be controlled in children.

Conclusion

The results of this study demonstrate that PAHs are widely distributed in varied environmental media in the aquatic ecosystem of the Beibu Gulf. The concentration of PAHs in the water revealed significant spatial differences—the Σ_{16} PAHs were significantly higher in the estuaries than on the coast in summer. The concentration of PAHs in marine organisms was notably different. The source apportionment results identified spilled oil, biomass, and coal burning as the main sources of PAHs in water, whereas spilled oil, fossil fuel burning, and vehicle emissions were identified as the primary pollutants in sediments. Bio-accumulation of the 16 PAHs was not observed in marine organisms. The ecological risk assessment shows that the PAHs in the Beibu Gulf pose very low to no risk. Although the consumption of seafood does not pose a health risk, it is suggested that shellfishes intake be monitored in children of the age group 2–5.

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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 analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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