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Distributions and potential sources of polycyclic aromatic hydrocarbons in surface sediments from an emerging industrial city (Xinxiang)

Jinglan Feng · Nannan Xi · Fei Zhang · Jiahui Zhao · Pengtuan Hu · Jianhui Sun

Abstract To investigate the distributions, degree, and possible sources of polycyclic aromatic hydrocarbons (PAHs) in bed sediments from four rivers of Xinxiang, 18 sediment samples were analyzed. The concentrations ranged from 4.45×10^3 to 29.0×10^3 ng/g for $\sum$15PAHs (sum of US Environmental Protection Agency (EPA) priority PAHs apart from naphthalene (Nap)) and 3.37×10^3 to 23.5×10^3 ng/g for $\sum$7carPAHs (including benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), and indeno[1,2,3-cd]pyrene (InP)) with average concentrations of 10.7×10^3 and 7.99×10^3 ng/g, respectively. Compared with those from other rivers in China, sediments from four rivers of Xinxiang were severely polluted with PAHs. Pearson correlation analysis showed that $\sum$15PAHs concentrations had a significant positive correlation with black carbon content. Four- to six-ring PAHs accounted for 83.4 % of total PAHs, which indicated that the main source of PAHs in the studied area could be pyrogenic contamination. Source apportionment using PCA/MLR and UNMIX revealed that coal and biomass combustion contributed 64.4–67.1 %, gasoline vehicle 23.2–27.2 %, and diesel vehicle 5.70–12.4 % of the total PAHs, respectively. The effects range low/effects range median (ERL/ERM) values showed that there was a high level of toxicity risk for BaA. The ecological risk assessment by mean effects range median quotients (*mERMQ*) revealed a medium ecological risk of $\sum$15PAHs in sediments from four rivers of Xinxiang, manifesting that a close attention should be paid to pollution of PAHs in the studied area.

Keywords PAHs · Surface sediment · Xinxiang · Distribution characteristics · Source apportionment · PCA/MLR · UNMIX · *mERMQ*

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), ubiquitous environmental contaminants, are a large group of chemicals composed of multiple aromatic rings fused together (Neff 1979). Due to their toxic, carcinogenic, and mutagenic characteristics, PAHs have raised great concerns around the world and 16 of them are included in the priority pollutants list of the US Environmental Protection Agency (USEPA) (Brown and Maher 1992; Pereira et al. 1996; Yang 2000; Lima et al. 2003). PAHs could be introduced into the environment through natural processes and anthropogenic activities (Harrison et al. 1996; Mai et al. 2003). Anthropogenic activities, which are generally considered to be the major sources of PAHs, release PAHs mainly to the atmosphere through various ways and eventually deposit in soils

or sediments of aquatic systems (Christensen et al. 1997). In such a way, sediments represent the most important reservoirs of PAHs in the environment (Budzinski et al. 1997), which are a source of PAH exposure directly or indirectly (e.g., via resuspension) to benthic organisms. As these chemicals are biologically available, PAH-contaminated sediments could adversely affect biota or result in high concentrations in the tissues of indigenous organisms (Meharg et al. 1998; Kipopoulou et al. 1999). Due to their high lipophilicity, PAHs are also preferentially accumulated in the lipids of organisms (Huang et al. 2012). It is well known that even moderate concentrations of certain PAHs in the sediments could pose a detrimental threat on aquatic organisms (Wang et al. 2010a).

Most of the previous studies indicate that high-level PAHs in the sediments are recorded at the highly industrialized and urbanized locations (Guo et al. 2007). PAH pollution in Xinxiang may be a potential major environmental problem. Xinxiang locates in the north of Henan Province, China, and is one of the primary industrial bases in Henan Province. Accordingly, Xinxiang has hosted development associated with a wide range of industrial sectors, including electric power industry, chemicals, coal chemical industry, construction materials, textiles, and pharmaceuticals. The growth of the GDP in recent years is over 14.0 % per year. In addition, over the past 30 years, the builtup area of Xinxiang increases from 34.2 km^2 to approximately 100 km^2. With the rapid industrialization and urbanization, intensive human activities and large energy consumption are likely to introduce a large quantity of chemical pollutants (such as PAHs) to the surface water and then pose a threat to the local aquatic system and human health.

The objectives of this study are as follows: (1) to investigate the PAH levels in bed sediments from four rivers of Xinxiang, (2) to identify their possible sources, and (3) to determinate the potential ecotoxicological impact of PAHs due to the urbanization and economy expansion in this studied area.

Experimental methods

Sample collection

Eighteen bed sediment samples (0–20 cm) were collected from four rivers of Xinxiang using a stainless grab sampler (Eijkelkamp, Netherlands) in January 2007.

Meanwhile, handheld GPS was used to determine the geographical coordinates of sample sites, which were plotted in Fig. 1. All sediment samples were freeze-dried after being transferred to the laboratory, and then kept in the dark glass bottles and stored at −18 °C until analysis.

Experimental materials

A mixed standard of 16 US EPA priority PAHs was purchased from Ultra Scientific Inc. (North Kingston, RI, USA). The priority PAHs include naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), benzo[ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (InP). Naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} used as surrogate standards were obtained from Ultra Scientific Inc. (North Kingston, RI, USA). In addition, hexamethylbenzene (99 %) used as an internal standard was bought from Aldrich Chemical, Gillingham, Dorset, USA. Solvents used in the experiment including dichloromethane, n-hexane, methanol, and acetone were HPLC grade. Silica gel (80~100 mesh) and anhydrous sodium sulfate (analytical grade) were baked at 450 °C for 4 h before use.

PAH analysis

The pretreatment procedure of PAHs in the sediments was a modification of the method described previously (Sun et al. 2009). Fifteen grams of freeze-dried, homogenized sediment, which was spiked with a known amount of surrogate standards, was Soxhlet-extracted for 48 h with 120 mL of dichloromethane. Two grams of activated Cu was added for desulphurization. The extracts were concentrated to 1–2 mL by a rotary evaporator and subject to a solvent exchange to hexane. The concentrated extract was passed through a 1:2 alumina/silica gel glass column with 1 cm anhydrous sodium sulfate on the top for cleanup and fractionation. Elution was performed with 70 mL hexane/dichloromethane (7:3, v/v). Elutes were concentrated to 1–2 mL, subject to a solvent exchange to hexane, and then concentrated to 0.2 mL with a gentle stream of purified nitrogen. The internal standard was added to the sample prior to GC-MS analysis.
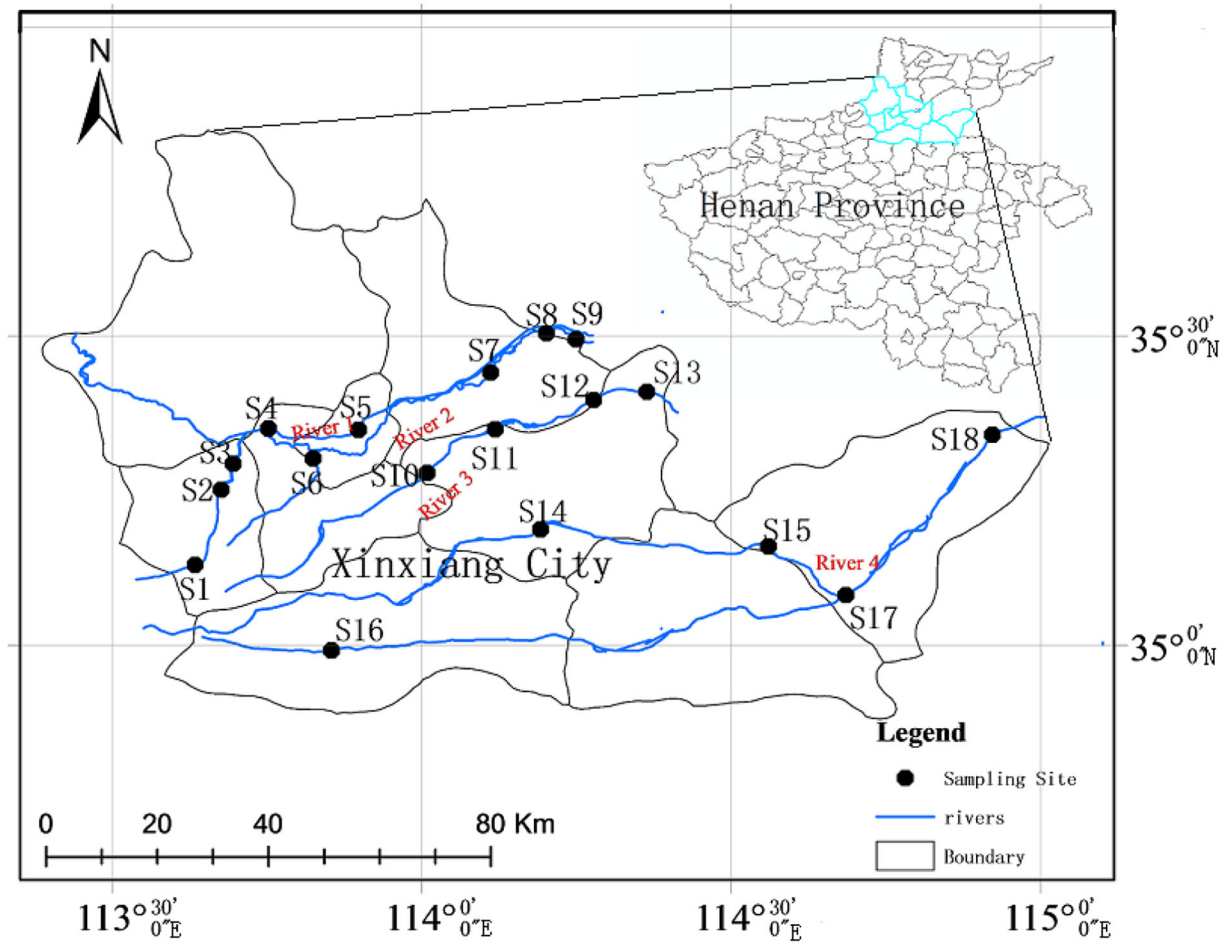
Fig. 1 Sampling sites in the studied area.

PAHs were quantified on a Hewlett-Packard 5890 gas chromatography coupled with 5972 mass selective detector (GC-MSD). The separation column was a HP-5MS fused silica column (30 m × 0.25 mm × 0.25 μm). Instrumental conditions were as follows: The injector port was maintained at 280 °C. Column temperature was programmed to increase from 60 °C (hold for 2 min) to 290 °C at 3 °C/min and then was held isothermal for 30 min. The carrier gas was helium at a constant flow rate of 1.0 mL min^{-1}. One microliter of each sample was injected in the splitless mode. The MSD was operated in the electron impact mode at 70 eV, and the ion source temperature was 180 °C. The mass scanning ranging between m/z 50 and m/z 500 was used for quantitative determinations, and concentration of individual PAHs was obtained by the six-point calibration curve.

Analytical quality control

All analytical data were subjected to strict quality control procedures. Procedural blanks, spiked blanks, matrix spiked duplicates, and sample duplicates were analyzed routinely with field samples. Deuterated surrogate standards were used to monitor procedural performance and matrix effects. Surrogate standards in sediment samples were determined with good precision. The mean recoveries of naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, chrysene-d$_{12}$, and perylene-d$_{12}$ were 41.7 ±7.57, 61.3±6.33, 86.7±9.21, 92.4±12.0, and 102±10.9 %, respectively. The method detection limit (MLD) of PAHs ranged from 0.56 to 3.07 ng g^{-1}. Each of the 18 sediment samples was analyzed in duplicate and relative standard deviations were less than 10 %.

Black carbon

Three grams of sediment from each sample was placed in 50-mL Teflon centrifuge tubes. The sediments were first treated with 3 mol/L HCl (48 h) and followed with 10 mol/L HF and 1 mol/L HCl (12 h). The acid-treated sediments were then oxidized using a mixing solution of 0.1 mol/L $K_2Cr_2O_7$:2 mol/L H_2SO_4 for 200 h at 25 °C to remove organic matter according to Masiello and Druffel (2001). After the oxidation steps, sediments were centrifuged, washed three times with Milli-Q water, and dried at 60 °C. Organic carbon left after this oxidation step was operationally defined as black carbon (BC), and the content was measured using a PE-2400 elemental analyzer (PerkinElmer 2400, USA).

Receptor models

Receptor models, such as principal component analysis (PCA)–multiple linear regressions (MLR) and UNMIX model, may assist in the identification of PAH sources and quantify their relative contributions to the receptor (Hopke 2003; Sofowote et al. 2008; Li et al. 2009; Zhang et al. 2012).

PCA/MLR

PCA/MLR is widely used to quantitatively determine sources of PAHs in the sediments (Zhang et al. 2012). Factor loadings and score matrices can be obtained through the input of PAH concentrations dataset (Eq. (1)):

$$X = L \times T \tag{1}$$

where X is the concentration matrix of PAHs, L is the factor loading matrix, and T is the factor score matrix. The potential sources of PAHs in the sediments can be determined by the factor loading matrix. Mass apportionment of possible sources to the total PAHs in each sample is obtained through MLR analysis, which uses the total concentrations of PAHs as the dependent variable and the factor scores of each source as the independent variable. A MLR of elements in the factor score matrix (t_k) against the normal standard deviation (Z) of the total PAH concentration is carried out to obtain the best correlation between observed and predicted total PAH concentration for each sample (Eq. (2)). The coefficients (B_k) of each factor are determined by the MLR

with a stipulated minimum 95 % confidence limit. The mean percent contribution of each source is calculated using Eq. (3):

$$Z_{\sum\text{PAHs}} = \sum B_k \times t_k \tag{2}$$

mean contribution of source $k(\%)$

$$= B_k \Big/ \sum B_k \times 100 \tag{3}$$

UNMIX

Unmix model is a PCA-based receptor model with nonnegative constraints, indicating that negative results would not be obtained by UNMIX model. For a dataset with n samples and m PAHs, UNMIX model first decreases the number of sources by performing a singular value decomposition of the data matrix. And then, UNMIX further reduces source compositions by projecting the dataset to a plane perpendicular to the first axis of N-dimensional space, which the edges of the projected data suggest the samples that determine the sources (Larsen and Baker 2003). Further details of the Unmix model can be found in the references (Larsen and Baker 2003; Zhang et al. 2012). In this work, EPA Unmix 6.0 model was used.

Ecological risk assessment

Ecological risks of PAHs in the sediments from four rivers of Xinxiang were evaluated by applying the effects range low (ERL) and effects range median (ERM) thresholds, which were established using the 10th and 50th percentiles in a database of increasing concentrations associated with adverse biological effects, respectively (Long et al. 1998). PAH concentrations below ERL were considered not to be harmful to organisms, while those above ERM were considered to be harmful frequently. PAHs with concentrations between ERL and ERM were considered to be harmful occasionally. In addition, calculation of the mean effects range median quotients ($mERMQ$) (Long et al. 1998, 2000, 2006), according to the formulas (4) and (5), provided a quantification of the probability for significant harmful effects on the ecosystem

in the studied area due to the synergistic action of individual PAHs:

$$mERMQ = \left(\sum_{i=1}^{n} ERM{-}Q_i \right) \Big/ n \qquad (4)$$

$$ERM{-}Q_i = \frac{C_i}{ERM_i} \qquad (5)$$

where C_i is the actual measured concentrations of individual PAHs, ERM_i is the ERM thresholds of individual PAHs, ERM-Q_i is the ERM quotients of individual PAHs, and n is the number of PAHs. In reference to literature (Long et al. 1998, 2000, 2006), four relative priority levels for contaminated areas had been defined: (a) high ($mERMQ > 1.5$), (b) medium high ($1.5 > mERMQ > 0.51$), (c) medium low ($0.5 > mERMQ > 0.11$), and (d) low ($mERMQ < 0.1$).

Data analysis

All statistical analyses were performed using EXCEL 2010 (Microsoft Inc., Redmond, WA, USA) and SPSS 13.0 (SPSS Inc., Chicago, IL, USA). Before statistical analysis, Kolmogorov–Smirnov (K–S) test is carried out to test the frequency distribution of PAH concentrations, which suggest that all of the variables achieve a normal distribution with $p > 0.05$.

Results and discussion

Levels of PAHs in the sediments

The concentrations of PAHs in sediments from Xinxiang surface water are summarized in Table 1. As shown in Table 1, the detectable proportion of 16 PAHs was up to 100 %. However, due to its high abundance in the solvent blank, naphthalene had to be excluded from the target list. The sum of the other 15 PAHs and 7 carcinogenic PAHs (including BaA, Chr, BbF, BkF, BaP, DBA, and InP) is defined as $\sum$15PAHs and $\sum$7carPAHs, respectively. In the sediments from Xinxiang surface water ($n = 18$), the concentrations of $\sum$15PAHs ranged from 4.45×10^3 to 29.0×10^3 ng/g with a mean concentration of 10.7×10^3 ng/g. The concentrations of $\sum$7carPAHs were in the range of $3.37 \times 10^3 \sim 23.5 \times 10^3$ ng/g, with an average concentration of 7.99×10^3 ng/g, responsible for 52.3 to 81.6 % of

Table 1 Concentration of PAHs in sediments from four rivers of Xinxiang (ng/g)

PAHs	Content		
	Min	Max	Mean
Acy	14.1	1.89×10^3	687
Ace	45.1	867	347
Flu	42.9	308	105
Phe	155	3.54×10^3	775
Ant	67.4	1.01×10^3	408
Flua	60.9	1.27×10^3	325
Pyr	40.1	736	277
BaA	1.92×10^3	15.5×10^3	6.28×10^3
Chr	63.9	991	274
BbF	55.0	835	185
BkF	53.9	5.96×10^3	568
BaP	61.5	653	229
DBA	53.6	723	207
BghiP	88.8	2.04×10^3	359
InP	55.8	647	248
$\sum$15PAHs	4.45×10^3	29.0×10^3	10.7×10^3

the $\sum$15PAHs. In reference to Baumard et al. (1998), the contamination levels of PAHs in sediments could be classified into four groups: low (0~100 ng/g), moderate (100~1000 ng/g), high (1000~5000 ng/g), and very high (>5000 ng/g). Based on these definitions, most sample sites from Xinxiang surface water were severely contaminated with PAHs. Levels of PAHs in the sediments from four rivers of Xinxiang were only lower than those found in the Tianjing River (Shi et al. 2005) and Haihe river (Tianjing section) (Jiang et al. 2007), but higher than in most of other large rivers or coastal areas (such as Huaihe River, Qiantang River, Minjiang River, Daliao River watershed, Aojiang River, Pearl River, Huangpu River, Songhua river (Jilin section), Yellow River, Yangtze River, Tonghui River, Yangtze estuary, Qingtao coastal area, Zhejiang coastal areas, and Zhoushan coastal area) in China (Table 2) (Mai et al. 2002; Zhang et al. 2003; Zhang et al. 2004; He and Yan 2006; Chen et al. 2007; Guo et al. 2007; Feng et al. 2007; Liu et al. 2008; Sun et al. 2009; Yu et al. 2009; Li et al. 2010; Wang et al. 2010a; Chen et al. 2014; Jiang et al. 2014; Liu et al. 2014; Mu et al. 2015). Generally, levels of PAHs in sediments from four rivers of Xinxiang ranked as very high levels, which should arouse the attention of the authorities. This was

Table 2 Comparisons of $\sum$PAHs in sediments from rivers in different areas in China (ng/g)

| Rivers	Concentrations			References
	n	Range	Mean	
Xinxiang surface water	15[a]	$4.45 \times 10^3 \sim 29.0 \times 10^3$	10.7×10^3	This study
Tianjing River	16[b]	$787 \sim 1.94 \times 10^6$	11.0×10^3	Shi et al. (2005)
Haihe River	16[b]	$775 \sim 255 \times 10^3$	27.1×10^3	Jiang et al. (2007)
Huaihe River (M and L)	16[b]	$31.1 \sim 1.01 \times 10^3$	294	He and Yan (2006)
Qiantang River	15[c]	$91.3 \sim 614$	313	Chen et al. (2007)
Mingjiang River	16[b]	$112 \sim 877$	433	Zhang et al. (2003)
Daliao River watershed	18[d]	$619 \sim 841$	287	Guo et al. (2007)
Aojiang River	15[c]	$491 \sim 883$	n.r.	Li et al. (2010)
Qingtao coastal area	16[b]	$256 \sim 1.88 \times 10^3$	685	Wang et al. (2010b)
Pearl River	16[b]	$597 \sim 10.8 \times 10^3$	n.r.	Mai et al. (2002)
Huangpu River	16[b]	$313 \sim 1.71 \times 10^3$	1.15×10^3	Liu et al. (2008)
Yellow River (middle and lower reaches)	16[b]	$16 \sim 1.36 \times 10^3$	182	Sun et al. (2009)
Yellow River (Lanzhou)	16[b]	$464 \sim 2.62 \times 10^3$	1.42×10^3	Yu et al. (2009)
Yangtze River (Wuhan)	16[b]	$72.4 \sim 4.00 \times 10^3$	1.34×10^3	Feng et al. (2007)
Tonghui River, Beijing	16[b]	$127 \sim 928$	540	Zhang et al. (2004)
Haihe River	16[b]	$92.9 \sim 15.9 \times 10^3$	5.88×10^3	Liu et al. (2014)
Yangtze estuary and Zhejiang coastal areas	16[b]	$31.8 \sim 384$	131	Mu et al. (2015)
Songhua River (Jilin section)	16[b]	$1.19 \times 10^3 \sim 1.63 \times 10^3$	1.35×10^3	Chen et al. (2014)
Zhoushan coastal area	16[b]	$1.02 \times 10^3 \sim 3.05 \times 10^3$	2.02×10^3	Jiang et al. (2014)

Note: 15[a] , including 16 US EPA priority PAHs, apart from Nap; 16[b] , including 16 US EPA priority PAHs; 15[c] , including 16 US EPA priority PAHs, apart from Acy; 18[d] , including 16 US EPA priority PAHs plus 2-methylnaphthalene and 1-methylnaphthalene; n.r., not reported in the references

probably due to the rapid industrialization and urbanization in the studied area, which resulted in the large consumption of fossil fuel.

Distributions of PAHs in the sediments

Spatial differences of PAHs levels in sediments from four rivers of Xinxiang were investigated and plotted in Fig. 2. As shown from Fig. 2, PAHs varied significantly at different sampling locations. An increasing trend in concentrations of PAHs was observed from the sites S1 to S5 (river 1), whereas the concentrations of PAHs decreased from S10 to S13 (river 3; Fig 2). As for river 2 (S6~S9) and river 4 (S14~S18), irregular fluctuations of PAH levels were recorded along the river. The relatively high PAH concentrations in the studied area were measured from sites S4 and S5, which are located in the river 1. This river flows across Huojia County and Huixian County of Xinxiang, where a large cement

plant and an aluminum manufacturer exist. Therefore, relatively high PAH levels may mainly originate from these industrial waste discharges. In addition, the same trend for $\sum$7carPAHs was observed in this study (Fig. 2). There are many factors affecting PAH levels in the sediments, such as physicochemical properties of PAHs and sediment composition. Black carbon was considered as an important factor affecting PAH distributions in the sediments in the previous study (Sánchez-Garcíaa et al. 2010). The BC contents in the sediments from Xinxiang surface water were measured to range from 0.40 to 25.8 mg/g dw. Sediments with higher BC contents generally also contained elevated values of PAHs (S4 and S5; Fig. 2). The corollary was that lower BC contents were also generally observed as PAH levels decreased (i.e., S1 and S15). This trend suggested a coupling between BC and PAHs, as described previously for sediment studies (Gustafsson and Gschwend 1997; Persson et al. 2002; Oen et al. 2006). Pearson
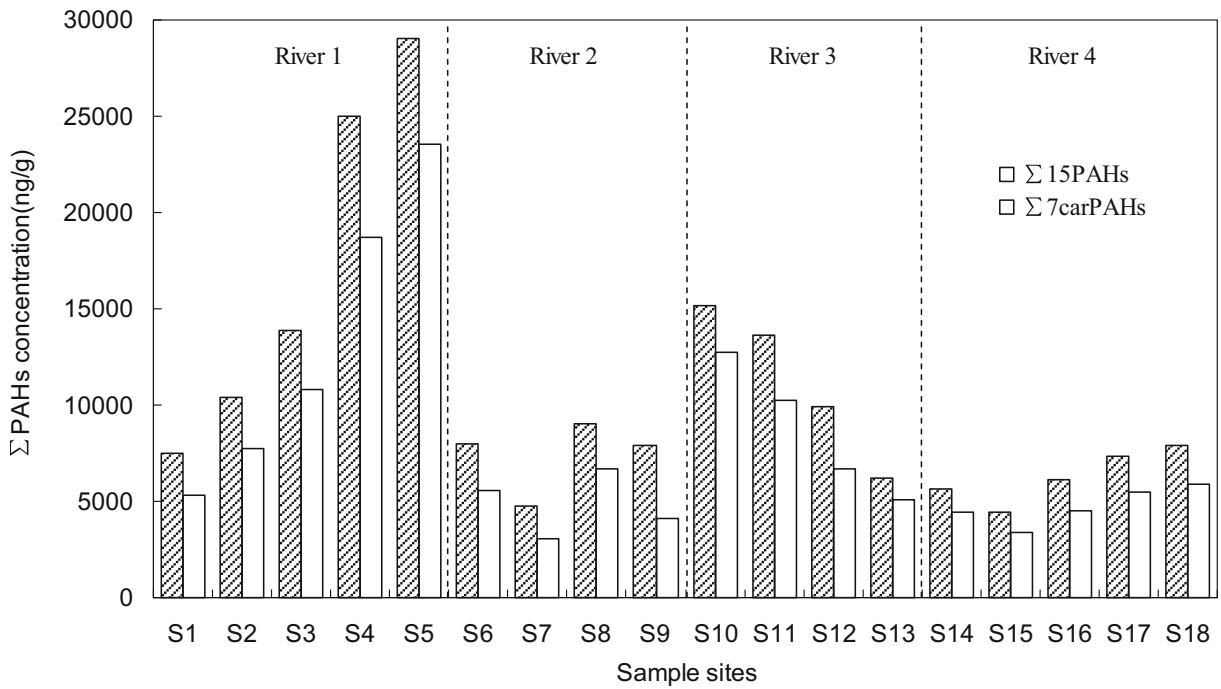
**Fig. 2** Distribution of $\sum$15PAHs and $\sum$7carPAHs in sediments from four rivers of Xinxiang

correlation analysis between $\sum$15PAHs and BC content shows a significant positive correlation ($r = 0.721$, $p < 0.01$) suggesting that BC concentrations may control the distribution of PAHs in the sediments in the studied area.

Composition characteristics of PAHs in surface sediments from Xinxiang

According to the number of aromatic rings, 15 PAHs were divided into four groups: (1) three-ring PAHs
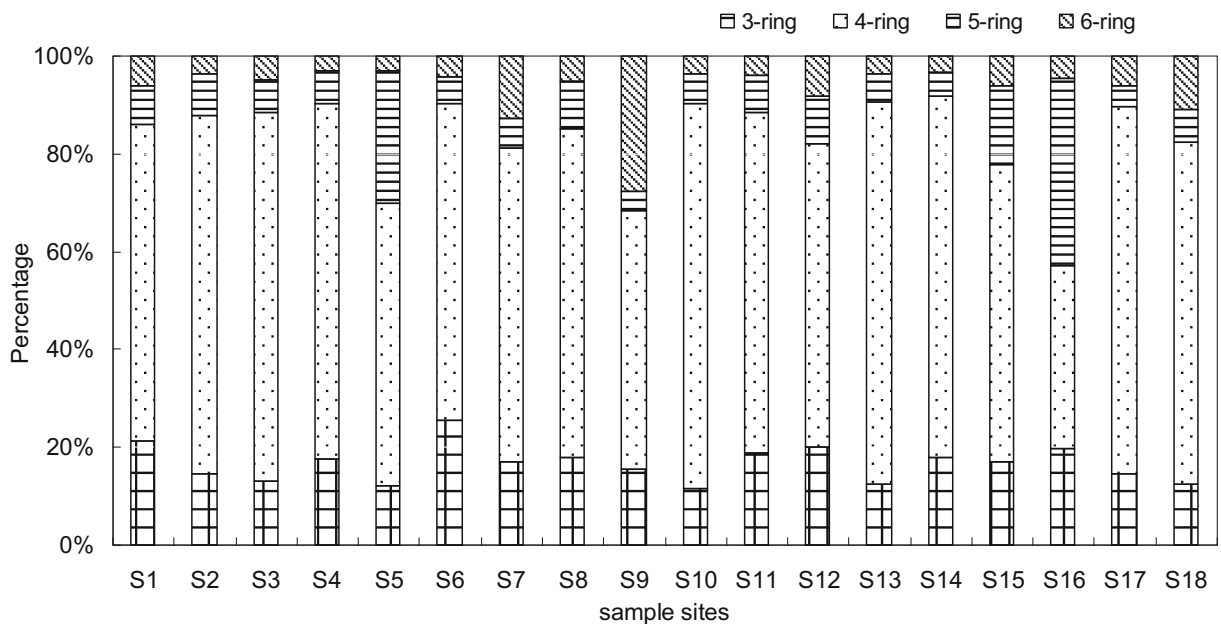
Fig. 3 Composition of PAHs in sediments from four rivers of Xinxiang
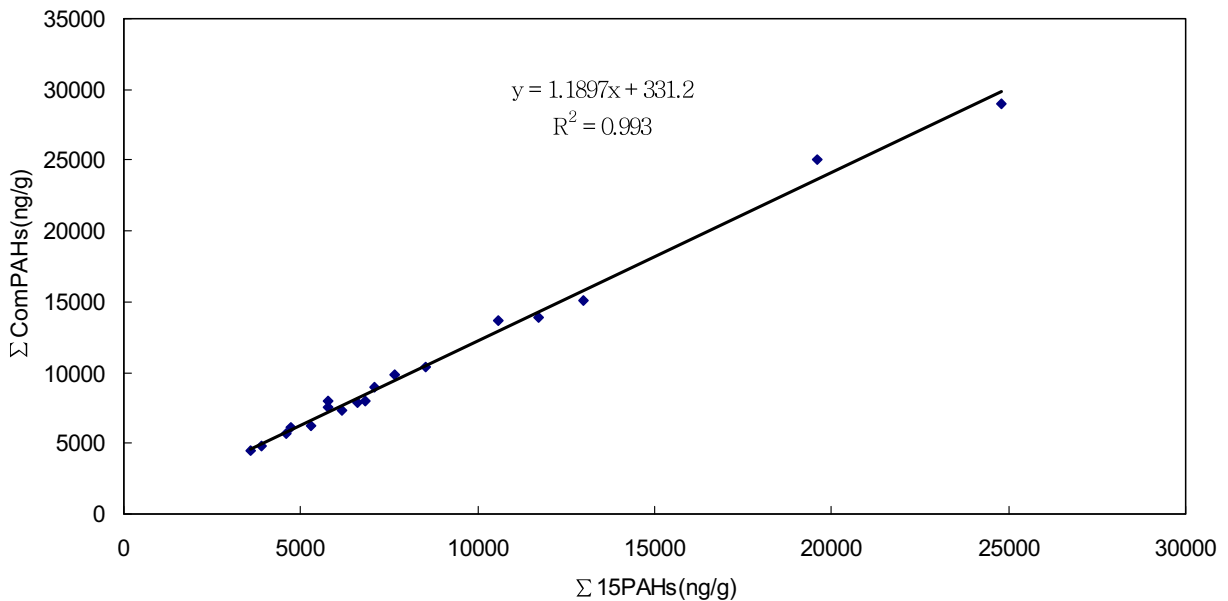
Fig. 4 Correlation between $\sum$15PAHs and $\sum$ComPAHs

(Acy, Ace, Flu, Phe, and Ant), (2) four-ring PAHs (Flua, Pyr, BaA, and Chr), (3) five-ring PAHs (BbF, BkF, BaP, and DBA), and (4) six-ring PAHs (BghiP and InP). Composition profiles of PAHs in sediment samples from four rivers in Xinxiang are illustrated in Fig. 3. As shown from Fig. 3, four-ring PAHs were the most abundant species with the mean of 66.5 % of the total PAHs, followed by three-ring PAHs (16.6 %), five-ring PAHs (10.1 %), and six-ring PAHs (6.72 %). In contrast to PAHs in surface water from Xinxiang (Feng et al. 2015), proportions of high molecular weight PAHs (four- to six-ring) increased while those of low molecular weight (three-ring PAHs) declined in the sediments. This phenomenon could be explained as follows. Due to their relatively low water solubility and high $LogK_{ow}$ and being nonbiodegradable, high molecular weight PAHs were difficult to dissolve, degrade, and transport in water (Hu et al. 2010; Chen and Chen 2011) and could easily reach the sediment and remain for a long period. In addition, PAHs from pyrogenic sources were abundant in high molecular weight PAHs, whereas the reverse was true of petrogenic origins (Zakaria et al. 2002). The predominance of high molecular weight PAHs in the studied area suggested that PAHs primarily derived from pyrogenic origin, such as coal, biomass combustion, or traffic

emission (Yunker et al. 2002). Moreover, the combustion-derived PAH (ComPAH) concentrations (Flua, Pyr, BaA, BbF, BkF, BaP, InP, DBA, and BghiP) (Prahl and Carpenter 1983) significantly correlated with the total PAH concentrations ($p < 0.01$; Fig. 4), further suggesting that pyrogenic PAH sources were important in the sediments from Xinxiang surface water. Furthermore, in reference to Rogge et al. (1993), $\sum$ComPAHs/$\sum$15PAHs were 0.30 for heavy-duty diesel trucks, while 0.41 for noncatalyst-equipped automobiles and 0.51 for catalyst-equipped automobiles. Relatively high $\sum$ComPAHs/$\sum$15PAHs (0.8–0.9) seemed to represent coal combustion (Cecinato et al. 1999). $\sum$ComPAHs/$\sum$15PAHs in the present study varied from 0.587 to 0.872 with average ratio of 0.794, suggesting that a considerable portion of PAHs could originate from coal combustion.

Source apportionment of PAHs in surface sediments

Based on the compositional analysis of PAHs, we have drawn the preliminary conclusion that PAHs in the studied area mainly derived from pyrogenic sources. However, it was only a qualitative diagnosis of the PAH origin (Li et al. 2006; Malik et al. 2011). In the next step, PCA/MLR and UNMIX are used to determine possible PAH sources in the sediments from four rivers

Table 3 Rotated component matrix of PAHs in sediments from four rivers of Xinxiang

PAHs	Factor		
	1	2	3
Acy	0.805	0.219	−0.017
Ace	−0.042	−0.204	−0.801
Flu	0.962	0.063	0.005
Phe	0.882	0.315	−0.033
Ant	0.065	−0.492	0.598
Flua	0.825	0.384	0.010
Pyr	0.654	0.397	0.062
BaA	0.923	0.153	0.050
Chr	0.957	0.158	−0.098
BbF	0.492	−0.072	0.823
BkF	0.309	0.060	0.888
BaP	0.724	0.453	0.006
DBA	0.932	0.055	−0.176
BghiP	−0.118	0.757	−0.066
InP	0.079	0.839	0.353
Estimated source variance	59.1 %	11.1 %	9.20 %
Possible sources	Coal and biomass	Gasoline vehicles	Diesel vehicles

of Xinxiang and quantify their relative contributions. Agreements between the methodologies reinforce the findings, while divergent solutions indicate areas of uncertainty or weakness in the models.
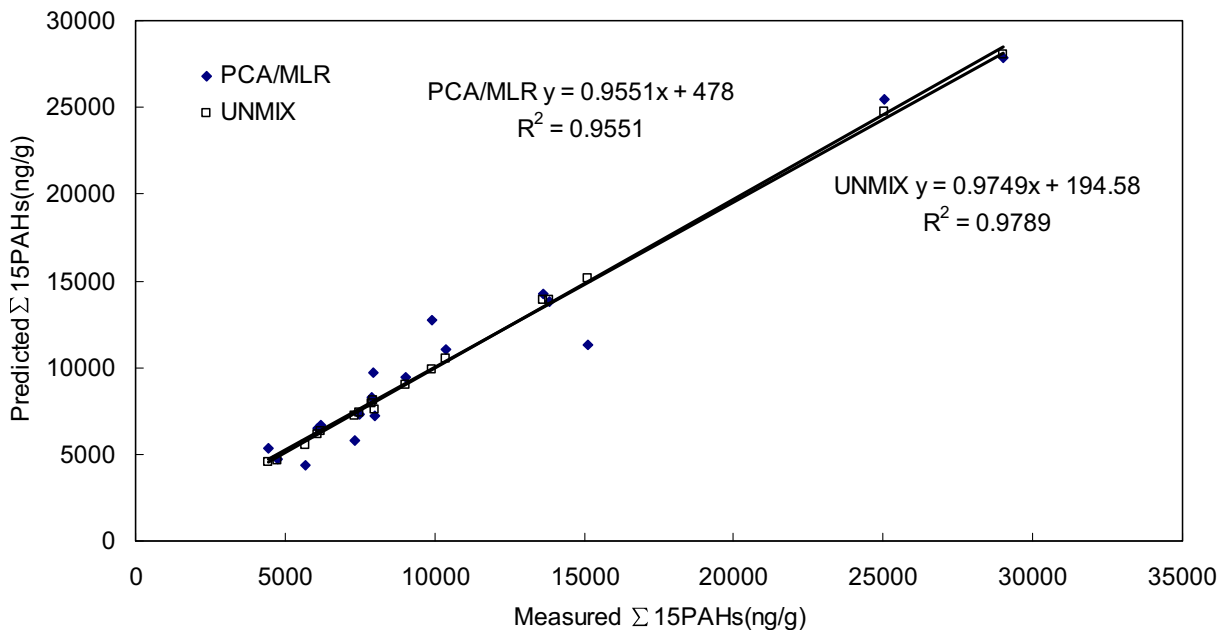
Fig. 5 Comparison of measured PAH concentration with predicted PAH concentration determined by PCA/MLR and UNMIX

Table 4 Source profiles obtained from UNMIX

PAHs	Factor		
	1	2	3
Acy	0.024	0.014	−0.011
Ace	0.149	−0.044	0.103
Flu	0.031	0.013	0.016
Phe	0.188	0.079	−0.008
Ant	0.111	0.192	0.113
Flua	0.078	0.071	−0.012
Pyr	0.106	0.054	−0.057
BaA	0.098	0.047	0.012
Chr	0.088	0.008	0.023
BbF	0.042	0.008	0.080
BkF	−0.013	−0.027	0.724
BaP	0.068	0.013	0.088
DBA	0.076	0.005	−0.011
BghiP	−0.036	0.575	−0.013
InP	0.088	0.038	−0.034
Estimated source	Coal and biomass	Gasoline vehicle	Diesel vehicle

Identification and source apportionment using PCA/MLR

In the present study, 15 PAH concentrations in sediments from four rivers of Xinxiang were used as variables for the PCA, which was conducted using factor extraction with eigenvalues >1 after Varimax rotation. Three factors were extracted, which accounted for 79.4 % of the total variance in the original data set of PAH concentrations (Table 3). As shown in Table 3, factor 1 explained 59.1 % of the total variance in the PAH concentrations data set, which was dominated by Acy (0.805), Flu (0.962), Phe (0.882), Flua (0.825), BaA (0.923), Chr (0.957), BaP (0.724), and Pyr (0.654). Research had shown that Acy, Phe, and Flu were associated with wood combustion (Duval and

Table 5 Average source contributions (%) from PCA/MLR and UNMIX model

Source	PCA/MLR	UNMIX
Coal and biomass burning	67.1	64.4
Gasoline vehicle	27.2	23.2
Diesel vehicle	5.70	12.4

Friedlander 1981; Jenkins et al. 1996; Rogge et al. 1993). In addition, the compounds of Flua, Pyr, BaA, Chr, and BaP were indicative of coal combustion origins (Venkataraman et al. 1994; Larsen and Baker 2003; Sofowote et al. 2008). Based on the above information, factor 1 probably represented a combination of coal combustion and biomass burning. Factor 2 was characterized by high positive loadings (>0.7) on BghiP (0.757) and InP (0.839). According to the source fingerprints summarized in literatures (Harrison et al. 1996), elevated levels of BghiP and InP were tracer of vehicular emissions, especially for gasoline vehicle. Therefore, factor 2 can be attributed tentatively to gasoline vehicle emission. Factor 3 was predominately weighted in BbF (0.823) and BkF (0.888). Emissions from diesel engines might have a more significant contribution to BbF and BkF (Homdutt et al. 2007). Thus, factor 3 may be related to diesel vehicle emission. Based on the PCA analysis, coal combustion, biomass burning, and traffic emission may be the main sources of PAH contamination in sediments from four rivers of Xinxiang. This was consistent with the results of PAHs in road dust from Xinxiang (Feng et al. 2013).

The contributions of each source to the sum of 15 PAH concentrations obtained from MLR were listed in Table 5. Moreover, the ratio of predicted concentrations of PAHs to those measured concentrations was close to 1 (Fig. 5, $R^2 = 0.955$), which suggested that all PAHs were well estimated by the PCA/MLR in this study. As shown from Table 5, the mean percent contribution was 67.1 % for coal and biomass combustion, 27.2 % for gasoline vehicle, and 5.70 % for diesel vehicle, respectively. The result was coinciding with the compositional analysis and the energy structure of Xinxiang. According to the statistical yearbook of Xinxiang (2014), coal was responsible for over 80 % of the total energy consumption and Xinxiang's personal vehicles surpassed 400,000, which resulted in the large consumption of fossil fuel. During the use of fossil fuel, abundant PAHs were introduced into the environment of Xinxiang.

Identification and source apportionment using UNMIX

UNMIX analyses were performed using 15 PAHs from 18 sites in the present study. The estimated PAH concentrations using UNMIX model versus the measured PAH concentrations was compared. Three factors that gave the best fitting ($R^2 = 0.979$) were chosen in the

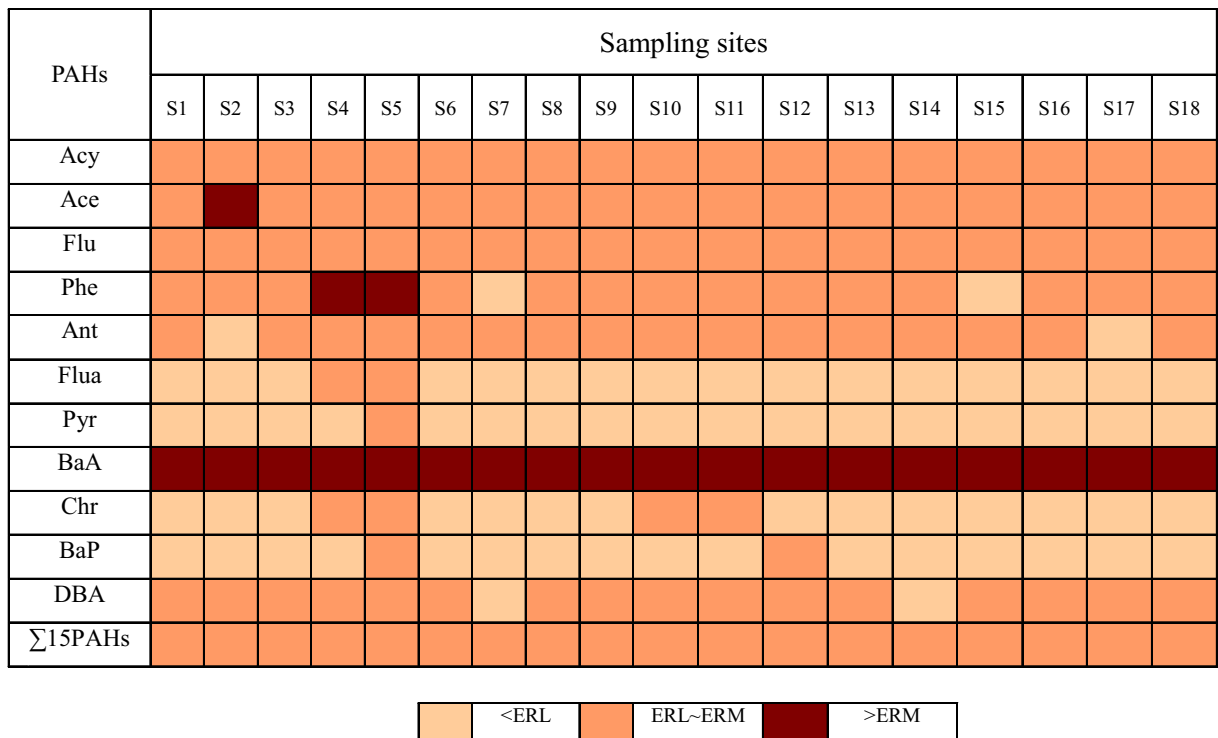| PAHs	Sampling sites																	
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18
Acy																		
Ace																		
Flu																		
Phe																		
Ant																		
Flua																		
Pyr																		
BaA																		
Chr																		
BaP																		
DBA																		
∑15PAHs																		

<ERL   ERL~ERM   >ERM

Fig. 6 Comparison of PAHs in the studied area with ERL/ERM

present study. Each factor was compared with source profiles of PAHs reported in the literature, and the results are shown in Table 4. As shown from Table 4, three distinct sources of PAHs were (1) coal combustion
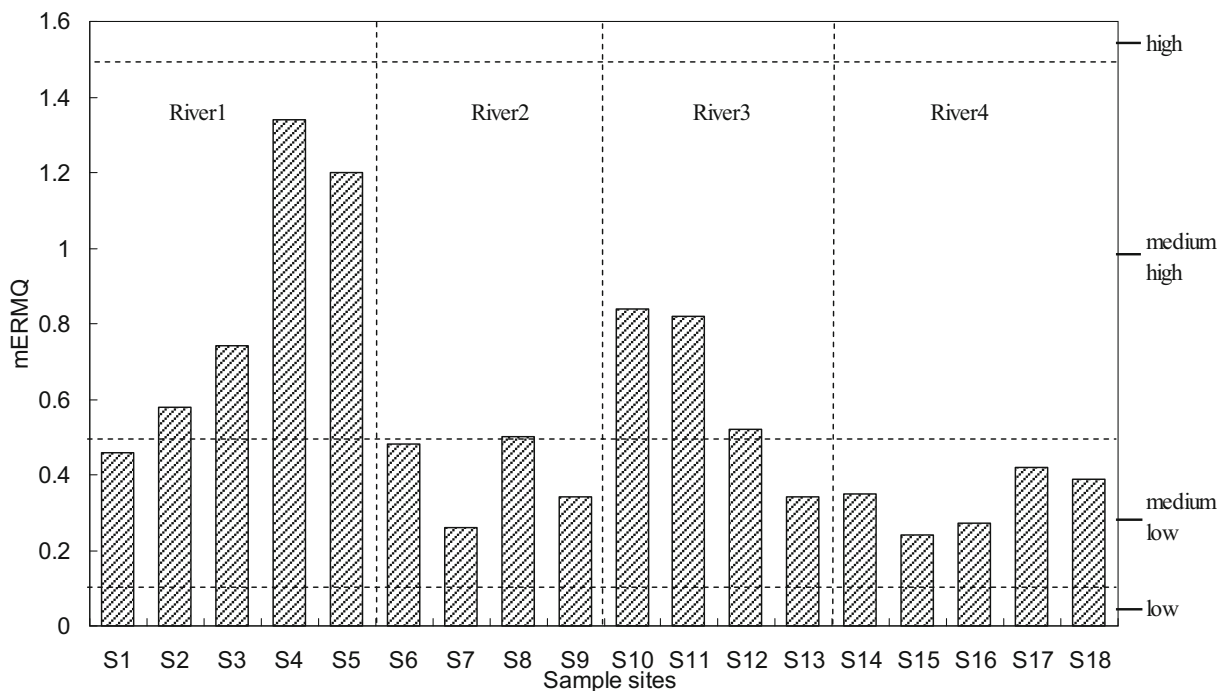
Fig. 7 Spatial distribution of *mERMQ* in the studied area

and biomass burning, (2) gasoline vehicle, and (3) diesel vehicle. Factor 1 was similar to coal and biomass signature with high levels of Ace, Phe, Ant, Pyr, Flua, BaA, and Chr. In a manner similar to the PCA/MLR analysis, it was clear that factor 2 had a gasoline vehicular signature with high levels of InP and BghiP. Factor 3 had high fractions of BbF and BkF, which was attributed to diesel vehicles. The estimated average contribution for three sources was in the order of coal and biomass (64.4 %), gasoline vehicle (23.2 %), and diesel vehicle (12.4 %; Table 5).

The estimated source contributions for PAHs were discussed here with the two receptor models. The measured and estimated total PAH concentrations from PCA/MLR and UNMIX match well with each other based on R^2 values ranging from 0.955 to 0.979 (Fig. 5). In addition, source contributions obtained by PCA/MLR and UNMIX were similar to each other, as shown in Table 5. Coal and biomass combustion were the most significant contribution source (64.4–67.1 %), followed by gasoline vehicle (23.2–27.2 %) and diesel vehicle (5.70–12.4 %).

Ecological risks of PAHs in the studied area

Using the ERL/ERM approach, Σ15PAHs concentrations generally varied between the ERL and ERM thresholds in the studied area (Fig. 6). This suggested the possibility for negative effects on aquatic animals without, however, causing irreversible damages to them. Nevertheless, if individual PAHs were considered, an exceedance of the ERM threshold in the studied area was observed, denoting great risk for irreversible impairment of the aquatic communities. This was primarily due to the excessive contents of BaA in all of the sampling sites. In contrast, Pyr, Flua, and BaP were not capable of posing serious risk to the local ecosystem, since their contents were below the ERL thresholds. As for other PAHs, such as Acy, Ace, Flu, Phe, Ant, and DBA, there were some possibilities for reversible harmful effects, since their loadings exceeded the ERL limit. The calculated *mERMQ* values in the studied area (Fig. 7) revealed that river 1 and river 3 may be considered as of medium high ecological risk while river 2 and river 4 may be classified as of medium low ecological risk.

Conclusion

This study investigated 15 PAHs in the sediments from four rivers of Xinxiang. Total concentrations of PAHs in sediments from Xinxiang surface water ranged from 4.45×10^3 to 29.0×10^3 ng/g with an average concentration of 10.7×10^3 ng/g. In comparison to other rivers in China, the levels of PAH contamination in the studied area ranked relatively high. BC may control the spatial distribution of PAHs at different sampling sites. The four-ring PAHs were the most abundant compounds in the sediments from four rivers of Xinxiang. Compositional analysis suggested that pyrogenic sources were major sources of PAHs. Further analysis using PCA/MLR and UNMIX indicated that coal and biomass combustion contributed 64.4–67.1 %, gasoline vehicle 23.2–27.2 %, and diesel vehicle 5.70–12.4 % of the total PAHs, respectively. The results demonstrated that rapid industrialization and large fossil fuel consumption were predominant factors of PAH pollution in sediments from Xinxiang surface water. Ecological risk posed by PAHs was assessed using ERL/ERM and *mERMQ*, which indicated medium ecological risk level of Σ15PAHs, but with a high risk level of BaA in sediments from Xinxiang surface water.

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