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Research Article

Distribution, Seasonal Variations, and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in the East Lake, China

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants and their presence in urban lakes is of great concern for human and ecological health. One hundred twenty-six surface water samples and 126 surface sediment samples were collected in winter 2012 and summer 2013, respectively, to investigate distribution patterns, seasonal variations, possible pollution sources, and potential ecological risks of 16 priority PAHs in the largest urban lake, East Lake in China. The total concentrations of 16 PAHs in water and sediment ranged from 10.2 to 525.1 ng L^{-1} and 10.9 to 2478.1 ng g^{-1} dry weight, respectively. The concentrations of $\sum$PAHs in sediment samples in summer were almost two times greater than those in winter, but the seasonal variations did not differ significantly in the water samples. Diagnostic ratios of indicator PAHs reflected a possibility of pyrolytic PAH input in sediment and a mixture of petroleum and combustion sources in water from the East Lake. The potential ecological risk assessment based on the risk quotient indicated relatively moderate ecological risks of PAHs in the East Lake.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are neutral, nonpolar organic contaminants that built from two or more benzene rings, which originate primarily from both natural and anthropogenic sources and the latter are by far the major contributors [1, 2]. Volcanic eruptions and forest fires are the major natural sources, while fossil fuel combustion, waste incineration, petroleum refining, coke and asphalt production, road runoff, and many other industrial activities have been identified as the important anthropogenic sources of PAHs [3, 4]. Due to their toxicity, carcinogenicity and mutagenicity, the European Community and the United States Environmental Protection Agency have listed 16

PAHs as priority pollutants [5]. Among them, two- and three-ring PAHs are less mutagenic, while four- to six-ring PAHs are highly carcinogenic and mutagenic [6].

PAHs are ubiquitous pollutants in the environment that can be introduced into aquatic environments through oil leakage, surface runoff, atmospheric deposition, and industrial effluents, etc. [7]. Because of their high partition coefficients, PAHs tend to associate with particles, which may finally accumulate in the sediments. Under certain conditions, the bound PAHs can be resuspended from the sediment to water [8]. Once entering into the water they may bioaccumulate in aquatic organisms owing to their low solubility and high lipophilicity, which would cause both acute and chronic effects in aquatic plants, fish, waterfowls, and other mammals that feed on aquatic organisms [9]. As rivers, lakes, and reservoirs are frequently used for potable water sources, their contamination is particularly undesirable [1]. Therefore, investigations of PAHs in aquatic environments are imperative, which are important to understand the status of contamination and evaluate the potential risk to the ecosystem.

The East Lake (30°33′ N, 114°23′ E) located in the northeast of Wuhan, the largest city in central China. The lake is the largest urban lake in China, covers an area of 33.7 km^2 and has a mean depth of 2.8 m with a maximum depth of 4.75 m. A number of roadway dikes have been constructed across the lake and divide it into several lakelets. Many industrial plants, such as cement plants, foundries, coal gasification, and coking plants, have been built around the lake. In addition, aquacultural and tourism activities have been rapidly expanded around the East Lake in the past three decades, which would potentially cause pollution [10]. However,

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Abbreviations: **Ace**, acenaphthene; **Acy**, acenaphthylene; **Ant**, anthracene; **BaA**, benzo[*a*]anthracene; **BaP**, benzo[*a*]pyrene; **BbF**, benzo[*b*]fluoranthene; **BghiP**, benzo[*g,h,i*]perylene; **BkF**, benzo[*k*]fluoranthene; **Chr**, chrysene; **DahA**, dibenz[*a,h*]anthracene; **dw**, dry weight; **Fla**, fluoranthene; **Flr**, fluorine; **GC-MS**, GC equipped with mass spectrometry; **GPS**, global position system; **HMW**, high molecular weight; **InP**, indeno[1,2,3-*cd*]pyrene; **LMW**, low molecular weight; **MDL**, method detection limit; **MPC**, maximum permissible concentration; **NA**, not available; **Nap**, naphthalene; **NC**, negligible concentration; **nd**, not detected; **PAH**, polycyclic aromatic hydrocarbon; **PCNB**, pentachloronitrobenzene; **Phe**, phenanthrene; **Pyr**, pyrene; **RQ**, risk quotient; **RSD**, relative standard deviation; **SD**, standard deviation; **TCmX**, 2,4,5,6-tetrachloro-*m*-xylene; **TEF**, toxic equivalency factor; **TOC**, total organic carbon

systematic studies of the distribution of PAHs in the East Lake have not been undertaken yet. Therefore, the main purpose of the present study was to determine the concentrations, distribution, and seasonal variations in surface water and sediment from the East Lake. Diagnostic ratios of indicator PAHs are applied to analyze possible sources in the aquatic environments. In addition, potential ecological risks of PAHs in the East Lake were assessed to provide important information for lake management.

2 Materials and methods

2.1 Standards and reagents

Reference PAHs (each at $500 \mu g \, mL^{-1}$) were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flr), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno-[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP), which were obtained from AccuStandard (AccuStandard, USA). The recovery surrogate and internal standard were 2,4,5,6-tetrachloro-m-xylene (TCmX) and pentachloronitrobenzene (PCNB), which were purchased from Ultra Scientific (North Kingstown, RI, USA). They were diluted to concentrations of working standard solutions with n-hexane to prepare calibration standards for gas chromatography equipped with mass spectrometry (GC-MS).

Other organic-solvents, including dichloromethane, n-hexane and acetone, were GC-MS grade (Fisher Scientific, USA). Florisil (60−100 mesh) and neutral silica gel (100−200 mesh) were activated in a drying oven at 150°C for 10 h and 180°C for 4 h, respectively. Anhydrous sodium sulfate was baked at 450°C for 4 h before use.

2.2 Sample collection and preparation

One hundred twenty-six surface water samples and 126 surface sediment samples were collected at 42 sampling sites in winter (November and December) 2012 and summer (May and June) 2013, respectively from five main lakelets of the East Lake: Guandu, Guozheng, Tangling, Niuchao and Houhu (Fig. 1). Each site was marked and located with the help of global position system (GPS). Water samples were collected in pre-cleaned glass bottles and sediment samples were collected with a grab sampler in polytetrafluoroethylene bags. All samples were transported immediately to the laboratory in Wuhan Botanical Garden, Chinese Academy of Sciences, China. In the laboratory, water samples were filtrated under vacuum through 0.45 μm glass fiber filters (Millipore) and stored at 4°C before extraction. Sediment samples were freeze-dried with a freeze-drier, sieved through 60-mesh nylon sieve and stored at −20°C before extraction.

2.3 Sample extraction, cleanup, and analysis

A liquid−liquid extraction method was used to extract the water samples. A 1 L water sample with a known amount of TCmX as a surrogate in a separatory funnel with Teflon stopcocks and stoppers was extracted with 40 mL dichloromethane three times. The combined extracts were passed through anhydrous sodium sulfate and then concentrated with a rotary evaporator to approximately 5 mL, followed by column cleanup. A column (8 mm id) was packed with 4 g neutral alumina, 4 g neutral silica and 2 g anhydrous sodium sulfate from the bottom to the top. The column was eluted with 20 mL of a mixture of dichloromethane and hexane (1:1, v/v). The eluent was concentrated to 100 μL under a gentle high purity nitrogen stream for analysis.

Sediment samples were extracted according to matrix solid-phase dispersion method [11]. One gram of sediment samples was blended thoroughly with a specific amount of TCmX and 3 g C$_{18}$ (Silicycle, Canada) as dispersion sorbent in a glass mortar using a glass pestle for 5 min to obtain a homogeneous mixture. The mixture was transferred into a polyethylene syringe barrel-column (10 mL) which contained a membrane filter (0.22 μm). The column was packed with 1 g anhydrous sodium sulfate, 1 g Florisil, 1 g neutral silica gel, and 2 g activated copper powder from the bottom to top. Another membrane filter was placed on top of the column after the column was packed. Elution was made by gravity flow with 20 mL of dichloromethane. The eluent was concentrated with a gentle stream of high purity nitrogen followed by addition of internal standard (PCNB) and adjusted to 100 μL for GC-MS analysis.

All samples were analyzed on an Agilent 5975 GC-MSD (Agilent, USA). The column was a HP-5 (Agilent, 30 m × 0.25 mm id × 0.25 μm) capillary column and was used for the separation of the analytes.
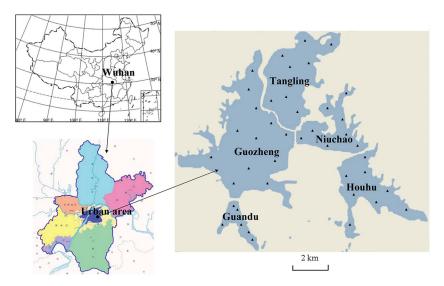

Figure 1. Locations of the sampling sites in the East Lake, China.

The carrier gas was high purity helium gas set at a constant flow rate of 0.8 mL/min. Samples (1 μL) were injected in splitless mode and the injector temperature was 250°C. The column temperature started at 50°C for 3 min, increased to 200°C at a rate of 10°C/min, followed by a rate of 5°C/min until 280°C and held for 10 min. All data were acquired and processed with Chemstation software (Agilent, USA).

The total organic carbon (TOC) contents of sediments were analyzed with the Shimadzu TOC analyzer (Shimadzu, Japan) with the solid sample model (SSM-5000A).

2.4 Ecological risk assessment

Based on the negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) of PAHs in water and sediment, the risk quotient (RQ) approach was used to assess the potential ecological risk of PAHs in the water and sediment from the East Lake [12]. The RQ_{NCs} and RQ_{MPCs} were calculated as follows:

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV(NCs)}} \tag{1}$$

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV(MPCs)}} \tag{2}$$

where C_{PAHs} was the detected concentration of certain PAH in water and sediment samples, and $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ were the quality values of the NCs and MPCs of PAHs in water and sediment, respectively. To solve the problem of ecological risk for the other six individual PAHs using the RQ method, toxic equivalency factors (TEFs) of PAHs were used to infer NCs and MPCs of Acy, Ace, Flr, Pyr, BbF, and DahA [13, 14]. The toxicity of Acy, Ace, Flr, and Pyr was equal to Phe or Nap, BbF equal to BaA, and DahA equal to BaP. Furthermore, $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ were calculated as follows:

$$RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{16} RQ_{i(NCs)} \qquad (RQ_{i(NCs)} \geq 1) \tag{3}$$

$$RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{16} RQ_{i(MPCs)} \qquad (RQ_{i(MPCs)} \geq 1) \tag{4}$$

2.5 Quality assurance and quality control

All analytical procedures were monitored with strict quality assurance and control measures. The instruments were calibrated daily with calibration standards. Average PAHs recoveries and relative standard deviation (RSDs) were first obtained to evaluate the method performance by multiple analyses of ten samples spiked with PAHs standard. A solvent blank and matrix blank were analyzed through the entire procedure prior to and after every 10 samples. The limits of detection of PAHs were defined as three times of the signal-to-noise ratio (S/N). The RSDs for the method were <15%. The recoveries ranged from 78 ± 9 to 116 ± 8% for water samples and ranged from 81 ± 7 to 108 ± 10% for sediment samples. The concentrations of all sediment samples were calculated with respect to the dry weight (dw).

2.6 Statistical analysis

The total PAHs in water and sediment samples were tested for their seasonal variations using SPSS for statistical process (SPSS, USA).

Independent samples t-test was used to compare the difference of total PAHs in water and sediment samples between winter and summer, respectively. The level of statistical significance was defined at $p < 0.05$. The concentrations of compounds that were not detected were replaced as zero for statistical analyses and risk calculations. As for sources analysis, the sampling sites were excluded when Ant, Phe, Fla, or Pyr were not detected.

3 Results and discussion

3.1 Occurrence levels of PAHs

Table 1 shows the method detection limits, concentration ranges, mean values, and standard deviations in surface water in winter and summer from the East Lake. The total concentrations of PAHs in water ranged from 10.2 to 525.1 ng L^{-1} from all sampling sites. It could be seen from Tab 1 that PAHs were present in the majority of the water samples. Nap was observed to have the highest concentration (23.6 ng L^{-1}), followed by BbF, Phe, and BkF, with concentrations of 14.5, 13.8, and 13.6 ng L^{-1}, respectively. The concentration of Nap in water was more than the other PAHs, possibly due to its higher solubility, vapor pressure and input. Total concentrations of potential carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, InP, and DahA) ranged from 42 to 138.7 ng L^{-1} with the mean value of 59.4 ng L^{-1} in winter and ranged from 4.1 to 116.4 ng L^{-1} with the mean value of 13.3 ng L^{-1} in summer, accounting for 59 and 15%, respectively, of the average concentration of $\sum$PAHs. The average concentration of BaP was 0.8 ng L^{-1} which was less compared with the environmental quality standard for surface water of China (2.8 ng L^{-1}, GB3838-2002, China).

Table 2 illustrates the concentrations of PAHs in sediment samples from the East Lake in winter and summer. The concentrations of $\sum$PAHs ranged from 10.9 to 2478.1 ng g^{-1} dw with a mean value of 685.8 ng g^{-1}. BkF was observed to have the highest concentration (101.2 ng g^{-1}), followed by Phe, Ant, and BbF, with concentrations of 98.5, 84.8, and 80.1 ng g^{-1}, respectively. Total concentrations of potential carcinogenic seven PAHs ranged from 8.3 to 531.9 ng g^{-1}

Table 1. Concentrations of PAHs (ng L^{-1}) in surface water of the East Lake

PAHs	MDLs	Winter (2012)			Summer (2013)		
		Range	Mean	SD	Range	Mean	SD
Nap	1.3	nd−108.2	30.1	25.4	nd−92.8	17.1	24
Acy	0.93	nd−3.6	0.2	0.8	nd	NA	0
Ace	0.56	nd−27.5	2.5	6.4	nd−4.3	0.3	0.9
Flr	0.49	nd−19.8	4.6	5.5	nd−24.8	3.8	5.1
Phe	0.8	nd−12.1	1	2.7	nd−137.3	26.6	27.8
Ant	0.29	nd−8.3	0.4	1.5	1.1−32.7	1.5	6.6
Fla	0.37	nd−37.3	2.5	7.5	1.6−81.6	11.1	12.8
Pyr	0.3	nd−8.5	0.3	1.3	1.2−55.1	9.2	9.8
BaA	0.28	0.9−31.7	3.5	5.6	2.4−16.2	4.4	2.4
Chr	0.66	nd−28.2	2	5	1.7−38	4.6	5.6
BbF	0.92	20.7−51.6	27.3	5.5	nd−28	1.7	4.6
BkF	0.74	21.1−51.7	25.5	5.5	nd−28.2	1.8	4.7
BaP	0.86	nd−33.1	1	5.1	nd−9.0	0.6	1.8
InP	1.2	nd−3.4	0.1	0.5	nd−3.9	0.1	0.6
DahA	1.64	nd	NA	0	nd	NA	0
BghiP	1.5	nd−2.7	0.2	0.7	nd−6.4	0.2	1
$\sum$PAHs		42−214.1	101	39.9	10.2−525.1	86.4	87.8

Table 2. Concentrations of PAHs (ng g^{-1} dw) in surface sediments of the East Lake

PAHs	MDLs	Winter (2012)			Summer (2013)		
		Range	Mean	SD	Range	Mean	SD
Nap	0.32	nd–59.9	22.7	18	nd–135	41.9	33.5
Acy	0.04	nd–1	0.02	0.2	nd–12.1	1.8	2.9
Ace	0.12	nd–13.4	1.2	2.5	nd–17	5	4.4
Flr	0.24	nd–44	8.2	15.8	nd–94.7	31.1	24.7
Phe	0.18	nd–134.6	82.4	35	nd–286.9	114.5	55.8
Ant	0.01	0.1–133.6	78.7	36	nd–283.8	90.8	67.5
Fla	0.15	nd–96.9	50.2	24.7	nd–254.2	79.2	62.8
Pyr	0.26	nd–85.5	22.2	26	nd–219.8	42.5	53.5
BaA	0.14	2.2–45.4	18.5	14.3	2–151.2	39.3	31
Chr	0.08	1.7–83.7	32.7	25.6	1.3–259.2	64.6	53.5
BbF	0.3	1.8–124.6	44.3	38.4	2.7–338.7	115.8	75.4
BkF	0.28	1.1–199.3	77.3	45.1	2–376.2	125	83.4
BaP	0.35	nd–93.3	36.2	22.5	1.6–183.7	61.6	42.3
InP	0.21	0.9–14.6	4.6	3.1	0.9–139.9	23.7	30.1
DahA	0.16	0.5–23.9	5.7	5.8	0.5–94	10.8	18.5
BghiP	0.02	nd–0.7	0.1	0.2	nd–190.2	39.2	48.6
$\sum$PAHs		16–932.6	484.8	229.1	10.9–2478.1	886.7	526.3

with the mean value of 219.2 ng g^{-1} in winter and ranged from 10.9 to 1321.6 ng g^{-1} with the mean value of 440.7 ng g^{-1} in summer, accounting for 45 and 50%, respectively, of the average concentration of $\sum$PAHs. The hydrophobic organic compounds were generally much related to the sediments organic carbon contents [15, 16]. The TOC of sediments from the East Lake ranged from 1.84 to 7.74%. However, no correlations were found between PAH concentration and TOC ($p < 0.05$). With PAHs concentrations influenced by the import of pollution sources and sediments derived from different locations. In addition, sediment and water in the East Lake undergo dynamic adsorption and desorption, which makes it difficult to achieve adsorption equilibrium among all sediments. Therefore, it is not surprising that there is no obvious correlation between PAH concentration and TOC. A similar phenomenon was also observed in the Qiantang River, China [17] and Lake Thun, Switzerland [18].

PAHs pollution of surface water and sediment has been well documented around the world in recent years (Tab 3). The results demonstrated that the level of PAHs in water from the East Lake was higher than the Seine River, France [19], but much lower than the Great Bitter Lake, Egypt [21] and the Yangtze River, China [15]. The total PAH concentrations in water from the East Lake were similar to those found in the Luan River, China [13]. It is obvious that PAHs concentration in water from the East Lake is not very high. The concentration of PAHs in sediment from the East Lake was higher than Todos Santos Bay, Mexico [24] and Luan River, China [13], although the concentration of PAHs in water was similar to the Luan River. However, the level of sediment by PAH in the East Lake was substantially lower than Eire Lake [23] and Yangtze River, China [15].

3.2 PAHs distribution and seasonal variations

Figure 2 shows the profiles of $\sum$PAHs in water and sediment among different sampling sites in winter and summer from the East Lake. The seasonal variation of PAHs was obvious in sediment and the

Table 3. Concentration ranges and mean values of PAHs in water and sediment collected from different locations

Medium	Location	$\sum$PAHs (ng L^{-1}, ng g^{-1})[a]		Reference
		Range	Mean	
Water	Seine River, France	4–36	20	[19]
	St. Lawrence River, Canada	109–1131	326	[20]
	Great Bitter Lake, Egypt	280–39 570	12 380	[21]
	Yangtze River, China	321.8–6234.9	2095.2	[15]
	Qiantang River, China	70.3–1844.4	283.3	[17]
	Luan River, China	37.3–234	99.4	[13]
	Lake Chaohu, China	95.2–370.1	181.5	[22]
	East Lake, China	10.2–525.1	93.7	This study
Sediment	Eire Lake	224–5304	2088	[23]
	Todos Santos Bay, Mexico	7.6–813	96	[24]
	Kyeonggi Bay, Korea	9.1–1400	120	[25]
	Yangtze River, China	72.4–3995.2	1334.5	[15]
	Qiantang River, China	91.3–614.4	313.3	[17]
	Luan River, China	20.9–287	115.3	[13]
	Lake Chaohu, China	60.8–10 200	1230	[26]
	East Lake, China	10.9–2478.1	685.8	This study

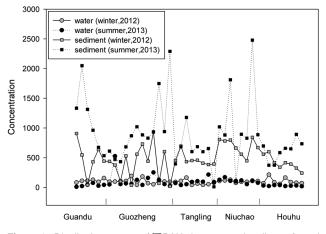[a] Unit: ng L^{-1} for water samples and ng g^{-1} for sediment samples.

Figure 2. Distribution pattern of $\sum$PAHs in water and sediment from the East Lake.

concentrations of PAHs in 86% of the sampling sites were higher in summer than in winter. The sediment concentrations of $\sum$PAHs in summer were almost two times greater than those in winter ($p = 0.000$). The difference of $\sum$PAHs in water samples between winter and summer were compared by independent samples t-test. The probabilities (p-value of two-tailed significance) for $\sum$PAHs between winter and summer were 0.328, >0.05, indicating $\sum$PAHs in water samples were not much different in winter and summer.

For the five lakelets, the maximum PAH level in water was found in Guozheng Lake (116.2 ng L^{-1}), followed by Niuchao Lake (107 ng L^{-1}) and Tangling Lake (88 ng L^{-1}), whereas the maximum PAH level in

sediment was found in Niuchao Lake (903.6 ng g^{-1}), followed by Guandu Lake (822.6 ng g^{-1}) and Guozheng Lake (689.3 ng g^{-1}). These lakelets are located in a more industrialized and urbanized region and used to tourism, the PAHs were probably related to sewage outfalls, discharged wastewater and urban runoffs. In addition, there were lots of boats traveling in these lakelets, which may contribute to the higher concentrations of PAHs. Houhu Lake was observed to have the lowest levels of PAHs in both water and sediment, which was agreed with the status that the lake was used to fishery.

The mean compositional profiles of PAHs by ring size are shown in Fig. 3, which showed that the most abundant ring in winter were five-rings followed by two-ring PAHs, and three-ring PAHs are the most abundant PAHs in summer, followed by 2-ring PAHs. In sediment samples, three- and five-ring PAHs were the most abundant both in winter and summer. On the whole, high molecular weight PAHs (HMW, 4- to 6-ring PAHs) predominated in sediment samples, accounting for 60 and 68% in winter and summer, respectively. PAHs composition in sediment from the East Lake was consistent with the typical PAHs composition in other studies [27, 28]. This may be because HMW PAHs are resistant to degradation and more easily adsorbed in sediment. In comparison, water samples were dominated by low molecular weight PAHs (LMW, two- and three-ring PAHs) in summer but abundant with HMW PAHs in winter. This can be explained by different input sources in winter and summer due to water receives direct PAHs input from various sources.

3.3 Analysis for sources of PAHs

The sources of PAHs are mainly from anthropogenic PAHs, mainly derived from two mechanisms: discharged crude oil or its products
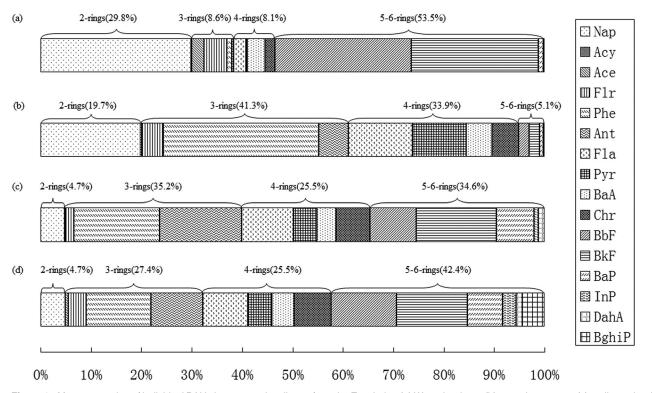

Figure 3. Mean proportion of individual PAHs in water and sediment from the East Lake. (a) Water in winter, (b) water in summer, (c) sediment in winter, and (d) sediment in summer.

(petrogenic) and combustion of organic matter (pyrolytic) [29]. Indicator PAHs molecular ratios were used to distinguish these various origins, such as Fla/Pyr, Phe/Ant, Chr/BaA, Pyr/BaP, and Nap/Fla [30–33]. Among these molecular ratios, Fla/(Fla + Pyr) and Ant/(Ant + Phe) are more widely used. A ratio <0.4 indicates pollutants mainly from petroleum, 0.4 < the ratio <0.5 indicates mainly from liquid fossil fuel combustion such as vehicle and crude oil, while the ratio >0.5 indicates mainly from combustion of grass, wood, and coal [30, 34]. In addition, the ratio of Ant/(Ant + Phe) <0.1 indicates mainly from petroleum contamination, whereas Ant/(Ant + Phe) >0.1 indicates mainly from combustion sources [35, 36].

In the present study, the ratios of Ant/(Ant + Phe) for the sediment ranged from 0.01 to 0.58 and 89.6% and the ratios of Ant/(Ant + Phe) were >0.1, clearly indicating combustion as the source in sediment. Ratios of Fla/(Fla + Pyr) were >0.4 with an average of 0.69, suggesting that combustion of grass, wood, and coal may be potential pollution sources of PAHs in sediment from the East Lake. However, the ratios of Ant/(Ant + Phe) in water samples ranged from 0.05 to 0.75 and

51.2% of the ratios of Ant/(Ant + Phe) were <0.1, proving petroleum source as one of the PAH sources accounts for a considerable proportion, reflecting its emission such as the lots of boats traveling in the lake. Ratios of Fla/(Fla + Pyr) were between 0.29 and 0.61 and 85.4% of the ratios of Fla/(Fla + Pyr) were >0.5, indicating that the sources of PAHs in water could be combustion of organic matter. As a whole, the results from PAHs cross-plots for Ant/(Ant + Phe) versus Fla/(Fla + Pyr; Fig. 4) showed that sediment from the East Lake were mainly contaminated by pyrolytic PAHs from the incomplete combustion of fossil fuels. In addition, the results showed the signature of a mixture containing petroleum and combustion sources in water from the East Lake.

3.4 Potential ecological risk assessment

The mean values of RQ_{NCs} and RQ_{MPCs} in water and sediment are listed in Tab 4. The suggested risk classification of individual PAHs and $\sum$PAHs is listed in Tab 5. In general, risk free indicates the risk
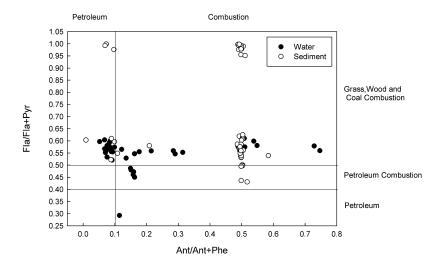

Figure 4. Ratios for Ant/(Ant + Phe) vs. Fla/(Fla + Pyr) in water and sediment from the East Lake.

Table 4. Mean risk quotients of PAHs in water and sediment from the East Lake

PAHs	TEFs	Water (ng L^{-1})		Sediment (ng g^{-1})		Water		Sediment	
		NCs	MPCs	NCs	MPCs	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}
Nap	0.001	12	1200	1.4	140	2	0	23.1	0.2
Acy[a]	0.001	3	300	1.4	140	0	0	0.6	0
Ace[a]	0.001	3	300	1.4	140	0.5	0	2.2	0
Flr[a]	0.001	3	300	1.4	140	1.4	0	14	0.1
Phe	0.001	3	300	5.1	510	4.6	0	19.3	0.2
Ant	0.01	0.7	70	1.2	120	3.9	0	70.7	0.7
Fla	0.001	3	300	26	2600	2.3	0	2.5	0
Pyr[a]	0.001	3	300	1.4	140	1.6	0	23.1	0.2
BaA	0.1	0.1	10	3.6	360	40	0.4	8	0.1
Chr	0.01	3.4	340	107	10 700	1	0	0.5	0
BbF[a]	0.1	0.1	10	3.6	360	145	1.5	22.2	0.2
BkF	0.1	0.4	40	24	2400	34	0.3	4.2	0
BaP	1	0.5	50	27	2700	1.6	0	1.8	0
InP	0.1	0.4	40	59	5900	0.3	0	0.2	0
DahA[a]	1	0.5	50	27	2700	0	0	0.3	0
BghiP	0.01	0.3	30	75	7500	0.7	0	0.3	0

[a] NCs and MPCs of six PAHs were inferred (values of Acy, Ace, Flr, and Pyr = value of Phe (water)/Nap (sediment), value of BbF = value of BaA, value of DahA = value of BaP).

Table 5. Risk classification of individual PAHs and $\sum$PAHs

Individual PAHs			$\sum$PAHs		
	RQ_{NCs}	RQ_{MPCs}		$RQ_{\sum PAHs(NCs)}$	$RQ_{\sum PAHs(MPCs)}$
Risk free	<1	<1	Risk free	<1	<1
			Low risk	≥1; <800	<1
Moderate risk	≥1	<1	Moderate risk-I	≥800	<1
			Moderate risk-II	<800	≥1
High risk	≥1	≥1	High risk	≥800	≥1.0

might be negligible. Moderate risk indicates a moderate degree of contamination which needs monitoring and remedial actions. While high risk suggests that the contamination of PAHs would be severe and strict management measures and remedial actions must be taken at once.

It could be observed from Tab 4 that in water samples the RQ_{MPCs} of individual PAHs were all <1 except for BbF, which indicated that certain ecological risk might be caused to aquatic organisms by BbF. The mean values of RQ_{NCs} of Acy, InP, DahA, and BghiP in water and sediment were all <1, indicating these compounds caused risk might be negligible. Nap, Flr, Phe, Ant, Fla, Pyr, BaA, BkF, and BaP showed moderate ecological risk in both water and sediment. Chr showed moderate ecological risk in water but could be negligible in sediment; Ace showed moderate ecological risk in sediment but could be negligible in water. It is noteworthy that BaA, BbF, and BkF are of particular concern due to their carcinogenicity.

Comparing Fig. 5 with Fig. 3, it can be seen that the value of composition of LMW PAHs in water samples in summer is higher, while the value of RQ_{NCs} of HMW PAHs in winter is higher. Four- and

five-ring PAHs account for a higher proportion of RQ_{NCs} of PAHs in water, while three- and four-ring PAHs presented higher ecological risk in sediment from the East Lake. Therefore, remedial actions and management must be taken to decrease the concentrations of three-, four-, and five-ring PAHs.

For all sampling sites, RQ_{MPCs} of $\sum$PAHs in sediment in winter and summer were >1 accounting for 5 and 26%, respectively, and RQ_{NCs} of $\sum$PAHs were all <800. This result indicated that the ecological risk of $\sum$PAHs was moderate risk-II at these sampling sites and the other sampling area was low. However, RQ_{MPCs} of $\sum$PAHs in water in winter were all >1, indicating that the $\sum$PAHs in winter of the East Lake resulted in moderate risk-II, while in summer the RQ_{MPCs} of $\sum$PAHs was only at one sampling site >1, suggesting the ecological risk in water in summer was low. Comparing Fig. 6 with Fig. 2, it can be seen that due to different compositions of PAHs in different sampling sites in winter and summer lead to the seasonal changes of ecological risk in the East Lake. Although $\sum$PAHs in water samples were not much different between winter and summer, the mean ecological risk in winter was four times more than that in summer.
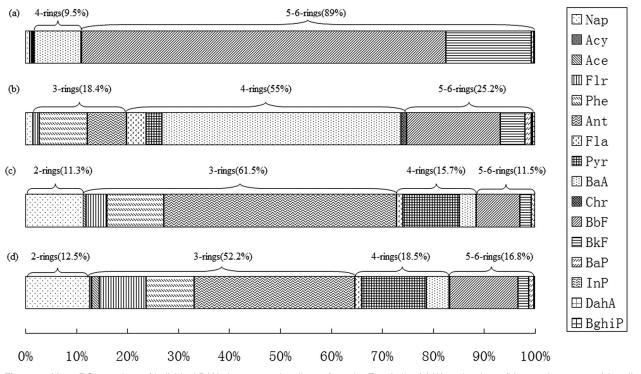

Figure 5. Mean RQ_{NCs} values of individual PAHs in water and sediment from the East Lake. (a) Water in winter, (b) water in summer, (c) sediment in winter and (d) sediment in summer.
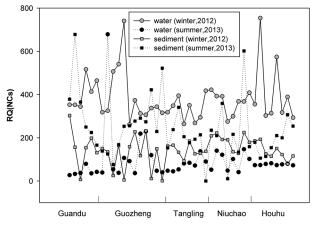
Figure 6. RQNCs of $\sum$PAHs ($RQ_{\sum PAHs(NCs)}$) in water and sediment from the East Lake.

4 Concluding remarks

The residues of 16 PAHs detected in surface water and surface sediment collected from the East Lake, China, indicated a wide occurrence of PAHs in this study area. In water samples, the most abundant rings in winter were five- and two-ring PAHs, while three- and two-ring PAHs were the most abundant PAHs in summer. In sediment samples, three- and five-ring PAHs were the most abundant both in winter and summer. The concentrations of $\sum$PAHs in sediment samples in summer were almost two times greater than those in winter, but the seasonal variations were not much different in water samples. The molecular ratios of Ant/(Ant + Phe) and Fla/(Fla + Pyr) showed that pyrolytic PAHs from incomplete combustion of fossil fuels predominated in sediment and mixture sources of pyrolytic and petrogenic in water from the East Lake. The RQ_{NCs} and RQ_{MPCs} values indicated relatively moderate ecological risks of PAHs in the East Lake. Although $\sum$PAHs in water samples were not much different between winter and summer, the mean ecological risk in winter was four times more than that in summer. Therefore, management strategies should be taken to protect the water ecosystem of the East Lake.

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