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RESEARCH ARTICLE

Distribution, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in surface sediments from the Haihe River, a typical polluted urban river in Northern China

Xiao Qian[1] · Baocui Liang[1] · Xuan Liu[2] · Xinhui Liu[1] · Juan Wang[1] · Fei Liu[1] · Baoshan Cui[1]

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Abstract The distribution, sources, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) were investigated in surface sediments from the Haihe River. Total PAH concentrations varied from 171.4 to 9511.2 ng g^{-1} with an average of 2125.4 ng g^{-1}, suggesting serious pollution of the Haihe River in comparison with other reported rivers worldwide. PAH contaminants differed significantly among 17 sampling locations with high values occurring in industrial areas and densely populated areas. The composition of PAHs was characterized by high abundance of 4-ring and 5-ring PAHs, and benzo[a]anthracene, chrysene, and benzo[a]pyrene were the predominant components. Molecular diagnostic ratios have confirmed that PAHs in Haihe River sediments resulted from mixed sources, primarily including various combustion processes. Ecological risk assessment using the Sediments Quality Guidelines indicated that PAHs in sediments could cause certain negative effects on aquatic organisms in most survey regions.

Keywords Polycyclic aromatic hydrocarbons · Sediments · Urban river · Source identification · Ecological risk assessment

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✉ Xinhui Liu
xhliu@bnu.edu.cn

[1] State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Beijing Normal University, Beijing 100875, People's Republic of China

[2] Département Génie Mathématique, Institut National des Sciences Appliquées de Rouen, Normandie, France

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons composed of two or more fused benzene rings. As one of the most important classes of persistent organic pollutants, PAH compounds are ubiquitous in the environment and originate from both natural processes and anthropogenic activities (Elie et al. 2013). Due to their carcinogenic, teratogenic, mutagenic, and other properties such as bioaccumulation and biomagnification (Xu et al. 2013; Lau et al. 2014; Liu et al. 2015a), 16 of them have been listed as priority pollutants by United States Environmental Protection Agency (US EPA) (Gu et al. 2016). PAHs can be generated continuously during the processes of utilizing carbonaceous materials such as coal, petroleum, and wood (Zhang and Tao 2008; Dong et al. 2013). Hundreds of thousands of tons of PAHs are released into the environment worldwide each year and difficult to be eliminated completely (Zhang and Tao 2009). Consequently, PAHs are still of significant concern with high detection rates at present.

Urban river system, a special ecosystem around cities, has important landscape values and ecological functions and is deeply impacted by human activities. With increasing urbanization and industrialization, the environmental quality in cities has been deteriorating seriously (Guo et al. 2011). Large amounts of contaminants such as nutrients, heavy metals, antibiotics, surfactants, and toxic organic compounds are discharged into urban rivers, resulting in serious ecological hazards (Bao et al. 2010; Li et al. 2011; Islam et al. 2015; Xu et al. 2016). PAHs in urban areas are mainly from anthropogenic activities such as domestic heating, industrial emission, traffic-related fuel combustion, electrical power generation, and waste incineration (Ma et al. 2010; Liu et al. 2012). Then they can be emitted into urban rivers through multiple ways of wastewater discharge, atmospheric deposition, oil

spillage, and stormwater runoff. When entering into urban river environment, due to the high hydrophobicity (log K_{ow} from 3.37 to 6.75), PAHs are easily adsorbed on particulate matters and finally deposited into the sediments (Neff and Burns 1996; Hussain et al. 2015; Wang et al. 2016). Under proper conditions, sedimentary PAHs will remobilize into the overlying water and further threaten urban river ecosystem and even human health through food chains (An et al. 2016). That is, sediments can act as both a sink and a source of PAHs in urban rivers.

Tianjin is situated on the north of China. It is one most economically advanced city in China with an area about 11,946 km^2 and a population of 15 million. Its urban areas have been heavily polluted by the development of industry and the expansion of urban scale. Industry, traffic, and residents living are the primary pollution reasons. However in the suburban areas, agriculture is the major land-use type and causes pollution (Gong et al. 2004). The Haihe River flows through the Tianjin District, gathers several branch streams, and finally empties into the Bohai Bay. It receives domestic, industrial, and agricultural pollutants not only from Tianjin but also the surrounding Beijing and Hebei Province. As a result, the Haihe River has become a seriously polluted river with high loads of environmental pollutants (Cao et al. 2005). Levels of pollutants in surface sediments can reflect the current pollution status. Many studies have been focused on the occurrence and environmental fate of PAHs in surface sediments from various aquatic environments, such as lakes (Yuan et al. 2016), rivers (Deng et al. 2014), reservoirs (An et al. 2016), and coastal bays (Gu et al. 2016). Among these matrices, PAHs in urban river sediments are much more significant as urban river pollution can do harm to human health directly or indirectly. A previous study on the Haihe River has reported the distribution and sources of PAHs in surface sediments, but further toxicity and ecological risk were not assessed (Jiang et al. 2007). The reported data probably have turned inapplicable with time and new investigations on urban river sediments should be performed.

The objectives of this study were to (1) clarify the spatial distribution and composition characteristics of PAHs in urban river sediments via a scientific survey of the Haihe River, (2) identify the possible PAH sources using molecular diagnostic ratios, and (3) assess the potential toxicological and ecological effects related to PAHs. To achieve these goals, 16 priority PAHs, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), 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), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP) were selected and analyzed. This work will provide valuable information for PAHs pollution management to improve the environmental quality of the Haihe River.

Materials and methods

Study area and sediments sampling

As the largest water system in North China, the Haihe River is the most important freshwater reservoir to Tianjin and plays a vital role in maintaining the rapid urban development (Jiang et al. 2007). The mainstream is 73 km, the watershed area is 2066 km^2 and the annual average runoff is 26.4 billion cubic meters. Haihe River Basin has a typical mainland monsoon climate with distinct four seasons, sufficient sunshine, and moderate rainfall (Cao et al. 2005). The annual average temperature is 13.1 °C and the annual mean rainfall is 539 mm. The rainy, ordinary, and dry seasons are from June to August, September to November, and December to May, respectively.

Surface sediment samples were successively collected along Haihe River mainstream using a stainless steel grab sampler in June 2011. A sampling strategy was designed to cover the whole river from the headwater to the estuary. To explore the effects of urban structure on river sedimental PAHs distribution, 17 sampling sites were finally set up and divided into three categories, including two sampling sites (H1–H2) in Tianjin central urban area (TC), ten sampling sites (H3–H12) in Tianjin suburban area (TS), and five sampling sites (H13–H17) in Binhai New Area (BN). The detailed sampling locations are shown in Fig. 1 and synchronized latitude and longitude pairs of all sites were recorded by a global positioning system (Table S1). Once grabbed, approximately the top 5 cm of sediments were removed carefully with a stainless steel spoon, mixed well, and put in pre-cleaned aluminum containers. All sediment samples were transported immediately to the laboratory in a cooler box with ice packs and then kept at −20 °C until further extraction. The grain size of river sediments was determined by a Laser Particle Size Analyzer, and the particle was divided into three size fractions: clay (<63 μm), silt (63–2000 μm), and sand (>2000 μm) (Evans et al. 1990).

Sample extraction and cleanup

All sediment samples were freeze-dried using a vacuum freeze-drier (FD-1A, China). After removing stones and residual roots, the samples were ground into fine powders with a porcelain mortar and fully homogenized. Then the powders were sieved through a 100-mesh stainless steel sieve (<150 μm). Extraction and cleanup of PAHs were performed by the method published previously (Qiao et al. 2006). Dichloromethane, acetone, and hexane used in the analysis

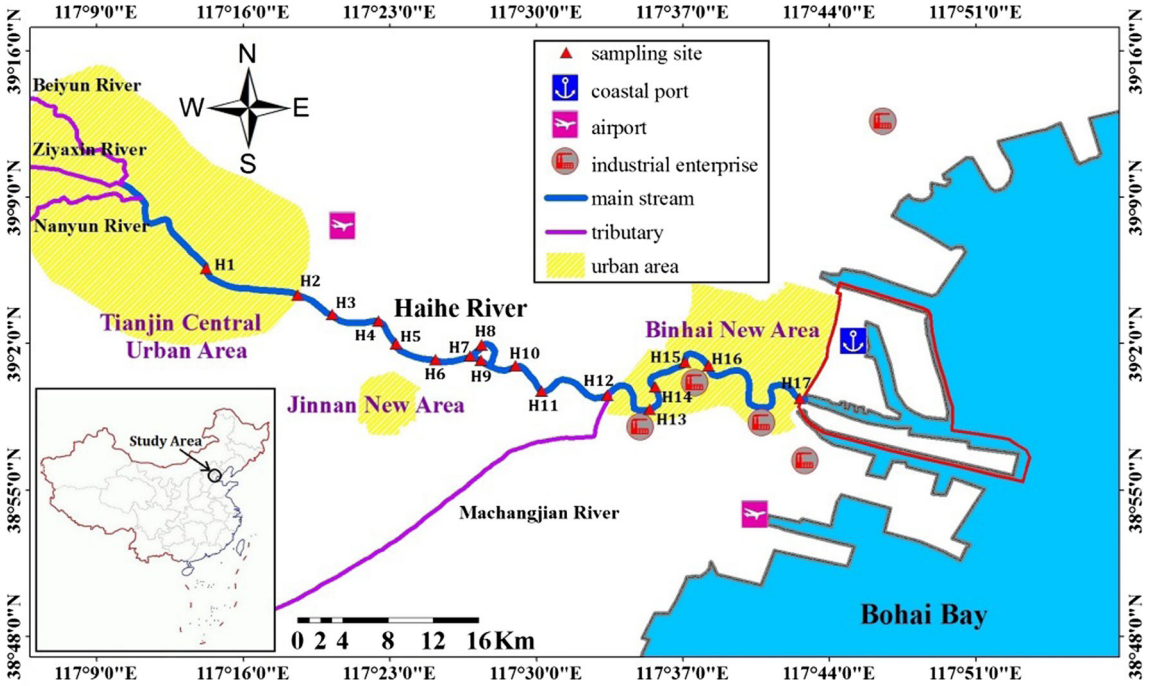

Fig. 1 Sketch map of the Haihe River showing the sampling sites of surface sediments (H1–H17) with *red triangles*

were of HPLC grade and obtained from Fisher Science Company. Unless otherwise indicated, the other chemicals used were of analytical grade. Briefly, 20 g of river sediment was spiked with five recovery surrogates (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, 300 ng, purchased from J&K Chemical, Beijing, China) and Soxhlet extracted with 200 mL dichloromethane/acetone (1:1, *v*/*v*) for 72 h. Elemental sulfur was removed by the addition of 2 g activated copper. After extraction, the sample extract was concentrated by a rotary evaporator, solvent exchanged to hexane, and further reduced to approximately 2 mL. An alumina/silica gel glass column containing 1 cm anhydrous sodium sulfate on the top was used to clean up the hexane extract. And the fraction containing PAHs was collected by eluting with 70 mL dichloromethane/hexane (3:7, *v*/*v*). Then the eluting solution was evaporated again to 5 mL, dried under a gentle stream of nitrogen and finally dissolved in 1 mL hexane. A known quantity of hexamethylbenzene (200 mg L^{-1}, 5 μL) was added to the sample as the internal standard prior to instrumental analysis.

Instrumental analysis

The concentrations of 16 PAHs were measured by gas chromatography (Agilent 6890 GC) in conjunction with mass spectrometry (Agilent 5973 MS). An HP-5MS capillary column (30 m × 0.25 mm diameter, 0.25 μm film thickness) was used. The GC carrier gas was high purity helium at a constant flow rate of 1.0 mL min^{-1}. A 1.0-μL sample was injected in the splitless mode. The chromatographic conditions were programmed as follows: initial temperature at 60 °C for 2 min, increased to 120 °C with a rate of 10 °C min^{-1}, and held 5 min, then increased to 290 °C with a rate of 4 °C min^{-1} and held 10 min finally. The injector and detector temperatures were 270 and 280 °C, respectively. The MS was operated in electron impact ionization mode at 70 eV and the scan to determine appropriate masses for selected ion monitoring ranged from 45 to 400 amu. Identification of individual PAH compounds was based on the selected ions and the comparison of relative retention times between sample and the standard solution.

Quality assurance (QA) and quality control (QC)

All analytical data were subjected to strict quality assurance and control. Method blanks (solvent), spiked blanks (standards spiked into solvent), sample duplicates, and a National Institute of Standards and Technology (NIST) standard reference material (SRM 1941b) were processed in the same procedures used for field samples in this study. Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} were added to the samples to correct procedural performance and matrix effects. The mean recoveries were 88.2 ± 7.8% for naphthalene-d8, 79.4 ± 6.2% for acenaphthene-d10, 81.9 ± 9.0% for phenanthrene-d10, 103.6 ± 9.5% for chrysene-d12, and 90.6 ± 7.6% for perylene-d12, respectively (Table S2). Quantification of individual PAHs was conducted by the internal calibration method based on five-point calibration curves. The relative standard deviations in sample duplicates were <15%. The recoveries of

all PAHs in the SRM 1941b samples were between 65.2% (Flu) and 110.4% (IcdP) of the certified values (Table S3). Detection limits (DLs) were calculated as three times of the signal-to-noise (S/N) ratios in blank samples and varied from 0.2 to 1.1 ng g^{-1} for individual PAHs (Table S2). All reported concentrations were corrected by surrogate recoveries and expressed on a dry weight (dw) basis.

Data statistical analysis

Statistical analyses of the results were performed using the Microsoft Excel 2010 (Microsoft Co., Redmond, WA, USA) and SPSS 18.0 for Windows (SPSS Inc., Chicago, IL, USA). Pearson correlation coefficient with two-tailed test (*t* test) was used to characterize the relationships between different sets of data. Four molecular ratios of Fla/(Fla + Pyr), Ant/(Ant + Phe), IcdP/(IcdP + BghiP), and BaA/(BaA + Chr) were used to identify the possible PAH sources.

Toxicity and ecological risk assessment

In general, low molecular weight (LMW, 2–3 rings) PAHs exhibit significant acute toxicity, whereas high molecular weight (HMW, 4–6 rings) PAHs are characterized by potential carcinogenic toxicity. As molecular weight increases, the carcinogenicity of PAHs also increases with reducing acute toxicity (Kim et al. 2013). In this study, the carcinogenic potency of sedimental PAHs was estimated by BaP equivalent (BaP_{eq}) concentrations calculated using BaP toxic equivalency factors (TEFs) (Nisbet and Lagoy 1992; Wang et al. 2013; Ning et al. 2014). In detail, BaP_{eq} concentration of each PAH was calculated by multiplying the concentration with corresponding TEF, and the carcinogenic potency of total PAHs could be defined as the sum of BaP_{eq} concentrations of 16 individual PAHs (Ning et al. 2014).

PAH contaminants in the sediments can be used by benthic organisms, then enter into food chains and pose potential risk to aquatic ecosystem (Dudhagara et al. 2016). The Sediments Quality Guidelines are useful tools to evaluate the risk of PAHs to organisms and ecosystem and widely applied for sediment quality assessment in aquatic environments (Qiao et al. 2006; He et al. 2014). Effects range-low (ERL) values and effects range-median (ERM) values which were established by 10 and 50% effective concentrations respectively were used in this study (He et al. 2014). PAH concentrations lower than ERL values were considered to be harmful rarely to organisms, concentrations higher than ERM values were considered to be harmful frequently, and concentrations between ERL values and ERM values were considered to be harmful occasionally (Long et al. 1995; MacDonald et al. 1996).

Table 1 Descriptive statistics for PAH concentrations (ng g^{-1}, dw) in surface sediments from the Haihe River

PAHs	Abbreviation	Ring	Min	Max	Mean	Median	SD	CV (%)
Naphthalene	Nap	2	17.0	200.0	67.1	50.6	53.0	78.9
Acenaphthylene	Acy	3	35.9	79.8	55.9	51.6	14.1	25.1
Acenaphthene	Ace	3	0.9	131.0	18.9	4.4	37.3	196.9
Fluorene	Flu	3	1.1	33.6	10.9	5.2	11.5	104.8
Phenanthrene	Phe	3	3.8	84.4	30.5	15.4	27.1	88.8
Anthracene	Ant	3	7.5	12.0	11.7	12.0	1.1	9.3
Fluoranthene	Fla	4	19.2	880.0	187.2	84.8	248.1	132.5
Pyrene	Pyr	4	2.8	257.0	47.6	17.6	68.9	144.7
Benzo[a]anthracene	BaA	4	16.4	1546.0	337.8	92.2	513.0	151.9
Chrysene	Chr	4	13.0	1357.0	280.8	76.0	433.8	154.5
Benzo[b]fluoranthene	BbF	5	2.8	1042.0	207.8	50.8	315.6	151.8
Benzo[k]fluoranthene	BkF	5	3.8	936.0	215.7	53.6	311.1	144.2
Benzo[a]pyrene	BaP	5	5.4	1362.0	270.1	71.4	412.6	152.7
Dibenzo[a,h]anthracene	DahA	5	1.4	816.0	159.6	37.2	251.8	157.7
Benzo[g,h,i]perylene	BghiP	6	ND[a]	424.0	86.7	40.8	113.0	130.3
Indeno[1,2,3-cd]pyrene	IcdP	6	1.2	656.0	136.8	32.0	218.3	159.6
∑CPAHs[b]	–	–	44.0	7715.0	1608.7	479.6	2429.4	151.0
∑PAHs	–	–	171.4	9511.2	2125.4	762.8	2913.1	137.1

[a] Below the detection limit

[b] The sum concentration of seven carcinogenic PAHs

Results and discussion

Levels and spatial distribution of PAHs

Sixteen priority PAHs were investigated in surface sediments from different sampling locations of the Haihe River. Descriptive statistics for the concentrations of individual PAHs, seven carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IcdP) and total PAHs are provided in Table 1. All PAHs were detected at 17 sampling sites except that BghiP was not found at site H6. The mean detection rate of 16 individual PAHs was 99.6%. As listed in Table 1, there were obvious differences on individual PAH concentrations among all samples. BaA had the highest concentrations varying from 16.4 to 1546.0 ng g^{-1} with a mean value of 337.8 ng g^{-1}. Flu, Ant, and Ace had relatively low concentrations of 10.9 ± 11.5, 11.7 ± 1.1, and 18.9 ± 37.3 ng g^{-1}, respectively. BaP, one of the most toxic PAHs, was detected in all samples and ranged from 5.4 to 1362.0 ng g^{-1} with a mean value of 270.1 ng g^{-1}. In brief, HMW PAHs exhibited relatively higher levels than LMW ones. The decreasing order based on mean concentrations was: BaA > Chr > BaP > BkF > BbF > Fla > DahA > IcdP > BghiP > NaP > Acy > Pyr > Phe > Ace > Ant > Flu. In addition, the coefficients of variation (CVs) of individual PAHs were calculated and ranged from 9.3 to 196.9%. Most of individual PAH values (13 of the 16) displayed a high spatial variability with CV >100%. To some extent, the large CV could reflect that the occurrence of PAHs in surface sediments from the Haihe River might be related to anthropogenic activities and energy consumption structure along the river (Sun et al. 2015).

The spatial distributions of total PAHs and seven carcinogenic PAHs in surface sediments from the Haihe River are shown in Fig. 2. Total PAH concentrations varied greatly depending on sampling locations and ranged from 171.4 to 9511.2 ng g^{-1} with a mean value of 2125.4 ng g^{-1}. The highest concentration was observed at site H17 (9511.2 ng g^{-1}) followed by H16 (7695.0 ng g^{-1}) and H13 (6669.4 ng g^{-1}), while the lowest was recorded at site H6 (171.4 ng g^{-1}). The maximum value was over 50-fold higher than the minimum value. Sites H13, H16, and H17 were all located close to large-scale industrial enterprises, which was the main reason of high concentrations under the influence of industrial emission. Slightly high concentrations of total PAHs were also found at sites H1 and H2, two sites in densely populated urban areas (TC), due to the secondary environment problems (e.g., traffic

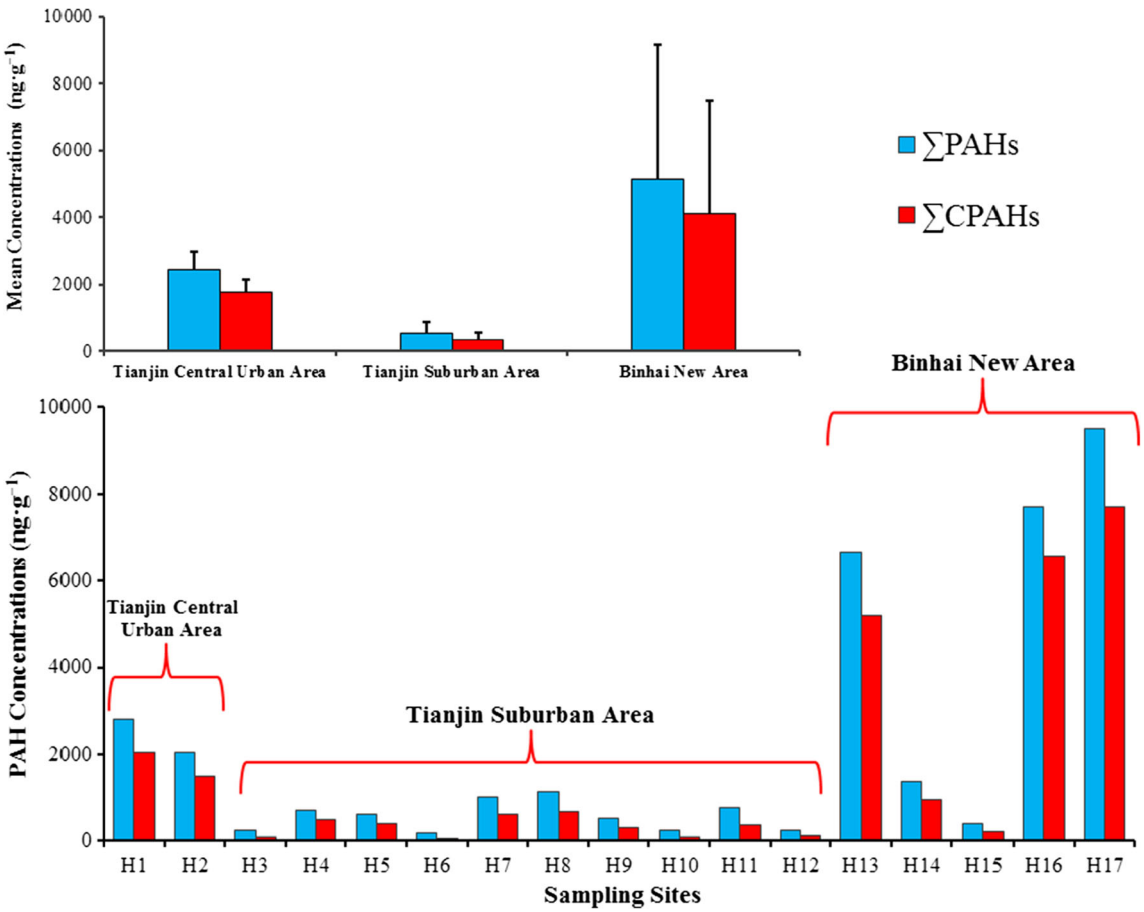

Fig. 2 Concentrations of total PAHs and seven carcinogenic PAHs in 17 surface sediments

emission, fuel consumption, and domestic sewage discharge) caused by the large population. On the contrary, low concentrations observed at some sites in TS could be explained by fewer pollution sources in such agricultural cultivation regions. The concentrations of seven carcinogenic PAHs ranged from 44.0 to 7715.0 ng g^{-1} with a mean value of 1608.7 ng g^{-1}, and shared similar distribution characteristics to total PAH concentrations. On average, seven carcinogenic PAHs accounted for 75.7% of total PAHs in all samples. The percentage was highest at site H16 (85.3%) and lowest at site H6 (25.7%). These seven PAHs were the major contributors to total PAHs in surface sediments from the Haihe River and should be paid more attention.

For three particular sampling regions, the mean concentrations of total PAHs in surface sediments occurred in the following order: BN (5127.0 ± 4024.2 ng g^{-1}) > TC (2436.4 ± 540.0 ng g^{-1}) > TS (562.4 ± 340.5 ng g^{-1}). The mean concentrations of seven carcinogenic PAHs of TC, TS, and BN were 1766.5 ± 400.9, 335.8 ± 223.9, and 4129.0 ± 3366.3 ng g^{-1}, respectively. The general tendency of PAH contaminants was decreased at first and then sharply increased in the process of runoff flowing from upstream to estuary. Binhai New Area, located in the coastal region of the Bohai Bay, is one of the most rapidly developing areas in China. Severe PAHs pollution happening in this area was reasonable and could be attributed to three factors. Firstly, this area is densely populated and characterized by flourishing industrial activities. Many large-scale industrial enterprises such as shipbuilding plants, petrochemical plants, metal manufacturing plants, and steel mills are concentrated along

Table 2 Comparison of total PAH concentrations (ng g^{-1}, dw) in surface sediments from different locations worldwide

Locations	N^a	Total concentrations	Mean concentrations	Pollution levels	References
Haihe River, China, 2011	16	171.4–9511.2	2125.4	Moderate to very high	This study
Haihe River, China, 2004	16	774.81–255,371.91	27,074.08	Moderate to very high	Jiang et al. 2007
Beiyun River, China	16	171–8650	4241	Moderate to very high	Shen et al. 2009
Ziyaxin River, China	16	326.89–11,296.66	2926.40	Moderate to very high	Liu et al. 2013a
Bohai Bay, China	16	140.6–300.7	188.0	Moderate	Hu et al. 2010
Bohai Sea, China	16	97.2–300.7	175.7	Low to moderate	Hu et al. 2013
Lijiang River, China	16	160–602	329	Moderate	Xue et al. 2013
Songhua River, China	16	68.25–654.15	234.15	Low to moderate	Zhao et al. 2014
Shenzhen River, China	16	1028–1120	1074	High	Deng et al. 2014
Liangtan River, China	16	69–6250	2040	Low to very high	Liu et al. 2013b
Aojiang River, China	15	490.6–883.4	740.6	Moderate	Li et al. 2009
Dongjiang River, China	16	100–3400	880	Moderate to high	Zhang et al. 2011
Huangpu River, China	16	313–1707	1154	Moderate to high	Liu et al. 2008
Xihe River, China	16	340–12,900	5593	Moderate to very high	Guo et al. 2011
Luan River, China	16	20.9–287.0	115.3	Low to moderate	Cao et al. 2010
Huaihe River, China	16	95.2–877.5	370.8	Low to moderate	Feng et al. 2012
Erjen River, Taiwan	16	22–28,622	737	Low to very high	Wang et al. 2015a
Hyeongsan River, Korea	16	5.3–7700	2200	Low to very high	Koh et al. 2004
Chao Phraya River, Thailand	17	33–594	263	Low to moderate	Boonyatumanond et al. 2006
Prai River, Malaysia	16	1102–7938	4357	High to very high	Keshavarzifard et al. 2014
Malacca River, Malaysia	16	716–1210	1023	Moderate to high	Keshavarzifard et al. 2014
Gomti River, India	16	5.24–3722.87	697.25	Low to high	Malik et al. 2011
Tiber River, Italy	6	157.8–271.6	215.2	Moderate	Patrolecco et al. 2010
Ammer River, Germany	16	112–22,900	8770	Moderate to very high	Liu et al. 2013b
Arc River, France	16	151–1257	549	Moderate to high	Kanzari et al. 2012
Huveaune River, France	16	572–4235	1966	Moderate to high	Kanzari et al. 2014
Savannah River, USA	24	29–5375	1216	Low to very high	Sanders et al. 2002
Iguaçu River, Brazil	16	131–1713	554	Moderate to high	Leite et al. 2011
Biobio River, Chile	16	15–276	104	Low to moderate	Barra et al. 2009

[a] Number of PAH compounds analyzed in each study

the river banks. Large amounts of domestic and industrial wastewater is discharged through drain outlets into the Haihe River. Secondly, water activities brought by tourism and transportation are frequent in this river section and result in accidental oil spillage sometimes. Thirdly, the Haihe River is a sluice-controlled river. The presence of sluice at the river mouth weakens the water exchange ability with adjacent sea areas, which is not conducive to the dispersion of PAH contaminants. Generally, the accumulation of PAHs in surface sediments from the Haihe River was affected by multiple anthropogenic activities with industrial pollution as the major contributor.

A comparison of total PAH concentrations in surface sediments collected from different locations (including two tributaries of the Haihe River, some adjacent sea areas and other rivers around the world) is given in Table 2 and Fig. S1. The levels of sediment pollution evaluated by total PAH concentrations could be classified as: low, 0–100 ng g^{-1}; moderate, 100–1000 ng g^{-1}; high, 1000–5000 ng g^{-1}; and very high, >5000 ng g^{-1} (Baumard et al. 1998). The pollution levels of surface sediments from the Haihe River in this study were moderate to very high. Surface sediment samples from the Haihe River were taken previously in 2004 and the mean concentration of total PAHs was 27,074.1 ng g^{-1} (Jiang et al. 2007), approximately 13 times higher than that in this study. The difference might be attributed to desilting works and renovation implemented in recent years. The mean concentration of total PAHs in this study was slightly lower than those in two tributaries, but higher than those in adjacent sea areas. The continuous inflow of tributaries could exacerbate PAHs pollution of the Haihe River, and similar situation would happen in the offshore areas influenced by the Haihe River. In addition, compared with other rivers around the world, the mean concentration of total PAHs in this study was similar to those in the Liangtan River, Hyeongsan River, and Huveaune River, lower than those in the Xihe River, Prai River, and Ammer River, but higher than those in other rivers. Obviously, the comparison indicated that PAHs pollution in the Haihe River was already at a relatively serious level and further treatment measures should be adopted to protect this significant urban ecosystem. Such comparison of reported data could be subjective and slightly inaccurate sometimes because of variances in the numbers and types of individual PAHs investigated, the numbers of sediment samples taken, the sediment fractions analyzed, and the analytical methods used.

Composition pattern of PAHs

Composition pattern of PAHs contains much important information on different sources that contribute PAH contaminants to environmental samples (Cao et al. 2005). Based on the number of aromatic rings, the 16 PAHs could be divided into five groups: 2-ring, 3-ring, 4-ring, 5-ring, and 6-ring PAHs. The relative abundance of PAHs by ring size is illustrated in Fig. 3. The concentrations ranged from 17.0 to 200.0 ng g^{-1}

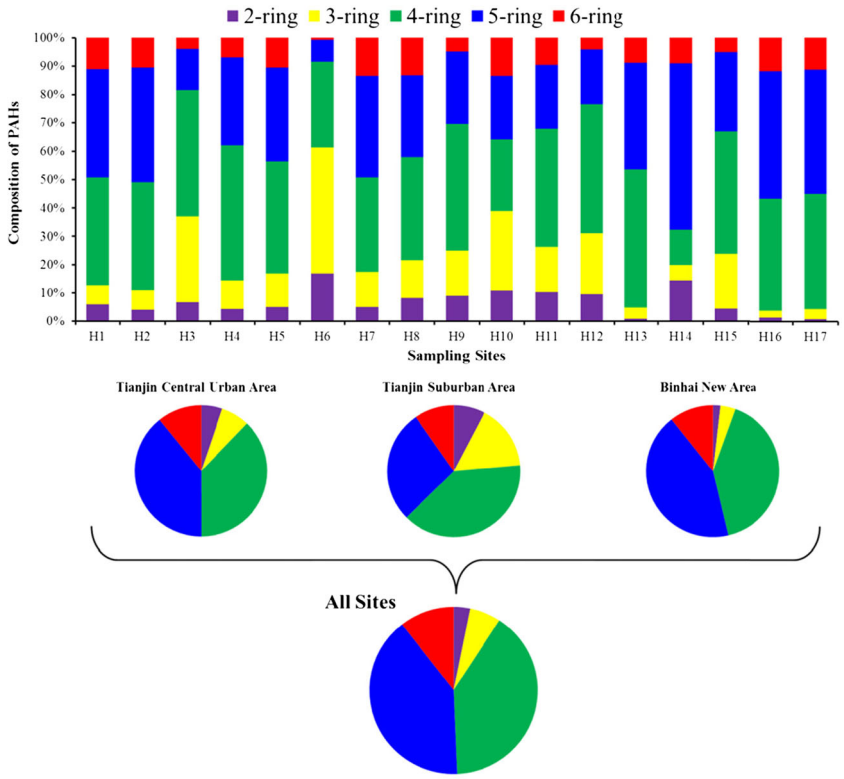

Fig. 3 Composition profiles of PAH compounds in surface sediments from the Haihe River

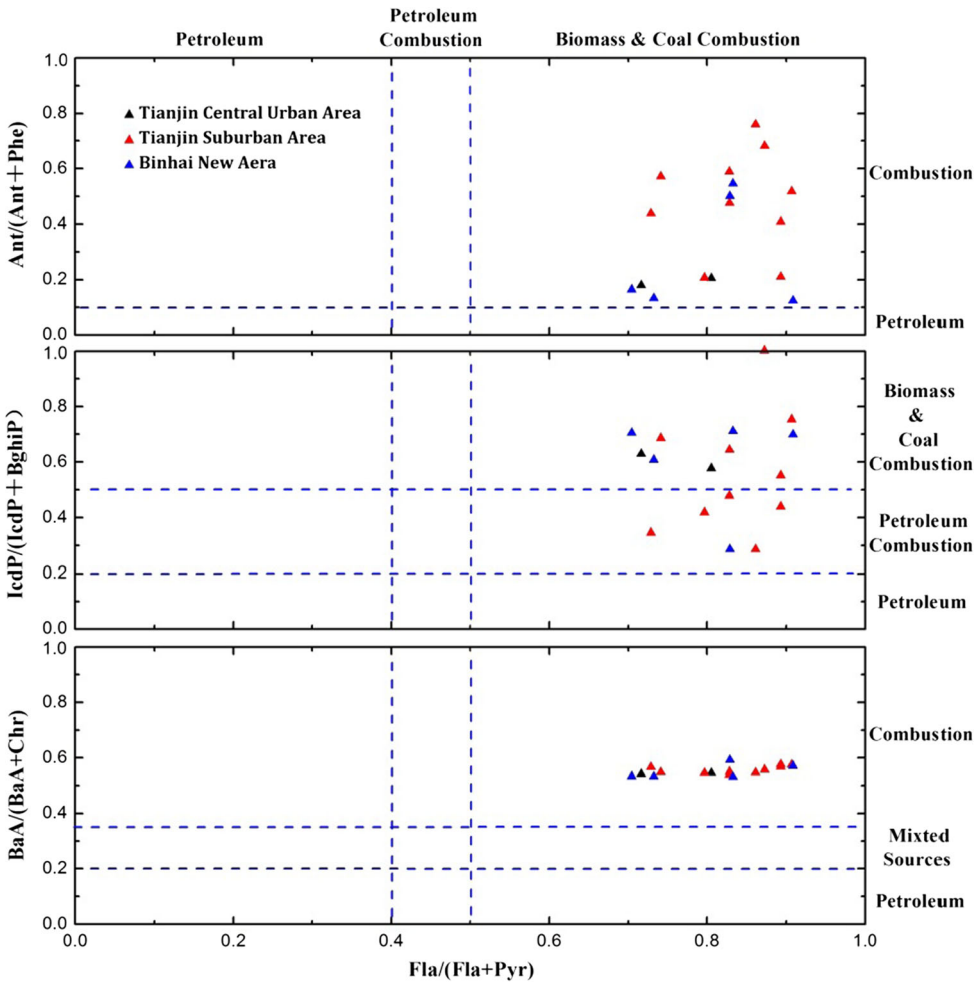

Fig. 4 Plots of four isomeric ratios in surface sediments from the Haihe River

for 2-ring PAHs, from 52.4 to 330.0 ng g^{-1} for 3-ring PAHs, from 51.4 to 3863.0 ng g^{-1} for 4-ring PAHs, from 13.4 to 4156.0 ng g^{-1} for 5-ring PAHs, and from 1.2 to 1080 ng g^{-1} for 6-ring PAHs. In general, 4-ring and 5-ring PAHs were the predominant compounds for all samples, followed by 6-ring and 3-ring PAHs, while the relative abundance of 2-ring PAHs was the lowest. Numerically, 4-ring and 5-ring PAHs jointly accounted for 80.3% of total PAHs on average, among which the percentages of BaA, Chr, BaP, BkF, and BbF were 15.9, 13.2, 12.7, 10.2, and 9.8%, respectively. It should be noted that the general composition characteristics above were just suitable to most samples. LMW PAHs had relatively higher percentages in sediment samples of TS (mean 23.6%) much more than TC (mean 12.2%) and BN (mean 5.5%). More significantly at sites H6 and H10, 3-ring PAHs were even the most abundant PAHs. LMW PAHs are considered to originate from both petrogenic and low-temperature combustion sources, whereas HMW PAHs have predominantly high-temperature pyrolytic sources (Mai et al. 2003). High percentages of LMW PAHs at some sites indicated the contribution of petrogenic processes. Furthermore, HMW PAHs are more resistant to degradation and more hydrophobic to be accumulated in the sediments (Liu et al. 2015b). As a result, higher concentrations of HMW PAHs than LMW PAHs have been commonly observed in surface sediments from freshwater and marine environments (Liu et al. 2015b; Yuan et al. 2016; Zhang et al. 2016). The composition of PAHs in this study showed a significant difference between proportions of HMW PAHs (90.8%) and LMW PAHs (9.2%), which was in agreement with the universal result found in aquatic surface sediments.

Source identification of PAHs by isomer ratios

Identifying the possible sources of PAHs is extremely important in understanding the fate of PAH contaminants and how the processes occurring in the designated area contribute to PAHs pollution (Maciel et al. 2015; Yang et al. 2015; Gu et al. 2016). Anthropogenic PAHs in the environment are mainly from incomplete combustion processes and the release of petroleum and its products (Mai et al. 2003). Molecular indices based on ratios of isomeric concentrations have been widely applied to distinguish PAHs from pyrolytic and petrogenic

sources (Yunker et al. 2002; Li et al. 2015; Wang et al. 2015b; Gu et al. 2016). In order to determine the possible PAH sources in surface sediments from the Haihe River, four isomer ratios of Fla/(Fla + Pyr), Ant/(Ant + Phe), IcdP/(IcdP + BghiP), and BaA/(BaA + Chr) were selected, calculated, and plotted in Fig. 4. Phe is thermodynamically more stable than Ant and the more existence of Phe indicates that PAHs are mainly the result of petrogenic activities (Yang et al. 2013). Indeed, petroleum products usually exhibit a quite low Ant/(Ant + Phe) ratio. It is accepted that the ratio of Ant/(Ant + Phe) <0.10 is indicative of petroleum sources while the ratio of Ant/(Ant + Phe) >0.10 suggests combustion sources of PAHs contamination (Yunker et al. 2002). In addition, for Fla/(Fla + Pyr) and IcdP/(IcdP + BghiP), the ratios below 0.40 and 0.20 suggest petroleum sources; the ratios over both 0.50 are considered to be associated with grass, wood, and coal combustion; and other intermediate ratios (0.40–0.50 and 0.20–0.50) are characteristic of petroleum (e.g., liquid fossil fuel, vehicle, and crude oil) combustion (Yunker et al. 2002). In the case of BaA/(BaA + Chr), the ratio <0.20 is usually taken to indicate petroleum origins, the ratio >0.35 is probably attributable to combustion origins, and the ratio between 0.20 and 0.35 means PAHs from either petroleum or combustion (Yunker et al. 2002; Wang et al. 2015b).

In this study, the ratios of Fla/(Fla + Pyr) ranged from 0.70 to 0.91 with a mean of 0.80 (much higher than 0.50), which indicated that PAHs contamination from biomass and coal combustion. For Ant/(Ant + Phe), the ratios in all samples were higher than 0.10 (from 0.12 to 0.76), suggesting pyrolytic sources (e.g., petroleum, wood, and coal combustion). More accurately to different regions, the mean ratios of Ant/(Ant + Phe) in TC, TS, and BN were 0.19, 0.40, and 0.20, respectively. Low values near 0.10 were mainly found in urban areas such as sites H13, H17, H16, H1, and H2, implying the slight contribution of petroleum products. For IcdP/(IcdP + BghiP), the ratios ranged from 0.29 to 1.00 with a mean of 0.61. The IcdP/(IcdP + BghiP) ratio >0.50 indicated that the main sources at most sites (11 of the 17) were biomass and coal combustion, whereas the rest six sites were contaminated by petroleum combustion. The ratios of BaA/(BaA + Chr) were in the stable range of 0.53 to 0.59 (>0.35), indicating combustion sources of PAHs. Overall, the above data demonstrated that PAHs in surface sediments from the Haihe River originated from mixed combustion of petroleum, grass, wood, and coal to a large degree.

In addition, the correlations between above four isomer ratios were analyzed. It was found that the correlations between any two of Fla/(Fla + Pyr), Ant/(Ant + Phe), IcdP/(IcdP + BghiP), and BaA/(BaA + Chr) were very poor (R^2 < 0.10), except for the correlation of Fla/(Fla + Pyr) and BaA/(BaA + Chr) (Table S4). The correlation analysis revealed that molecular ratios were not an unequivocal method to recognize PAH sources due to the complexity of parameters determining PAHs distribution in the Haihe River (Wang et al. 2015b). Inconsistent results could be observed when using different isomer ratios. To enhance the reliability of source apportionment and better understand the potential PAH sources, more precise analytical methods with comprehensive data should be applied in the future researches.

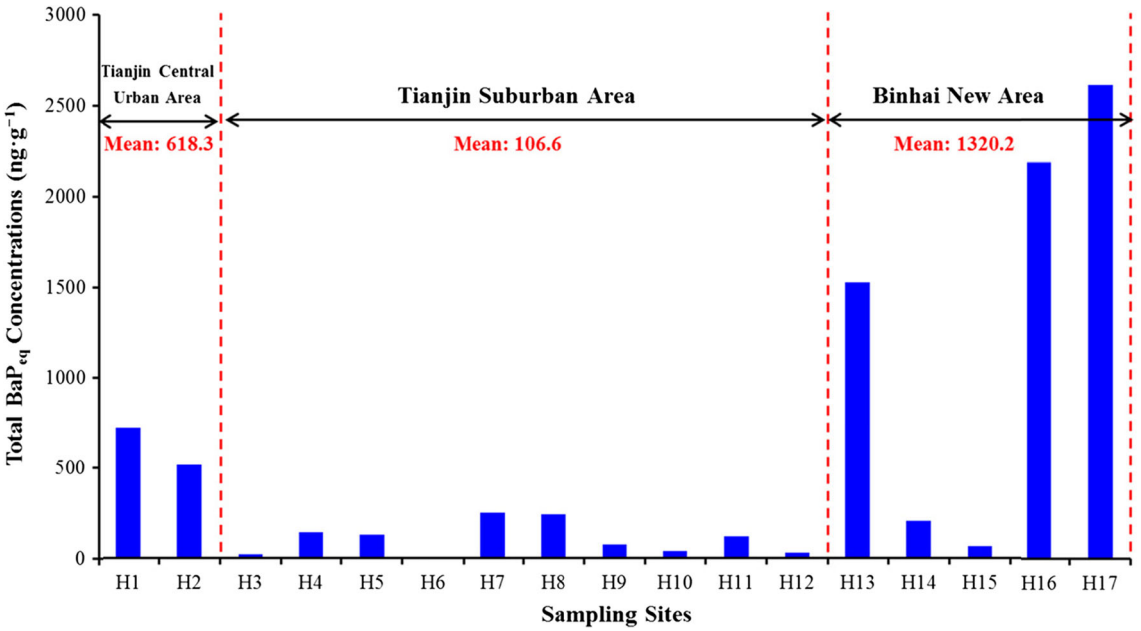

Fig. 5 Total BaP_{eq} concentrations in surface sediments from the Haihe River

Toxicity and potential ecological risk

Toxicity based on the BaP_{eq} concentrations

The TEF values used in this study and carcinogenic potencies of PAHs in surface sediments are provided in Table S5. Total BaP_{eq} concentrations ranged from 9.6 to 2615.3 ng g^{-1}, with a mean value of 523.8 ng g^{-1}. The BaP_{eq} concentrations of seven carcinogenic PAHs ranged from 9.4 to 2609.6 ng g^{-1}, with a mean value of 522.4 ng g^{-1}, which were much higher than those in surface sediments from the Songhua River (mean 13.2 ng g^{-1}) (Zhao et al. 2014). Seven carcinogenic PAHs were the main contributors to total carcinogenic potency and the mean BaP_{eq} concentration of seven carcinogenic PAHs accounted for 99.7% of total PAHs. For individual carcinogenic PAHs, the mean BaP_{eq} concentrations decreased in the following order: BaP (270.1 ng g^{-1}) > DahA (159.6 ng g^{-1}) > BaA (33.8 ng g^{-1}) > BkF (21.6 ng g^{-1}) > BbF (20.8 ng g^{-1}) > IcdP (13.7 ng g^{-1}) > Chr (2.8 ng g^{-1}).

The spatial distribution of total BaP_{eq} concentrations is shown in Fig. 5. The highest value at site H17 was approximately 250-fold higher than the lowest value at site H6. The mean total BaP_{eq} concentrations in TC, TS, and BN were 618.3, 106.6, and 1320.2 ng g^{-1}, respectively. High carcinogenic toxicity appeared primarily in surface sediments from urban river sections (TC and BN). Considering the different harmfulness among various PAHs, the BaP_{eq} concentrations calculated by toxic equivalency factors could reflect the potential risk to organisms with a more accurate perspective than total PAH concentrations in surface sediments to some extent.

Potential ecological risk of PAHs

The measured concentrations of individual PAHs, LMW PAHs, HMW PAHs, and total PAHs were compared with ERL values and ERM values in 17 surface sediments (Table 3). As shown, the concentrations of Acy at most sampling sites (14 of the 17 except for sites H3, H4, and H12) were of the intermediate range (ERL–ERM), indicating that adverse biological effects related to Acy would occur occasionally in most regions of the Haihe River. The concentrations of Phe, Ant, and Pyr at all sites were lower than corresponding ERL values, indicating that aquatic organisms could rarely affected by these three PAHs. The concentrations of DahA higher than ERM value at sites H13, H16, and H17 had adverse biological effects on organisms frequently, between ERL value and ERM value at sites H1, H2, H7, and H8 had adverse biological effects occasionally, and lower than ERL value at other ten sites had adverse biological effects rarely. For NaP, Ace, Flu, Fla, BaA, Chr, and BaP, the

Table 3 Comparison of PAH concentrations with ERL and ERM guideline values in surface sediments from the Haihe River (ng g^{-1}, dw)

PAHs	ERL[a]	ERM[a]	Concentration range	Number of sampling sites		
				<ERL	ERL–ERM	>ERM
Nap	160	2100	17.0–200.0	15	2	0
Acy	44	640	35.9–79.8	3	14	0
Ace	16	500	0.9–131.0	14	3	0
Flu	19	540	1.1–33.6	14	3	0
Phe	240	1500	3.8–84.4	17	0	0
Ant	85.3	1100	7.5–12.0	17	0	0
Fla	600	5100	19.2–880.0	15	2	0
Pyr	665	2600	2.8–257.0	17	0	0
BaA	261	1600	16.4–1546.0	12	5	0
Chr	384	2800	13.0–1357.0	14	3	0
BbF	–	–	2.8–1042.0	–	–	–
BkF	–	–	3.8–936.0	–	–	–
BaP	430	1600	25.4–136.0	14	3	0
DahA	63.4	260	1.4–816.0	10	4	3
BghiP	–	–	ND–424.0	–	–	–
IcdP	–	–	1.2–656.0	–	–	–
LMW PAHs	552	3160	75.7–412.2	17	0	0
HMW PAHs	1700	9600	66.0–9099.0	12	5	0
∑PAHs	4022	44,792	171.4–9511.2	14	3	0

[a] Data from He et al. (2014)

concentrations between corresponding ERL values and ERM values at some sites (in a range from two to five) could cause adverse biological effects on organisms occasionally. For different sampling sites, 16 PAH concentrations were all below corresponding ERL values at sites H3, H4, and H12, and surface sediments from these sites presented almost no ecological risk. For other 14 sites, there was at least one PAH concentration above ERL value that would cause adverse biological effects. Especially at sites H13, H16, and H17 in BN, the concentrations of DahA were greater than ERM value and the concentrations of total PAHs were between ERL value and ERM value. Surface sediments from partial section of the Haihe River in BN had relatively high possibility of serious ecological risk. Generally, these findings mentioned above indicated that surface sediments from most survey regions of the Haihe River exhibited certain levels of ecological risk in terms of PAHs. More properly, ERL and ERM values are not threshold concentrations of sediment toxicity (O'Connor 2004). The assessment of PAHs in Haihe River sediments using these two values may overestimate or underestimate the quality of Haihe River sediments.

Conclusions

This study provided important data on the occurrence and distribution of PAHs in surface sediments from the Haihe River. Total PAH concentrations were relatively high in comparison with other reported rivers around the world, indicating serious PAHs pollution in the Haihe River. PAH concentrations in surface sediments varied significantly among sampling locations with high values in industrial areas (BN) and densely populated areas (TC). Four-ring and 5-ring PAHs were dominant in most samples, and BaA, Chr, and BaP exhibited the higher values. For molecular ratios, Fla/(Fla + Pyr), Ant/(Ant + Phe), IcdP/(IcdP + BghiP), and BaA/(BaA + Chr) were recorded at all sampling sites. The results suggested that PAHs originated mainly from various combustion sources. The mean total BaP_{eq} concentration was 523.8 ng g^{-1}, which was mostly contributed by seven carcinogenic PAHs. In relation to ecological risk assessment, there was at least one PAH concentration higher than ERL value at most sites, which could cause adverse effects on aquatic organisms. Urban river system plays an important role in substances circulation and can affect human health directly. Therefore, more attention should be paid and further researches should be continuously conducted in such important ecosystem.

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