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Spatial distribution and potential toxicity of polycyclic aromatic hydrocarbons in sediments from Liaohe River Basin, China

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Abstract The distribution and potential toxicity of polycyclic aromatic hydrocarbons (PAHs) in the sediments of Liaohe River Basin were investigated in this study. Total concentrations of 16 PAHs ($\sum PAH_{16}$) ranged from 82.5 to 25374.4 μg/kg averaging 3149.2 μg/kg. Three predominant PAHs were fluoranthene, phenanthrene, and pyrene. In Liao River, two-to-three-ring PAHs were dominant taking up 67.2–92.5 % of $\sum PAH_{16}$, whereas sediments in Daliao River system mainly contained four-to-six-ring PAHs ranging from 47.8 to 83.7 %. Both petrogenic and pyrogenic sources contributed to the PAH pollution based on diagnostic ratios. The empirical and mechanistic sediment quality guidelines were used to estimate the toxicity risk of PAHs to benthic organisms. The $\sum PAH_{16}$ in all sediments were significantly lower than probable effect concentrations (PEC), while $\sum PAH_{16}$ at nine sites of the Daliao River system were between threshold effect concentrations (TEC) and PEC, suggesting that adverse effects were possible at the nine sites. The only individual PAH was acenaphthene whose concentrations were above PEC at some sites, indicating its potential toxicity. Based upon equilibrium partitioning theory and narcosis model, the obtained toxic units for PAH mixtures at all sites were far less than one, implying that the levels of PAH mixtures were acceptable for the protection of benthic fauna. The two evaluation methods lead to the consistent results that benthic organisms inhabiting in the sediments of Liaohe River Basin have no or low risk of adverse effects resulting from exposure to PAHs.

Keywords Sediments · Polycyclic aromatic hydrocarbons · Toxicity · Sediment Quality Guidelines · Liaohe River Basin

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants, primarily originated from the incomplete combustion of fossil fuels and biomass and spillage of petroleum (Mastral and Callen 2000). These PAHs are released to the aquatic environments mainly through surface runoff and atmospheric deposition. Due to their low water solubility, less volatility, and high persistence, once PAHs are introduced into the aquatic system, they tend to be adsorbed onto particulates and subsequently deposited in sediments. In such a way, sedimentary PAHs will become a direct exposure to benthic organisms or an indirect exposure to pelagic organisms (e.g., via resuspension), leading to their acute

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or chronic toxicity. Moreover, PAHs in sediments entering into the food web may pose a potential risk to human health (Kannan et al. 2005). Therefore, researches on the contents and potential toxicity of PAHs in sediments are important and necessary.

Sediment Quality Guidelines (SQGs) provide a scientific tool to assess the adverse effects of sediment pollutants to aquatic life. The currently developed SQGs include the empirical and mechanistic ones. The empirical SQGs use a database of matched sediment chemistry and biological effects to derive the pollutant levels with varying likelihoods of causing adverse effects to benthic organisms. There have been many published empirical SQGs to predict whether PAHs in sediment will be toxic, exhibiting a great variability (Burgess et al. 2013). Therefore, consensus-based threshold effect concentrations (TEC) and probable effect concentrations (PEC) were developed trying to harmonize the existing values based on the geometric mean of SQGs and have been successfully applied in the toxicity evaluation of PAHs in sediments (Swartz 1999; MacDonald et al. 2000a, b; Veses et al. 2012). The mechanistic SQGs are based on the bioavailability of contaminants to determine whether the bioavailable fractions will be sufficient in quantities to result in adverse effects (Di Toro et al. 2005). For PAH mixtures, mechanistic SQGs were evolved from equilibrium partitioning (EqP) theory and narcosis model (Di Toro and McGrath 2000). EqP theory was employed to estimate the bioavailable concentrations. Since PAHs belong to type I narcotic chemicals, the critical effect concentration can be predicted from the relationship between PAH toxicity and the octanol-water partition coefficient (Verhaar et al. 1992). The toxicity unit (TU) for individual PAH was calculated and then summed on the basis of additive effect to determine the toxicity of PAH mixtures to benthic fauna. The empirical SQGs have been widely used in the prediction of toxic effects of PAHs in sediments, whereas there are relatively few studies applying the mechanistic SQGs, let alone considering the utilization of both approaches (Weinstein et al. 2010; Veses et al. 2012).

Liaohe River Basin is located in northeast China. It includes the Liao River and Daliao River system (Hun River, Taizi River, and Daliao River). As the important industrial bases for oil, chemical steel-iron, and machinery factories, Liaohe River Basin has been seriously polluted, especially by organic pollutants. PAH contamination in this basin has been concerned, and their levels in water and sediment, possible sources, and associated risk were also discussed (Guo et al. 2007; Zhang et al. 2013a; Lv et al. 2014). These studies, however, either focused on PAH pollution in water or in some tributaries. In terms of environmental risk, only empirical SQGs were used whereas the great variability of empirical ones makes the assessment results different. Since sediments are the ultimate sink and reservoir of PAHs, information on the toxicity risk of PAHs to the benthic organisms inhabited is unknown throughout the whole basin. The present work aims to determine the levels and distribution of 16 priority PAHs in the sediments of Liaohe River Basin and gain more reliable results of potential toxicity of PAHs to benthic organisms based on the empirical and mechanistic SQGs.

Materials and methods

Chemicals and reagents

The 16 mixed PAH standards and deuterated PAHs containing naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} were purchased from AccuStandard Inc. (USA). All solvents used were of high-performance liquid chromatography (HPLC) grade obtained from J. T. Baker.

Sample collection and preparation

Duplicate sediment samples (0–10 cm) were collected from 24 sites in Liaohe River Basin using a Van Veen Grab Sampler in June 2014 (Fig. 1). There were nine sites from Liao River (L1–L9), five sites from Hun River (H1–H5), six sites from Taizi River (T1–T6), and four sites from Daliao River (D1–D4). Each sediment sample was placed into sealed polyethylene bags, transferred to an ice box, and then immediately frozen and kept at −20 °C. All samples were freeze-dried, sieved, and stored at 4 °C in the dark until analysis.

Sample extraction and cleanup

An amount of 20 g sediment sample combined with 5 g of copper powder and 5 g of diatomite were extracted using hexane/dichloromethane mixture (50/50, *v*/*v*) in an accelerated solvent extraction (ASE, Dionex 300, USA; pressure, 1500 psi; temperature, 100 °C). A mix of deuterated PAHs as surrogate standards was added to all samples prior to extraction. The extracts were pre-

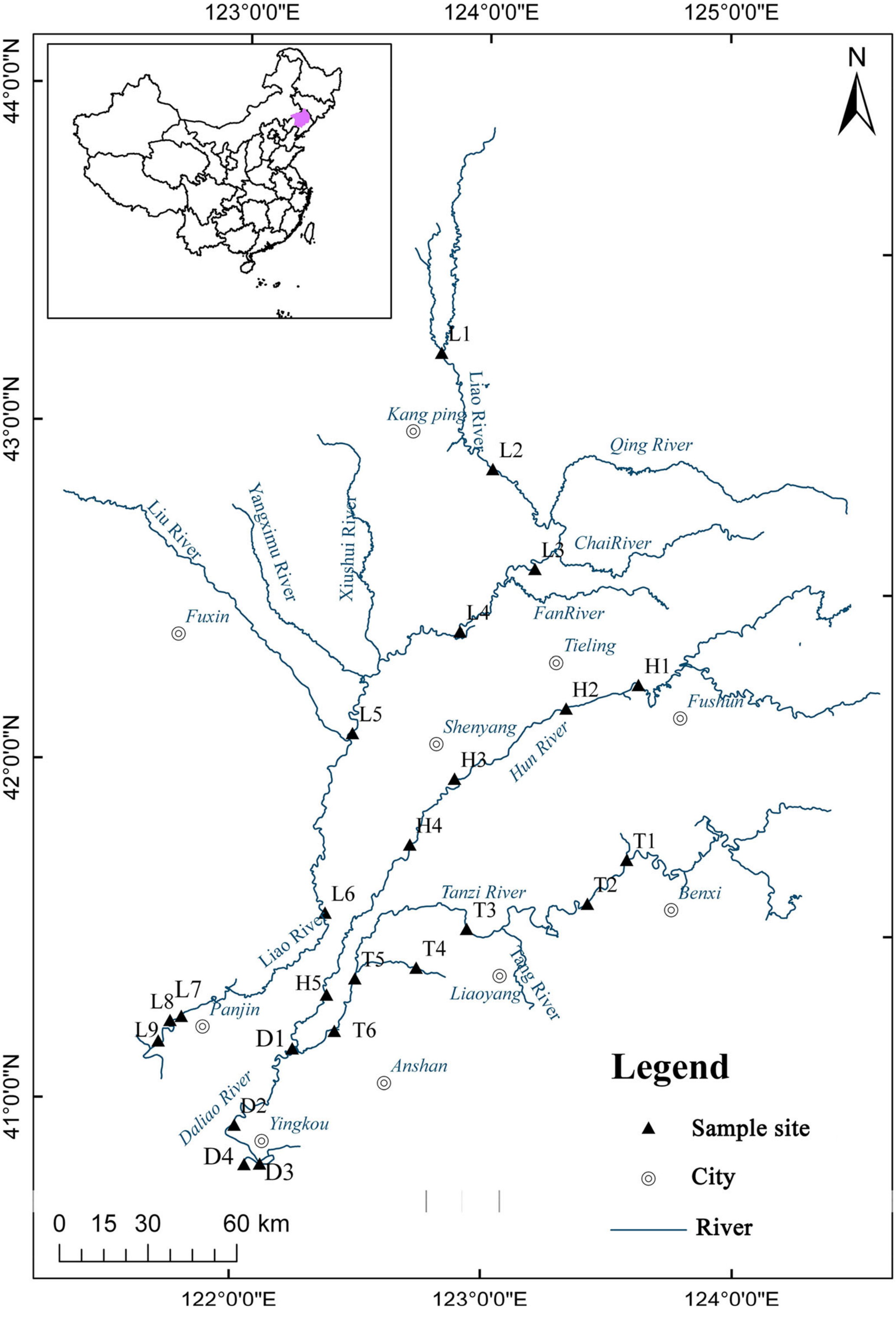


Fig. 1 Locations of sampling sites in Liaohe River Basin

condensed to approximately 2 mL with a rotary evaporator (R-210, Buchi, Swiss) and solvent-exchanged to hexane. The hexane extract was cleaned up by solid phase extraction (SPE) and concentrated to 1 mL with a gentle stream of purified nitrogen for analysis.

PAH analysis and quality control

The concentrations of PAHs was determined on a gas chromatography-mass spectrometer (GC-MS) (QP2010 Plus, Shimadzu, Japan) equipped with a fused silica capillary DB-5MS column (30 m × 0.25 mm inner diameter, 0.25 μm film thickness, Agilent, USA) under the selected ion monitoring mode (SIM). The carrier gas was Helium at a flow rate of 1.2 mL/min. The oven temperature was programmed from 60 °C (1 min) to 160 °C at 10 °C/min, increased to 260 °C at 8 °C/min, and then increased to 300 °C at 6 °C/min holding for 8 min. The injector and detector temperatures were 250 and 300 °C, respectively. The mass spectrometer was operated in scan mode with electron impact ionization of 70 eV and ion source at 230 °C. Splitless injection of 1 μL of the sample was conducted with an autosampler. Target analytes were indentified and verified by comparing the retention time and mass spectra of the samples with the standards and were quantified using the internal calibration based on the five-point calibration curves for individual PAH.

All the analytical procedures were subject to strict quality control, including analyses of method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, and sample duplicates. The PAHs in the blank sediments were all below the detection limits of the method, which were 0.1–2.0 ng/g. The average recoveries of standards in spiked matrix samples were in the range of 62.3–112.5 %. A mixture of five perdeuterated PAHs were added to each sample, and the surrogate recoveries were 72.3 ± 4.5 % for naphthalene-d_8, 80.5 ± 17.6 % for acenaphthene-d_{10}, 88.3 ± 8.6 % for phenanthrene-d_{10}, 90.4 ± 10.5 % for chrysene-d_{12}, and 79.0 ± 8.4 % for perylene-d_{12}, respectively. All results were expressed on a dry weight basis and corrected for surrogate recoveries.

Total organic carbon analysis

Total organic carbon (TOC) in the sediment samples was determined by potassium dichromate oxidation-ferrous sulfate titrimetry method (GAQS-IQ, 2008).

Results and discussion

Level and spatial distribution of PAHs

Sixteen PAH compounds were detected in all 24 surface sediments of Liaohe River Basin. The $\sum PAH_{16}$ (total concentrations of 16 PAHs) at 24 sites showed wide variations, ranging from 82.5 to 25,374.4 μg/kg, with an average value of 3149.2 μg/kg (Table 1). The spatial analysis revealed that the mean levels of $\sum PAH_{16}$ were ranked in the following order of Liao River < Daliao River < Taizi River < Hun River. This distribution trend reflected the serious PAH pollution of the Daliao River system, which flows through many important industrial cities. As exhibited in Fig. 2, the highest level of $\sum PAH_{16}$ (25,374.4 μg/kg) was at T2 located upstream of Taizi River near Benxi Iron and Steel Company, where PAHs were released from coke manufacturing, sintering, and iron and steel making. The high concentrations may be related to the atmospheric fallout and industrial effluent discharge, as well as urban off from Benxi City. High level of PAHs was also found at H3 (17,345.6 μg/kg) in Hun River. This site was located downstream of Shenyang City, the capital of Liaoning Province of China, which is the most important industrial base of northeast China, such as Tiexi Economic Development Area. Large amounts of industrial wastewater and domestic sewage from the dense population made important contributions to PAH levels at H3. In Daliao River, the highest concentration was observed at D1 (2046.5 μg/kg), locating at the confluence of Hun River and Taizi River. The PAH residues from the upstream of the two rivers could transport and deposit in the downstream sediment. Compared with the Daliao River system, the concentrations of PAHs in Liao River were much lower with the highest concentration at L9 downstream of Panjin City (623.1 μg/kg).

The PAH contamination levels can be classified into four categories: (a) low, 0–100 μg/kg; (b) moderate, 100–1000 μg/kg; (c) high, 1000–5000 μg/kg, and (d) very high, >5000 μg/kg (Baumard et al. 1998). Based on this classification, PAH pollution level in the basin was river-specific, which was moderate in Liaohe River (mean value of $\sum PAH_{16}$, 214.7 μg/kg), high in Daliao River (1079.3 μg/kg), and very high in Hun River (6538.5 μg/kg) and Taizi River (6106.5 μg/kg). Compared with other rivers in China, PAH levels in the sediments of Liaohe River Basin were lower than those of Tianjing River (Shi et al. 2005) and Pear River (Mai et al. 2002), but higher than those of Yellow River

Table 1 Concentrations of PAHs in the sediments of Liaohe River Basin plus selected benchmark references—TEC, PEC, and FCV

PAH	Mean (μg/kg)	Range (μg/kg)	TEC (μg/kg)	PEC (μg/kg)	$C_{OC,PAHi,FCVi}$ ($\mu g/g_{oc}$)[d]
Naphthalene (NAP)	171.5	45.3–1131.5	176[a]	561[a]	385
Acenaphthylene (ACY)	26.7	2.0–313.6	5.9[b]	128[b]	452
Acenaphthene (ACE)	75.5	2.4–773.2	6.7[b]	88.9[b]	491
Fluorene (FLO)	108.7	5.4–864.1	77.4[a]	536[a]	538
Phenanthrene (PHE)	441.4	14.1–2943.1	204[a]	1170[a]	596
Anthracene (ANT)	90.9	0.7–804.5	57.2[a]	845[a]	594
Fluoranthene (FLA)	447.8	4.4–3497.1	423[a]	2230[a]	707
Pyrene (PYR)	359.1	3.0–2678.2	195[a]	1520[a]	697
Benzo[a]anthracene (BaA)	264.2	0.5–2373.0	108[a]	1050[a]	841
Chrysene (CHR)	353.5	0.7–3056.2	166[a]	1290[a]	844
Benzo[b]fluoranthene (BbF)	260.5	0.6–2282.7	NA	NA	979
Benzo[k]fluoranthene (BkF)	129.0	0.3–979.0	240[c]	13400[c]	981
Benzo[a]pyrene (BaP)	108.8	0.1–929.0	150[a]	1450[a]	965
Dibenzo[a,h]anthracene (DahA)	50.1	0.04–528.0	33[a]	135[a]	1123
Indeno[1,2,3-cd]pyrene (IcdP)	104.4	0.3–982.1	200[c]	3200[c]	1115
Benzo[ghi]perylene(BghiP)	157.0	0.3–1370.1	170[c]	3200[c]	1095
ΣPAHs	3149.2	82.5–25374.4	1610[a]	22800[a]	/

[a] MacDonald et al. 2000b

[b] CCME 2002

[c] Persaud et al. 1993

[d] USEPA 2003

(Xu et al. 2007), Huai River (Fu et al. 2011), Huangpu River (Liu et al. 2008), Tonghui River (Zhang et al. 2004), Songhua River (Zhao et al. 2014), Xiangjiang River (Zhang et al. 2013b), and Yangtze River (Wuhan) (Feng et al. 2007) (Table 2). Overall, the whole basin has reached moderate to high levels of PAH contamination.

Composition of PAHs

The average concentrations of individual PAH in the sediments of Liaohe River Basin are shown in Table 1. It can be seen that fluoranthene (FLA) was the most abundant component, accounting for 14.2 % of $\sum PAH_{16}$. The concentrations of phenanthrene (PHE) and pyrene (PYR) were also high taking up approximately 14.0 and 11.4 % of the total PAHs, respectively. A similar typical pattern was found in the sediments of Bohai Sea and northern part of the Yellow Sea in China where the three PAHs accounted for 35.0–84.6 % (Li et al. 2015). High levels of FLA, PHE, and PYR provided the evidence of the PAH inputs from the coke oven emission, coal combustion, and vehicular PAH sources (Wilcke and Amelung 2000; Shi et al. 2005; Hu et al. 2010).

The composition profiles of PAHs according to the number of aromatic rings and their relative contribution to $\sum PAH_{16}$ along the river are presented in Fig. 2. It was obvious that low-molecular-weight PAHs (two to three rings) predominated in Liao River sediments, ranging from 67.2 to 92.5 % of $\sum PAH_{16}$, while in the Daliao River system, the high-molecular-weight PAHs (four to six rings) contributed 47.8 to 83.7 % of the total PAHs with the dominance of four-ring PAHs (accounting for 33.8–56.8%). Such a difference was probably attributed to different PAH inputs. In general, low-molecular-weight PAHs are indicative of petrogenic and low-temperature pyrolytic sources, whereas high-molecular-weight PAHs is the evidence of pyrolytic origin. It then can be concluded that PAHs in Liao River were mostly from crude oil and the refined oil products, as well as emissions of automobile or trucks (Zakaria et al. 2002). Coke emissions enriched in high-molecular-weight PAHs were mainly responsible for the serious pollution of the Daliao River system, where large-scale industries are located.

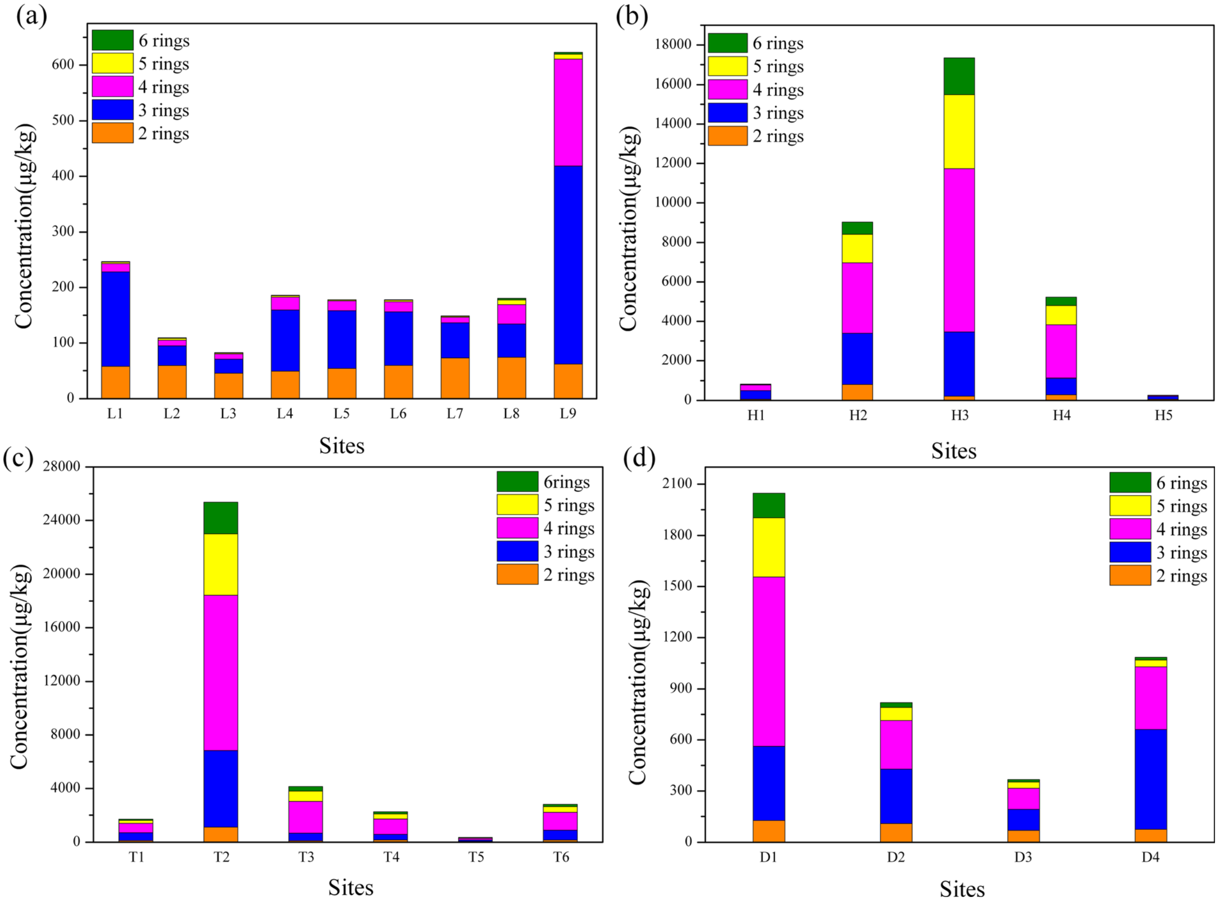


Fig. 2 Concentrations and compositions of $\sum PAH_{16}$ in the sediments of Liaohe River Basin: **a** Liao River; **b** Hun River; **c** Taizi River; and **d** Daliao River

Table 2 The comparison of total PAH concentrations in the surface sediments from different rivers in China

Location	Range (μg/kg)	Mean (μg/kg)	References
Yellow River	464–2621	1414	Xu et al. 2007
Huai River	62.9–2232.4	1056.8	Fu et al. 2011
Huangpu River	313–1707	1154	Liu et al. 2008
Tianjing River	787–1943000	10980	Shi et al. 2005
Tonghui River	127–928	540	Zhang et al. 2004
Songhua River	68.3–654.2	234.2	Zhao et al. 2014
Pearl River	1434–10811	4892	Mai et al. 2002
Xiangjiang River	190–983	452	Zhang et al. 2013b
Yangtze River(Wuhan)	72.4–3995.2	1334.5	Feng et al. 2007
Liaohe River Basin	82.5–25374.4	3149.2	This study

Source identification of PAHs

PAH isomeric ratios based on the relative abundance of individual PAH or groups of PAHs have been practically used to identify the potential sources of PAHs. In this study, two specific ratios of FLA/(FLA+PYR) and ANT/(ANT+PHE) were calculated to trace the possible sources of PAHs, and the PAH cross-plot is displayed in Fig. 3. A Flu/(Flu+Pyr) ratio <0.5 corresponds to the petroleum combustion; >0.5 represents biomass combustion (grass, wood, or coal). In the whole basin, all ratios of FLA/(FLA+PYR) were above 0.5 except one site indicating that the combustion of biomass and coal was the primary source of PAHs. This result is due to the energy consumption in China with the dominance of coal. In addition, biomass burning is very common in the villages of northeast China. The ANT/(ANT+PHE) ratio of 0.1 is defined as the petrogenic/pyrogenic origin transition point. In Liao River, the ANT/(ANT+PHE) ratios ranging from 0.02 to 0.05 implied the petrogenic origins, while the ratios at most sites of the Daliao River system sediments were above 0.1 suggesting the pyrogenic origins. The results were consistent with the PAH composition profile and further confirmed the discharge inputs of PAHs from factories along the Daliao River system. As discussed above, mixed sources contributed to the PAH pollution of Liaohe River Basin.

Toxicity assessment based on the empirical and mechanistic SQGs

The potential hazard of PAHs in sediments to benthic organisms was assessed based on the empirical and mechanistic SQGs. In this study, the empirical SQGs utilized consensus-based threshold and probable effect concentrations (TEC and PEC) to predict the adverse effects. TEC values represent a concentration below which harmful effects on sediment-dwelling organisms rarely occur, whereas PEC values represent a concentration above which adverse effects are expected to frequently occur. At levels between TEC and PEC values, there will be an occasional adverse effect. The numerical values of the guidelines are provided in Table 1. Due to the wide range of TOC values in the sediments of Liaohe River Basin (0.14–10.51 %), PAH levels were normalized to 1 % TOC except for sediments containing organic carbon <0.2 %. The low contents of organic carbon indicated that factors other than TOC were more important in determining the partitioning of PAHs to the pore waters (Di Toro et al. 1991). The mean TOC-normalized $\sum PAH_{16}$ values in this basin ranged from 0.15 to 6.7 µg/g$_{oc}$ (Fig. 4). Compared with guideline values, it is obvious that no sediments contained PAHs whose total levels exceeded the PEC value of 22,800 µg/kg. Nine sites in the Daliao River system had mean normalized $\sum PAH_{16}$ ranging between TEC (1610 µg/kg) and PEC values.

Fig. 3 Cross plot for the diagnostic ratios of ANT/(ANT+PHE) vs FLA/(FLA+PYR) in the sediments of Liaohe River Basin

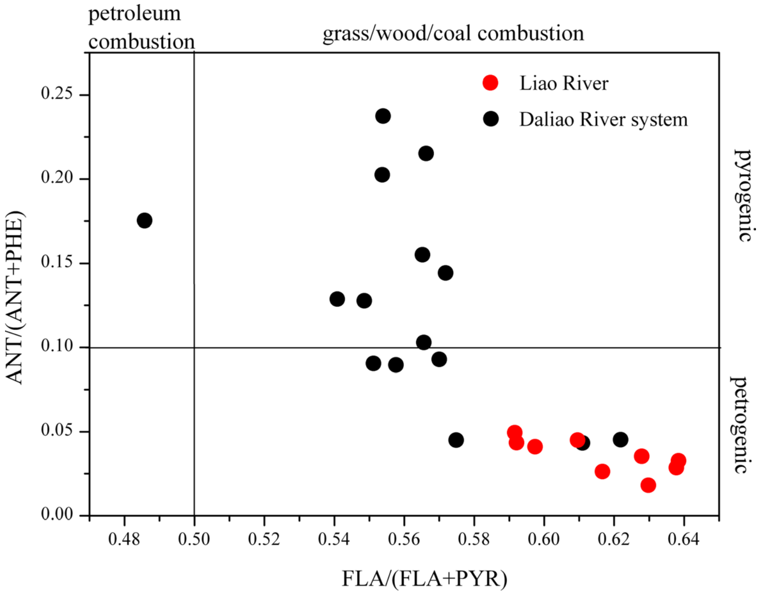
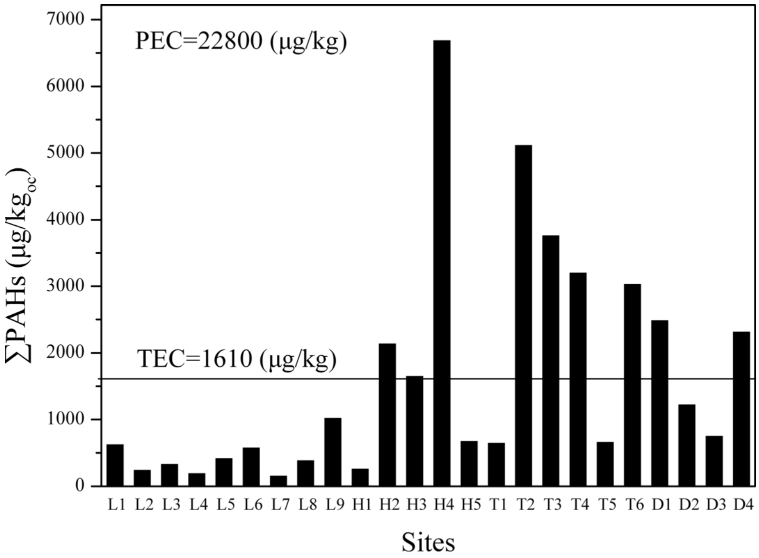


Fig. 4 The mean TOC-normalized $\sum PAH_{16}$ levels in Liaohe River Basin



Therefore, adverse biological effects related to PAHs would rarely occur for most sites whereas at the nine sites potential toxicity risk would occur occasionally. The distribution of the nine sites further emphasized the impacts of industrial and human activities on the PAH pollution and toxicity. For the individual PAH analytes, sediments in Liao River rarely exceeded their respective TEC values, except for naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), and PHE. In the Daliao River system, most sites had TEC exceedances for individual three-ring and four-ring PAHs, which may be possibly toxic to biota. Only ACE whose levels at T2, T6, and D1 were greater than the PEC value of 88.9 μg/kg, indicating its hazard to benthic fauna. As a constituent of coal tar, tobacco smoke, and automobile exhaust, ACE generated by combustion or pyrolysis of fossil fuels should deserve more attention (Pothuluri et al. 1992). In conclusion, sediments containing PAHs in Liaohe River Basin were either nontoxic or lowly toxic to benthic organisms.

The mechanistic SQGs utilized the equilibrium partitioning sediment benchmarks (ESB) derived for PAH mixtures (USEPA, 2003). Organic carbon is an important factor controlling the bioavailability of PAHs in sediments, so TOC-normalized concentrations were obtained as the bioavailable fractions (Ololade 2010; Veses et al. 2012). The PAH-specific final chronic value (FCV) was used as the narcosis-based toxicity effect concentration and summarized in Table 1. A TU for each individual PAH was defined as the bioavailable concentration of a specific PAH divided by FCV. Based upon the additive effects, the ΣESBTU for PAH mixtures were computed and the equation was expressed as follows:

$$\sum ESBTU = \sum_{i} \frac{COC, PAHi}{COC, PAHi, FCVi}$$

where $C_{OC,PAHi}$ is the TOC-normalized PAH concentration in sediments (μg/g$_{oc}$) and $C_{OC,PAHi,FCVi}$ is an effect concentration, above which a PAH will cause the sublethal toxicity (μg/g$_{oc}$).

The ESB for PAH mixtures were designed for a total set of 34 PAHs; however, only 16 PAHs were analyzed in this study. To prevent the underestimation of mixture toxicity, ∑ESBTU values for 13 PAHs (DahA, BghiP, and IcdP were excluded from the calculations) were multiplied by an uncertainty factor of 11.5 to obtain an estimation of ∑ESBTU for 34 PAHs ($\sum ESBTU_{34}$) with 95 % confidence (USEPA, 2003). The benchmark value for the protection of sensitive benthic organisms is considered to be 1. In sediments in which $\sum ESBTU_{34} > 1$, sediment toxicity caused by PAHs may occur. The obtained $\sum ESBTU_{34}$ values in this study were far less than 1 (0.004–0.098); hence, sediments were not likely to exhibit chronic toxicity to benthic organism exposure from PAHs. However, a high amount of uncertainty is associated with the predicted $\sum ESBTU_{34}$ based on the measurement of only parent PAHs. Sediment toxicity to benthic organisms might occur owing to the presence of unanalyzed PAHs, such as the PAH derivatives (nitro-, oxy-, and hydroxy-PAHs) (Hawthorne et al. 2006). It can be seen that consensus-based guidelines and ΣESBTU for PAH mixtures lead to the comparable results for the studied sediment samples. Definite conclusion was drawn from the two assessment methods that benthic organisms inhabiting in the sediments of Liaohe River Basin had no or low risk of toxic effects resulting from exposure to PAHs.

Generally, the empirical SQGs seek to predict whether sediment will be toxic, while mechanistic SQGs determine if a specific contaminant or mixture may be bioavailable to cause toxic effect (Burgess et al. 2013). The combination of empirical and mechanism approaches can be complemented with each other and will provide more reliable results about the estimation of adverse effects. They can also be used to prioritize sites in terms of their toxicity, thereby supporting the pollution control and biological resource protection. Though simple, inexpensive, and effective, the SQG approaches have some limitations, such as without considering the potential for bioaccumulation and trophic transfer of contaminants to aquatic life, and the interactions between contaminations (Weinstein et al. 2010). As a result, the application of sediment toxicity or bioaccumulation tests will increase confidence in the predictive ability of SQG approaches for the future ecotoxicity risk assessment.

Conclusions

In this study, 16 PAHs in the sediments of Liaohe River Basin were investigated and possible toxicity to benthic organisms was evaluated. High concentrations of PAHs were found in the sediments of this basin, and mixed inputs from petrogenic and pyrolytic origins were responsible for the contamination. Although high levels of PAHs were identified, benthic organisms inhabiting in sediments had no or low risk of toxic effects resulting from exposure to PAHs based on the empirical and mechanistic SQGs. The two methods give the consistent and definite results of PAH toxicity evaluation. SQGs combined with sediment toxicity or bioaccumulation tests could be helpful to fully understand the toxic effects of PAHs in sediments. This study will offer effective reference to develop management strategies for PAH control in the future.

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