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Baseline

Polycyclic aromatic hydrocarbons in surface sediment from Yangpu Bay, China: Distribution, sources and risk assessment

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ABSTRACT

The study investigated the occurrence of polycyclic aromatic hydrocarbons (PAHs) in the surface sediment from eleven sites in Yangpu Bay, China in December 2013 (winter) and July 2014 (summer). The 16 US EPA priority PAHs were found in the range of 1583.2–5701.7 ng/g dry weights with an average of 3134.7 ± 1241.3 ng/g in winter and ranged from 2161.8 to 4527.2 ng/g with an average of 3016.6 ± 748.0 ng/g in summer, respectively. The concentrations of the PAHs tended to be relatively high in comparison with other areas from the literatures. The identification using molecular indices analysis indicated that the PAHs originated mainly from pyrogenic and petrogenic sources in most of the sites. According to principle component analysis–multiple linear regression (PCA/MLR) for their source apportionment, the main sources of PAHs were vehicle emissions, petroleum products and biomass combustion. The risk assessment using international sediments quality guidelines and sediments quality criteria indicated that several PAHs, such as Nap, Flu, Phe, Ace, Acy and BghiP in most of the sites would potentially affect organisms in Yangpu Bay.

Polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants (POPs) containing two or more fused benzene rings. PAHs in the marine environment can derive from natural sources and anthropogenic activity. In general, the sources of PAHs can be classified into: pyrogenic sources like combustion of organic matter, petrogenic sources like crude and refined petroleum and diagenetic origins like short-term degradation of biogenic precursors (Wang et al., 2010; Botsou and Hatzianestis, 2012). Due to their potential mutagenic, carcinogenic and hazardous risks to organisms and human beings, PAHs have received special environmental concerns and 16 of them have been listed as priority control pollutants by the environmental protection agency of the USA (Manoli et al., 2000; Botsou and Hatzianestis, 2012).

The marine sediment is one of the most important reservoirs of environmental pollutants and can provide insights about the fate of these contaminants in the past (Guo et al., 2011). Because of their hydrophobicity and persistence, PAHs are readily absorbed to suspended particles and accumulated in sediment (Chiou et al., 1998). As a result, the contaminated sediments can directly affect bottom dwelling organisms. Moreover, the sediment can be resuspended and the contaminants would reenter the marine aquatic environment and circulate in ecosystems, resulting in second contamination (Zeng and Venkatesan, 1999). Therefore, distribution and sources of PAHs in sediment have been widely studied in coastal areas around the world (Huang et al., 2012; Sinaei and Mashinchian, 2014; Soliman et al., 2014). However, little data regarding the concentrations of PAHs in the sediment of Yangpu Bay, China have been reported.

Yangpu Bay is located at the northwestern section of Hainan Province with an area of 220 km^2. It is the busiest marine area near Yangpu economic development zone, with some large fish processing works, power stations, and petroleum and chemical storage facilities in addition to numerous industrial facilities. The bay is directly influenced by domestic wastewater, agricultural drainwater, and atmospheric fallout. Moreover, heavy industry, shipyard activities and the intensive navigation and shipping activities of Yangpu may also contribute to high level of pollution. Due to the potential impact of the pollution from anthropogenic sources on

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marine organisms, it is important to know the extent of the contamination. Therefore, it is necessary to identify the sources and distribution of PAHs, and assess the risk caused by anthropogenic pollution on the ecosystem of Yangpu Bay.

In our previous work, the spatial distribution and sources of PAHs in surface seawater of Yangpu bay have been reported, and PAHs pollution level was classified as moderate to heavy (Li et al., 2015). However, the state of PAHs in the local sediment is unknown. Therefore, the present study is to investigate the current state of PAHs concentrations in the surface sediment of Yangpu coastal area. The aim of the research was: (1) to determine seasonal variation of the concentrations and compositions of PAHs; (2) to elucidate the potential sources by PAHs diagnostic ratio analysis and carry out quantitative sources apportionment using principle component analysis–multiple linear regression (PCA/MLR), and; (3) to evaluate the possible ecological risk of PAHs in the sediment of Yangpu Bay.

Yangpu Bay locates at 19°11′N and 109°43′E. It has a tropical monsoon climate with clear rainy and dry seasons. The annual average rainfall is 1113.8 mm. The characteristic of the local tidal current is from southeast to northwest. The sampling stations are shown in Fig. 1. Twenty-two surface sediment samples (0–10 cm) were collected in December 2013 (water temperature was 18 °C) and July 2014 (water temperature was 31 °C) using a stainless steel grab sampler. All sediment samples were put into aluminum containers individually, then transported to the laboratory and stored at −20 °C for further analysis.

A composite standard solution of 16 US EPA priority PAHs (purity > 99%) was obtained from AccuStandard Chem. Co. (Connecticut, USA). The organic solvents including dichloromethane and hexane were chromatographic grade from Mreda Co. (USA). Anhydrous sodium sulfate (analytical grade) were heated at 450 °C for 6 h and stored in sealed containers. Silica gel (100–200 mesh, Aladdin) and Aluminum oxide (100–200 mesh, Aladdin) were precleaned by dichloromethane and hexane, then dried at 105 °C. Silica gel and Aluminum oxide were activated at 140 °C for 4 h and partially deactivated with 5% water. Activated elemental copper (analytical grade, Aladdin) was used to remove sulfur compounds avoiding potential interferences during gas chromatography.

Each sediment sample was homogenized and freeze-dried before extracting, then crushed into fine powders, and passed through a stainless steel sieve with the pore size of 150 μm. Two grams sample was extracted two times for 30 min by ultrasonication with 20 mL mixture of hexane/dichloromethane (1:1 ratio) and 0.5 g activated copper granules. The extract was then evaporated to 1–2 mL volume in a rotary vacuum evaporator. An alumina/silica gel (1:2) column with 1–2 g anhydrous sodium sulfate was used to clean-up and fractionate the extract. The sample was allowed to pass through the column. Then, the fraction containing PAHs was collected by eluting with 50 mL hexane/dichloromethane (1:1). The sample was concentrated again to 5 mL in the rotary evaporator. The concentrated extract was dried under a gentle gas stream of purified nitrogen. The residue was finally dissolved in 1 mL hexane for the gas chromatography–mass spectrometer (GC–MS) analysis.

The concentrations of PAHs in the extracts were determined using an Agilent 7890 gas chromatograph equipped with a split/splitless injector, a 7693 autosampler and a 7000 mass selective detector (MSD) under the multiple reaction monitoring (MRM) mode (Agilent, Palo Alto, CA, USA). An HP-5 fused silica capillary column (30 m × 0.25 mm × 0.25 μm, Agilent) was used for the separation. The injector temperature was maintained at 250 °C. The oven temperature was programmed as following: initial temperature at 100 °C for 2 min; then increased to 200 °C with a rate of 10 °C/min, then increased to 300 °C with a rate of 5 °C/min, and then isothermal pause 5 min at 300 °C. A volume of 1 μL extracted sample was injected in the splitless injector with a 1 min solvent delay. Helium was used as the carrier gas with a flow rate of 1.0 mL/min.

All results for the sediment samples were expressed with a dry-weight basis. For the quality control and assurance, the procedure blanks, standard-spiked blanks, and sample duplicates were routinely analyzed. The external standard method using a 16

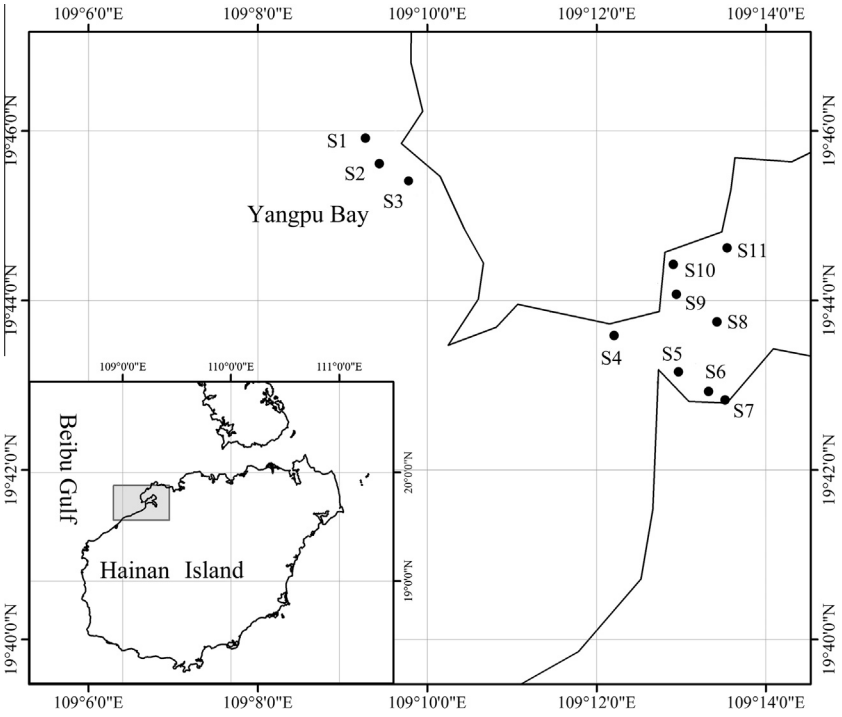

Fig. 1. Location of the sampling sites in Yangpu Bay.

PAHs reference material mixture was performed and the correlation coefficients for all calibration curves were higher than 0.999. The method described for the sample preparation was validated by a recovery investigation. The recoveries were monitored by adding standard compounds to each sample prior to extraction and the procedural blanks were analyzed with each set of samples. A satisfactory analytical quality control was achieved. The mean recoveries of sixteen individual PAHs ranged from 63.0% to 121.9%, and the relative standard deviation (RSD) varied from 1.28% to 11.21% ($n = 7$). The method detection limit (MDL) ranged from 0.10 to 4.09 ng/g.

Principal component analysis (PCA) followed by multiple linear regression (MLR) was performed for the data analysis using SPSS 19.0. The plots of data analysis were done using Origin 8.0.

The concentration of each PAH and total PAHs (in ng/g dry sediment) in the surface sediment of Yangpu Bay in winter and summer are presented in Table 1 and Fig. 2. The concentration of total PAHs (ΣPAHs) varied from 1583.2 to 5701.7 ng/g with a mean value of 3134.7 ± 1241.3 ng/g in winter and from 2161.8 to 4527.2 ng/g with a mean value of 3016.6 ± 748.0 ng/g in summer. The highest concentration of ΣPAHs in winter was detected at S9 (5701.7 ng/g), followed by S4 (4560.0 ng/g), and the lowest concentration was found at S6 (1583.2 ng/g). The highest concentration of ΣPAHs in summer was detected at S5 (4527.2 ng/g), followed by S9 (3599.6 ng/g), and the lowest concentration was found at S8 (2161.8 ng/g). Nap and Phe were predominant species in winter, accounting approximately for 18.5% and 12.4% of total PAHs, respectively. In addition, Nap and Phe were also prevalent in summer, accounted for 16.4% and 15.3% of total PAHs, respectively. The concentration of Ace was the lowest both in winter and summer, accounted for 1.1% and 0.4%, respectively. Among the 16 PAHs, BaA, Chy, BbF, BkF, BaP, InP and DahA were considered to have potential carcinogenicity according to IARC (1987). The total concentration of these seven potentially carcinogenic PAHs ranged from 298.0 to 3064.4 ng/g with an average value of 1176.3 ng/g in winter and from 476.7 to 2400.6 ng/g with an average value of 1178.0 ng/g in summer, respectively. Obviously, the potential carcinogenicity caused by PAHs in Yangpu Bay should be seriously considered both in winter and summer.

The relatively high individual PAHs and total PAHs concentrations were observed at S9, S4 and S5, which were seriously impacted by anthropogenic activities. Among the monitored sites, S9 was near a shipyard and factories, where the amount of PAHs could be related to industrial waste water and shipbuilding activities. S4 was near wharfs with frequent ship traffic, where oil spills and exhaust from engines may be the sources of the PAHs. S5 was near a fishing harbor and a flourishing town, where the sewage discharges and fishery activities might contribute to the input of the PAHs. In particular, the hydrological condition (e.g., tidal current) might also influence the distribution of PAHs (He et al., 2014; Lv et al., 2014). The lower concentrations of PAHs at S1, S2 and S3 might be due to higher tide currents with less sediment deposition than the sites located inside of the sheltered bay (S4–S11).

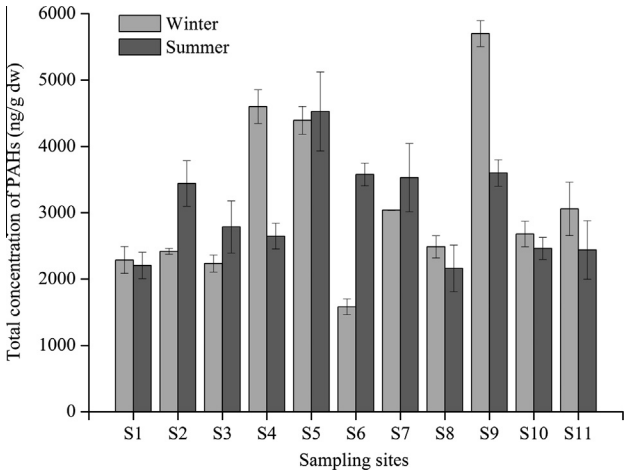

Fig. 2. Concentration of ΣPAHs at different sampling sites in winter 2013 and summer 2014 from Yangpu Bay.

Total concentrations of PAHs within 0–100, 100–1000, 1000–5000, and >5000 ng/g limits can be categorized as low, moderate, high, and very high, respectively (Baumard et al., 1998a, 1998b). According to this classification, PAHs concentration in the sediment in Yangpu Bay can be considered as high at most sites in winter and summer (1000 < ΣPAHs < 5000 ng/g), while at S9 in winter the concentration of PAHs was very high (ΣPAHs > 5000 ng/g).

A comparison of PAHs concentrations in surface sediment collected from different area around the world is shown in Table 2. The PAHs concentration in Yangpu Bay is higher than that in most other bays, e.g., Cyprus (Eastern Mediterranean) and Gorgan Bay, similar to the level in Yantai coastal area, China, but much lower than Osaka Bay, Japan, the harbor line of Mumbai, India, and Kaohsiung harbor in China. It shows that the current concentration of PAHs in the surface sediment in Yangpu Bay is relatively high in comparison with some areas in China as well as around the world.

Table 1
The concentration of 16 PAHs in the surface sediment in Yangpu Bay, China in winter and summer (ng/g dw).

PAHs	Abbreviation	Winter					Summer				
		Mean	Std.dev.	Min	Median	Max	Mean	Std.dev.	Min	Median	Max
Naphthalene	Nap	578.8	175.4	250.2	639.0	751.7	494.2	70.0	343.8	509.0	591.6
Acenaphthene	Ace	33.3	10.6	15.8	36.6	52.0	13.2	4.7	4.9	13.3	19.4
Acenaphthylene	Acy	53.4	10.9	33.1	52.6	68.7	31.2	8.5	20.4	29.2	42.7
fluorene	Flu	101.4	14.4	73.7	104.9	123.3	118.8	29.4	77.3	130.1	154.9
Phenanthrene	Phe	389.9	92.4	222.8	370.4	542.1	460.6	100.1	321.9	498.6	615.9
Anthracene	Ant	53.8	15.4	27.1	56.4	76.7	60.4	12.6	45.1	58.3	76.2
Fluoranthene	Flua	245.2	122.7	73.4	238.3	544.3	229.4	57.2	171.1	215.6	332.5
Pyrene	Pyr	339.2	123.2	128.6	313.8	537.5	352.5	99.1	212.1	339.6	527.9
Benzo[a]anthracene	BaA	175.0	120.2	44.2	136.9	390.9	199.3	65.8	109.9	185.9	333.4
Chrysene	Chy	219.8	188.7	45.0	162.6	560.7	274.5	89.6	104.9	268.3	427.4
Benzo[b]fluoranthene	BbF	207.6	162.9	57.7	174.6	533.9	128.2	76.3	46.1	109.8	318.5
Benzo[k]-fluoranthene	BkF	102.0	98.7	27.2	61.5	322.7	200.7	118.0	81.7	191.2	451.0
Benzo[a]pyrene	BaP	176.2	153.6	40.4	136.5	496.4	271.5	143.1	109.6	243.4	568.9
Indeno[1,2,3-c,d]pyrene	InP	220.4	193.7	59.7	162.7	569.0	82.0	57.5	24.4	61.8	218.0
Dibenzo[a,h]anthracene	DahA	75.3	59.3	23.8	56.0	190.8	21.8	23.7	0.0	16.3	83.3
Benzo[g,h,i]perylene	BghiP	163.5	125.4	55.1	122.7	396.5	78.3	61.1	10.4	54.1	219.7
	ΣPAHs	3134.7	1241.3	1583.2	2678.8	5701.7	3016.6	748.0	2161.8	2786.3	4527.2

Table 2
Comparison of total parent PAHs concentration (ng/g dry, wt) in surface sediment collected from different areas in the world.

Location	N*	ΣPAHs	Mean	References
Harbor line, Mumbai, India	15	17–134134	–	Dhananjayan et al. (2012)
Osaka Bay, Japan	18	6.40–7765	–	Miki et al. (2014)
Persian Gulf	16	113.50–3384.34	–	Sinaei and Mashinchian (2014)
Jinhae Bay, Korea	16	12.4–2430	208	Yim et al. (2014)
Peninsular Malaysia	15	12.3–1446	246 ± 401	Retnam et al. (2013)
Mediterranean Lagoon, Italy	16	nd–1056	208 ± 221	Acquavita et al. (2014)
Gorgan Bay, Caspian Sea	16	107.87–516.18	270.96 ± 150.47	Araghi et al. (2014)
Cyprus (Eastern Mediterranean)	16	4.9–76	–	Darılmaz et al. (2013)
Kaohsiung harbor, China	17	472–16201	5764	Chen and Chen (2011)
Yantai coastal area, China	16	450–4299	2492.9	Lang and Yang (2014)
Quanzhou Bay, China	16	9.48–108.35	39.63 ± 30.28	Yang et al. (2013)
Beibu Gulf, South China Sea	15	3.01–388	95.5	Li et al. (2014)
Yellow River Estuary	16	97.2–204.8	152.2	Hu et al. (2014)
Yangpu Bay, China (winter)	16	1583.2–5701.7	3134.7 ± 1241.3	This study
Yangpu Bay, China (summer)	16	2161.8–4527.2	3016.6 ± 748.0	This study

* *N*, number of PAH compounds.

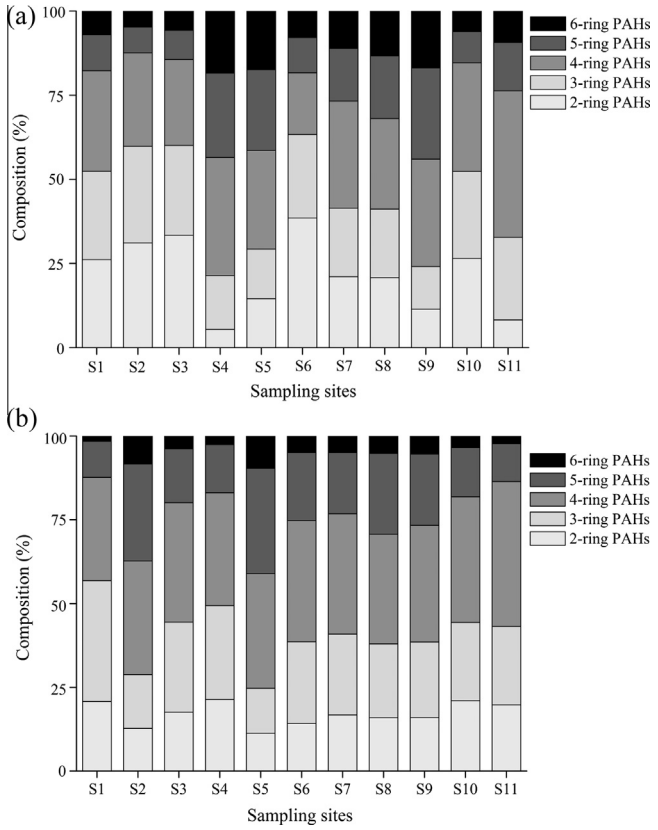

Fig. 3. The composition pattern of PAHs by ring size in the surface sediment in Yangpu Bay in winter 2013 (a) and summer 2014 (b).

The components of PAHs by ring size in the surface sediment in Yangpu Bay are shown in Fig. 3. The 4-ring PAHs were the most predominant compounds accounting for nearly 30.2% and 35.3% of the total PAHs in winter and summer, respectively. Whereas the 6-ring PAHs were the minimum compounds accounting for 10.7% and 4.7% in winter and summer, respectively. The PAHs with 2–3 rings were predominant at S1, S2, S3, S6 and S10, contributing to 52.3–63.3% of total PAHs in winter, while the other sites were abundant with 4–6 rings PAHs accounting for 58.5–78.7%. The PAHs with 4–6 rings were the most abundant one, contributing to 50.6–75.3% of total PAHs at each site, except at S1 (43.2%) in summer. Generally, PAHs with high molecular weight (4–6 ring PAHs) usually indicate a pyrogenic origin, while with low molecular weight (2–3 ring PAHs) indicate a petrogenic origin (Zhao et al., 2012). Therefore, the components of PAHs indicate that the contaminations of PAHs in the surface sediment in Yangpu Bay were probably due to a mix of petrogenic and pyrogenic origin in winter, and mostly pyrogenic origin in summer.

PAH molecular indices based on different thermodynamic stability have been widely used to identify potential PAH sources in marine environmental samples (Huang et al., 2012; He et al., 2014), such as Phe/Ant, Flua/Pyr, BaA/(BaA + Chr) and Flua/(Flua + Pyr). The ratio of Phe/Ant < 10 implies pyrolytic input, while the ratio > 10 suggests petroleum input or diagenetic input (Baumard et al., 1998a, 1998b). The Flua/Pyr ratio > 1 indicates combustion processes, while the ratio < 1 indicates a petrogenic origin. The ratio of Flua/(Flua + Pyr) < 0.4 is corresponded to petroleum pollution, from 0.4 to 0.5 indicates petroleum combustion, and higher than 0.5 suggests grass, wood or coal combustion. The ratio of BaA/(BaA + Chy) < 0.2 is attributed to petroleum, between 0.2 and 0.35 suggests petroleum combustion, and >0.35 implies pyrolytic origin (Yunker et al., 2002).

In order to identify the sources of PAHs in the surface sediment in Yangpu Bay, the ratios of Phe/Ant, Flua/Pyr, Flua/(Flua + Pry) and BaA/(BaA + Chy) were selected and plotted (Fig. 4). As shown in Fig. 4, the ratios of Phe/Ant plotted with Flua/Pyr present that most sites in Yangpu Bay were contaminated by mixed sources of pyrogenic and petrogenic PAHs in winter and summer. In detail, PAHs at S2 in summer and S9, S4 in winter were mainly originated from pyrolytic sources, while at S8 and S11 in winter and S1, S6 in summer were mainly from petrogenic sources. This kind of source is confirmed by the plot of Flua/(Flua + Pyr) and BaA/(BaA + Chy), which shows PAHs at S11 in winter were mainly from petroleum combustion, and S9 and S4 in winter and S2 in summer were probably contaminated by grass, wood or coal combustion.

In conclusion, the results from the ratio analysis show that both petrogenic and pyrogenic PAHs are dominant in surface sediments in this area. Yangpu Bay is not only an economic development area, but also an important fishing region and international transportation hub. Pyrolytic PAHs in this area may come from the heavy traffic, urban sewages and fossil fuels combustion from industrials. Petrogenic PAHs may come from oil/gas/diesel spills and oily sewage discharges.

For further exploring the possible sources of PAHs, principle component analysis and multiple linear regression (PCA/MLR) are used and the results are shown in Table 3. PCA/MLR are the most frequently used receptor models in apportionment of PAHs and quantitative assessment in environmental samples. PCA is a

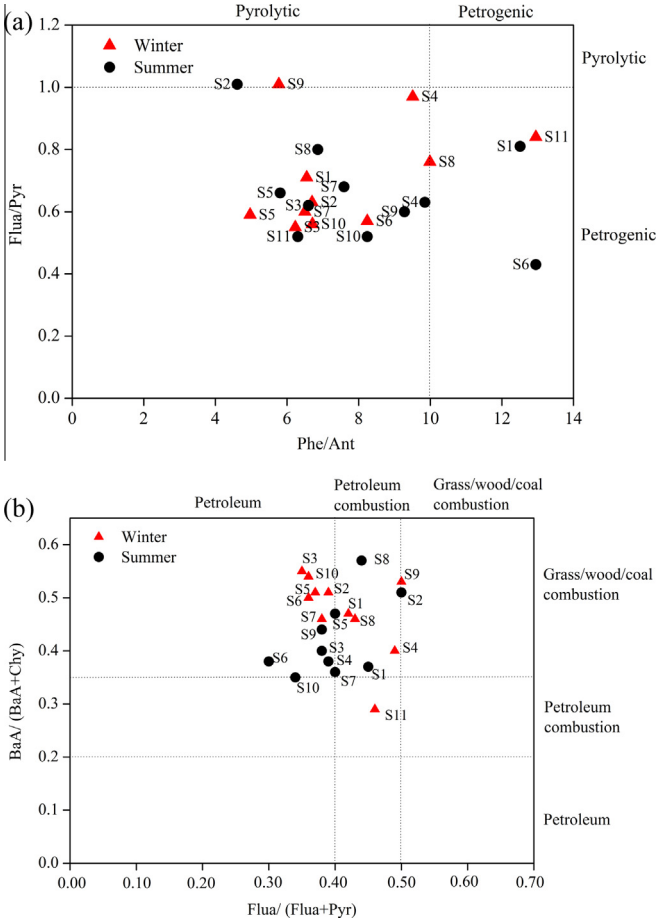

Fig. 4. Cross plots of molecular indices of Phe/Ant versus Flua/Pyr, Flua/(Flua + Pyr) versus BaA/(BaA + Chy).

statistical procedure to reduce a large number of original variables and to extract a small number of latent factors (called principal components, PCs) for analyzing relationship among the observed variables. The factor coefficients having a correlation > 0.75 are considered 'strong', those in the range of 0.74–0.50 are considered 'moderate' and 0.49–0.30 are considered 'weak' significant factor loadings (Liu et al., 2003).

In Table 3, PCA with varimax rotation revealed that three factors were extracted and the cumulative variances accounted for 95.52% and 88.61% of the total variation of PAHs in winter and summer, respectively. In winter, PC1 was responsible for 59.90% of the total variation, which was heavily loaded with 4- to 6-ring PAHs, including Flua, BaA, BbF, BkF, BaP, InP, DahA, BghiP. According to Larsen and Baker (2003), BghiP, BkF were identified as tracers for gasoline-powered engines, and InP and Pyr were found in both diesel- and gasoline-powered engines. Five or more ring PAHs has been demonstrated in the combustion of crude oil and diesel (Dobbins et al., 2006). Therefore, PC1 was inferred to indicate a vehicular combustion source of PAHs. PC2 accounted for 27.05% of the total variation heavily loaded with 3-ring PAHs of Ace, Acy and Flu. According to previous studies, Nap, Flu, Acy and Phe were the predominant profile of emissions of coke ovens, while 2–3 rings PAHs are the characteristic of the emissions from oil-burning power generation plants (Khalili et al., 1995; Larsen and Baker, 2003). Thus, PC2 suggests a source of petroleum oil product. PC3 contributed to 8.57% of the total variance with heavily loading of Phe and Chy, which indicates a source of coal combustion. The presence of Phe, Flua, Chy and Pyr were associated with coal combustion (Duval and Friedlander, 1981; Simoneit, 2002). In summer, PC1 was responsible for 54.02% of the total variance, which was also related to combustion of vehicular. PC2 accounted for 26.38% of the total variance, which was predominately weighted in Acy, Flu and Phe. This profile was indicative of petroleum oil product. PC3 was responsible for 8.21% of the total variance, which is predominately composed of Ace and Chy. It is suggested to be indicative of coal combustion.

Table 3
Component loadings of PAHs after varimax rotation for the surface sediment (high loadings >0.75 shown with bold) and relationship between ΣPAHs and PCs obtained by PCA/MLR.

PAHs	Winter			Summer		
	PC1	PC2	PC3	PC1	PC2	PC3
Nap	−0.126	0.659	−0.730	0.090	0.560	0.698
Ace	−0.105	**0.924**	−0.195	−0.202	0.291	**0.823**
Acy	−0.146	**0.850**	−0.220	0.130	**0.969**	0.077
Flu	−0.077	**0.936**	0.067	−0.085	**0.938**	0.255
Phe	0.325	0.108	**0.932**	−0.153	**0.919**	0.259
Ant	0.641	0.722	0.106	0.533	−0.211	0.324
Flua	**0.865**	0.291	0.316	**0.969**	0.020	−0.014
Pyr	0.699	0.649	0.177	0.619	0.263	0.530
BaA	**0.874**	−0.117	0.468	**0.938**	−0.062	0.295
Chy	0.472	−0.330	**0.807**	0.412	0.157	**0.835**
BbF	**0.976**	−0.031	0.196	**0.950**	0.094	0.177
BkF	**0.987**	−0.013	0.106	**0.984**	−0.049	−0.077
BaP	**0.976**	−0.050	0.199	**0.991**	−0.028	−0.069
InP	**0.967**	−0.116	0.202	**0.993**	−0.010	0.021
DahA	**0.959**	−0.150	0.202	**0.901**	0.042	0.216
BghiP	**0.979**	−0.062	0.167	**0.991**	−0.102	0.040
Eigenvalue	9.58	4.33	1.37	8.64	4.22	1.31
Variability (%)	59.90	27.05	8.57	54.02	26.38	8.21
Cumulative (%)	59.90	86.95	95.52	54.02	80.40	88.61
Estimated source	Vehicle	Petroleum	Biomass	Vehicle	Petroleum	Biomass
Standardized coefficient (β)	0.946	0.125	0.299	0.909	0.260	0.321
Standard error	0.013	0.013	0.013	0.019	0.019	0.019
t Value	78.281	10.375	24.723	48.769	13.951	17.225
Significant level (p)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Major contribution (%)	69.1	9.1	21.8	61.0	17.5	21.5

Table 4
Ecological risk assessment of PAHs in the surface sediment in Yangpu Bay.

PAHs	SQG* (ng/g)		Winter	Summer	Sites		
	ERL	ERM	ERM-q	ERM-q	<ERL	ERL-ERM	>ERM
Nap	160	2100	0.3	0.2	–	All sites	–
Ace	16	500	0.1	0.03	S4, S8	S1, S2, S3, S5, S6, S7, S9, S10, S11	–
Acy	44	640	0.1	0.05	S4, S5, S7, S8, S11	S1, S2, S3, S6, S9, S10	–
Flu	19	540	0.2	0.2	–	All sites	–
Phe	240	1500	0.3	0.3	–	All sites	–
Ant	85.3	1100	0.05	0.1	All sites	–	–
Flua	600	5100	0.05	0.04	All sites	–	–
Pyr	665	2600	0.1	0.1	All sites	–	–
BaA	261	1600	0.1	0.1	S1, S2, S3, S6, S7, S8, S10, S11	S4, S5, S9	–
Chy	384	2800	0.1	0.1	S1, S2, S3, S5, S6, S7, S8, S9, S10	S4, S11	–
BaP	430	1600	0.1	0.2	S1, S2, S3, S4, S6, S7, S8, S9, S10, S11	S5	–
InP	240	950	0.2	0.1	S1, S2, S3, S6, S7, S8, S10, S11	S4, S5, S9	–
DahA	63.4	260	0.3	0.1	S1, S2, S3, S6, S7, S8, S10, S11	S4, S5, S9	–
BghiP	85	330	0.5	0.2	S1, S3, S6, S10, S11	S2, S4, S5, S7, S8, S9	–
ΣPAHs	4022	44792	0.1	0.1	S1, S2, S3, S4, S6, S7, S8, S10, S11	S5, S9	–
m-ERM-Qs			0.17	0.13			

SQG, sediment quality guidelines.
ERL, effects range low.
ERM, effects range median.
NA, not available.
* According to Long et al. (1995) and Miki et al. (2014).

The percent contribution of different PAHs sources were quantified by MLR method. The factor scores from PCA for PC1–PC3 representing vehicle emission, petroleum product and coal combustion were used as independent variables, and the standard normalized deviate (Z) of Σ16PAHs as the dependent variables. The regression coefficients obtained by MLR were used to estimate the source mass contributions. The contribution of each PAH source in winter and summer was estimated by Eqs. (1) and (2), respectively:

$$Z = 0.946\mathrm{PC1} + 0.125\mathrm{PC2} + 0.299\mathrm{PC3}; \quad R^2 = 0.999, \quad p < 0.001 \tag{1}$$

$$Z = 0.909\mathrm{PC1} + 0.260\mathrm{PC2} + 0.321\mathrm{PC3}; \quad R^2 = 0.998, \quad p < 0.001 \tag{2}$$

The R^2 ($\geqslant 0.998$) and adjusted R^2 ($\geqslant 0.997$) values obtained in winter and summer indicate a good fit of the model. The standardized coefficients (β) of the model presented in Table 3 indicate the relative influence of the PCs to ΣPAHs. Positive β values indicate positive relationship between PCs and ΣPAHs. As shown in Table 3, vehicles have the greatest influence on the ΣPAHs as the values of β were 0.946 and 0.909 in winter and summer, respectively. Based on the results from PCA/MLR, the contributions of the PAHs sources in the surface sediment in Yangpu bay in winter and summer were calculated. The major contribution of the PAHs sources in winter came from vehicular emission (69.1%), followed by coal combustion (21.8%) and petroleum product (9.1%), while in summer the major source was vehicular emission (77.3%), followed by coal combustion (20.4%) and petroleum product (2.3%). The vehicle emission in Yangpu bay may be due to the industrialization and frequent marine transportation and fishing activities. The spill, volatilization or combustion of petroleum may be related to sewage of petrochemistry industries and shipping process. In addition, both of the molecular indices and PCA/MLR is effective for identifying the PAHs sources, and reveal that vehicle, petroleum and coal combustion as the main sources in the surface sediment.

Sediment quality guidelines (SQGs) developed on the basis of biological effects database for sediments (BEDS) are important tools for the assessment of contamination in marine and estuarine sediments (Long et al., 1995; Barhoumi et al., 2014). In order to evaluate the biological effects of the individual PAHs, the average concentrations of each PAH in winter and summer were compared with the effects range low (ERL) and the effects range medium (ERM) concentrations proposed by Long et al. (1995) and Miki et al. (2014) (Table 4). The concentrations of PAH lower than the value of ERL are considered not to be harmful to organisms, while higher than ERM value are considered to be harmful frequently, the value between ERL and ERM are considered to be harmful occasionally (Long et al., 1995). The mean ERM (m-ERM) quotients were calculated based on the ERM values to determine the likelihood of toxicity of pollutants. The m-ERM quotient value < 0.1 indicates the lowest probability (9%) of toxicity, the value between 0.11 and 0.51 implies a small degree of variability in toxicological responses, and the value from 0.51 to 1.5 indicates a medium to high probability (> 49%) of being toxic, the value > 1.5 suggests a highest probability (> 76%) of toxicity (Long et al., 2000).

As shown in Table 4, the concentrations of Nap, Flu and Phe at all sites, Ace, Acy and BghiP at most of the sites in Yangpu Bay are between the ERL and ERM, suggesting that biological effects related to these PAHs would occur occasionally. The concentrations of Ant, Flua and Pyr at all sites, BaA, Chy, BaP, InP and DahA at most of the sites are below the ERL, indicating that organisms could rarely affected by these PAHs. However, the concentrations of BaA at S4, S5 and S9, Chy at S4 and S11, Bap at S5, InP and DahA at S4, S5 and S9 could have biological effects on organisms occasionally. None of the PAHs concentration is above the ERM in Yangpu Bay. The concentrations of ΣPAHs only at S5 and S9 are above the ERL, suggesting that organisms could occasionally be affected by total PAHs at the two sites. The m-ERM-q values were 0.17 and 0.13 in winter and summer, respectively, suggesting a small degree of toxicity related to PAHs in Yangpu Bay.

To assess the marine sediment quality relative to individual PAHs contamination in Yangpu Bay, the sediment quality criteria (SQC) based on SQGs with the consideration of natural, economic, social, technical and other conditions were used. This standard contains five effect levels proposed by Macdonald et al. (1996), namely: the rate effect level (REL), threshold effect level (TEL), occasional effect level (OEL), probable effect level (PEL), frequent effect level (FEL).

Table 5 presents the criteria of marine sediment quality relative to 12 individual PAHs and identifies the sites in Yangpu Bay with the five effect levels. It is shown that the concentrations of Nap at all sites except at S11 are between the PEL and FEL, indicating

Table 5
The assessment of the surface sediment quality relative to PAHs in Yangpu Bay.

PAHs	SQC* (ng/g)					Sites					
	REL	TEL	OEL	PEL	FEL	<REL	REL-TEL	TEL-OEL	OEL-PEL	PEL-FEL	>FEL
Nap	17	34.6	120	391	1200	–	–	–	S11	S1–S9	–
Ace	3.7	6.71	21	88.9	940	–	–	S4, S8	S1, S2, S3, S5, S6, S7, S9, S10, S11	–	–
Acy	3.3	5.87	30	128	340	–	–	–	All sites	–	–
Flu	10	21.2	61	144	1200	–	–	–	All sites	–	–
Phe	23	86.7	250	544	2100	–	–	–	All sites	–	–
Ant	16	46.9	110	245	1100	–	S6, S8	S1, S2, S3, S4, S5, S7, S9, S10, S11		–	–
Flua	27	110	500	1494	4200	–	–	All sites	–	–	–
Pyr	41	153	420	1398	3800	–	–	S1, S2, S3, S4, S6, S7, S8, S10, S11	S5, S9	–	–
BaA	27	74.8	280	693	1900	–	–	S1, S2, S3, S4, S6, S7, S8, S10, S11	S5, S9	–	–
Chy	37	108	300	846	2200	–	–	S1, S2, S3, S6, S8, S10,	S4, S5, S7, S9, S11	–	–
BaP	34	88.8	230	763	1700	–	–	S1, S3, S6, S7, S8, S10, S11	S2, S4, S5, S9	–	–
DahA	3.3	6.22	43	135	200	–	–	S1, S2, S3, S6, S8, S10, S11	S4, S5, S7, S9	–	–

REL, rate effect level.
TEL, threshold effect level.
OEL, occasional effect level.
PEL, probable effect level.
FEL, frequent effect level.
NA, not available.
* According to Macdonald et al. (1996).

that Nap may have adverse effects at most of the sites. The concentrations of Acy, Flu and Phe at all sites, Ace at most of the sites are ranged from the OEL and PEL, suggesting that adverse effects of the four PAHs in the area are occasional. The concentrations of Flua at all sites, Ant, Pyr, BaA, Chy, BaP and DahA at most of the sites are between the TEL and OEL, indicating that adverse effects relative to these PAHs are unlikely. The results suggest that further assessment of the environmental risks, long-term monitoring and remediation associated with PAHs in this area are necessary.

The present study reveals that the 16 PAHs concentrations in the surface sediment in Yangpu Bay are relatively high in comparison with that in other research areas around the world. The source identification approaches found that both pyrogenic and petrogenic PAHs were dominant at many sites in winter and summer, which were probably due to the vehicle exhaust from diesel engines as well as the combustion from petrochemical industries, and petroleum sources from fuel spills, oil sewage and urban runoff. The ecotoxicological risk assessment based on international SQGs and SQC shows that the negative effects related to some PAHs (Nap, Flu, Phe, Ace, Acy and BghiP) would occur occasionally at many sites in Yangpu Bay.

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