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RESEARCH ARTICLE

Characteristics, source, and potential ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the Songhua River Basin, Northeast China

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Abstract The concentration characteristics, sources, and potential ecological risk assessment of 16 PAHs were investigated in the surface water from the Songhua River Basin, Northeast China. A total of 48 river water samples, including 16 from the main streams and 32 from the tributaries, were collected. Samples were separated into dissolved phases and suspended particle matter (SPM) via filtration with 0.47 μm glass fiber filters. Each phase was analyzed for PAHs. The total PAH concentration in the dissolved phase in the water ranged from 32.5 to 108 ng L^{-1} and from 0.3 to 62.3 μg g^{-1} (dry weight) in the suspended particle matter (SPM). The total PAH concentration in the main stream was lower than in the tributaries; the volume of annual runoff of rivers had a significant effect on the PAH in the rivers. The 2- and 3-ring PAHs dominated in both the dissolved phase and SPM, indicating a relatively recent local source of PAHs in the study area. The concentrations of PAHs in the Songhua River Basin are lower when compared with the values previously reported in the literature from other rivers around the world. The sources of PAHs were assessed by diagnostic ratios and principal component analysis (PCA), and the ecological risk of the PAHs was assessed based on the risk quotient (RQ). The diagnostic ratios and PCA indicated that the main sources of PAHs originated from pyrogenic and petrogenic sources, and pyrogenic sources had a greater impact. The ecological risk assessment indicated that the PAHs presented low ecosystem risk in the Songhua River Basin.

Keywords Songhua River Basin · PAHs · Diagnostic ratio · Principal component analysis · RQ

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Introduction

Due to the carcinogenic and mutagenic potential, polycyclic aromatic hydrocarbons (PAHs) have been identified as priority pollutants by the US Environmental Protection Agency and have attracted a great amount of attention. (Keith and Telliard 1979). PAH compounds are composed of two or more fused aromatic rings which are mainly produced during the incomplete combustion of fossil fuels and petroleum product release. Considering the fact that the major source of PAHs are of anthropogenic origin, they are now one of the ubiquitous pollutants in the environment (Yunker et al. 2002). The PAHs are introduced to aquatic environments through atmospheric deposition (dry and wet), surface runoff, oil leakage, and waste water discharge (Johnsen et al. 2005). These PAHs could

pollute sources of drinking water (Wu et al. 2011a, 2011b). Also, exposure of aquatic organisms (phytoplankton, zooplankton, benthic macrofauna, and fish) that dwell in the polluted aquatic environments to PAH, portends great danger to human health, due to possible bioconcentration and biomagnification of PAHs, as well as the critical role of these organisms in the food chain. (Patrolecco et al. 2010; Guo et al. 2011).

The Songhua River Basin (41°42′–51°38′N, 119°52′–132°31′E; Fig. 1) is the biggest tributary of the Amur River and is the third largest river basin in China, covering an area of 55.72×10^4 km^2. The basin flows through Inner Mongolia Municipality, Heilongjiang, Liaoning, and Jilin Provinces. The Songhua River Basin has two headstreams: the Nen River and the Second Songhua River. The Nen River is the northern headstream and originates in the Daxinganling Mountains. The southern headstream is the Second Songhua River in the Changbai Mountains. After their confluence, the river is called the Songhua River and follows into the Heilongjiang River.

The rainy season spans from June to September and accounts for 85% of annual rainfall. The ice-bound period lasts at least 5 months. The Songhua River Basin is one of the most important agricultural bases of China and is one of the three black soil terrains in the world. The Daqing Oilfield, which is the largest oilfield in China, is also located in the basin. The rivers of the Songhua River Basin are an important water resource in the area. Despite their strategic importance, rapid economic development and high-energy consumption in the region during the last several decades, and their attendant extensive human activities such as industrial and agricultural activities, urbanization, etc., have caused constant and increasing emission of pollutants into the rivers (Wang et al. 2012; Ministry of Environmental Protection of the People's Republic of China 2015; Wang et al. 2016).

Considering the nature of anthropogenic activities that is dominant in the region, certain degree of health risk associated with PAHs exists, especially in urban areas. A few studies have been conducted on the water quality in the rivers of Songhua River Basin; however, few have focused on PAHs (Liu et al. 2007; Voulvoulis et al. 2007; Wang et al. 2013; Wang et al. 2015a, 2015b; Cui et al. 2016; Wang et al. 2016). In the past, the investigations of PAHs were mainly focused on the concentrations and distribution in the sediments and coastal water (Dickhut et al. 2000; Wang et al. 2001; Mai et al. 2002; Yim et al. 2005); few investigations have accessed the distribution and ecosystem risk of PAHs in the rivers, especially in Northeast China (Chen et al. 2004; Patrolecco et al. 2010). It has been established that exposure of PAHs to organisms and human beings via water sources is the most significant routes of exposure (Okoli et al. 2015). Considering the potential toxicity effects of PAHs, it is necessary to analyze the characteristics and assess the ecological risk of the PAHs in the aquatic environments.

The present work presents a systematic research study on the PAHs of the Songhua River Basin. The objectives of this study were (1): to evaluate the distribution characteristics of PAHs in the dissolved form in the water and in SPM in the Songhua River Basin, (2) to trace the possible sources of the PAHs by molecular diagnostic ratios and PCA, and (3) to determine the contamination status and evaluate the potential environmental risks in the aquatic system.

Material and methods

Chemicals and materials

The 16 EPA priority PAHs measured in this study included naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (B[*a*]A), chrysene (Chr), benzo[*b*]fluoranthene (B[*b*]F), benzo[*k*]-fluoranthene (B[*k*]F), benzo [*a*] pyrene (B[*a*]P), indeno[*1,2,3-cd*]pyrene (Ipy), Dibenzo[*a,h*]anthracessne (DBA), and benzo[*g,h,i*]perylene (BPE). A mixed standard solution of 16 EPA priority PAHs, internal standards (2-fluorobiphenyl and *p*-terphenyl-d14) and surrogate PAH standards (naphthalene-D_8, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12}, and perylene-D_{12}) were purchased from Accustandard Inc. (New Haven, CT, USA). Hexane, dichloromethane (DCM), and methanol were purchased from Merck Inc. (New Jersey, NJ, USA). Neutral silica gel and aluminum oxide (Al_2O_3) were purchased from Silicycle Incorporation (Quebec, Canada). J.T. Baker C_{18} solid-phase extraction (SPE) cartridges (200 mg/6 mL) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). All glassware and Whatman glass fiber filters (GF/Fs, 0.47 μm) were heated at 450 °C for 5 h before use.

Sample collection

The surface water sampling sites were along the main streams of the Songhua River Basin, the Second Songhua River, the Nen River, and their major tributaries (Fig. 1). A total of 48 river water samples, including 16 from main streams and 32 from tributaries, were collected using the baked glass bottles on July 2010. Sites 1–5 were located in the main stream of the Songhua River (SHR), sites 6–9 in the Second Songhua River (SSHR), sites 10–16 in the Nen River (NR), sites 17–27 in the tributaries of the Songhua River (TSHR), sites 28–30 in the tributaries of the Second Songhua River (TSSHR), and sites 31–48 in tributaries of the Nen River (TNR). The sum of 16 PAH concentrations is designated ΣPAH.

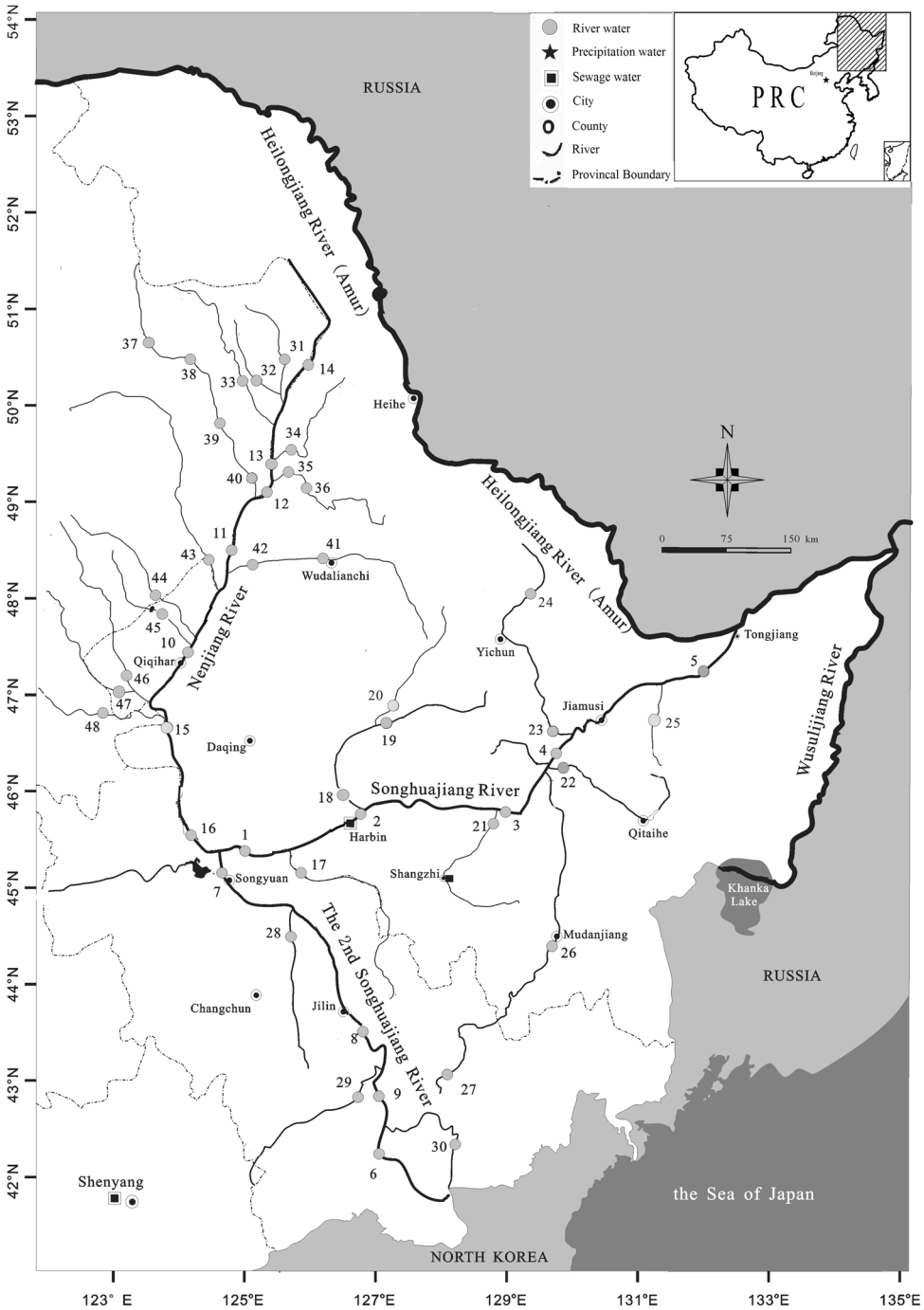

Fig. 1 Map showing the location of sampling sites in Songhua River Basin

Sample pretreatment

All samples were divided into two phases, the dissolved phase and SPM, via filtration with 0.47-μm glass fiber filters (GF/Fs); the volume of each sample was 2 L, and the surrogates were added before filtration. Each phase was analyzed for PAHs. Extraction of the dissolved phase PAHs was processed following the previously method (Hu et al. 2014). In brief, dissolved PAHs in the water were extracted with C_{18} SPE cartridges. The SPE columns were activated with 5-mL methanol, followed by 2.5-mL deionized water, and 12% methanol (*V*/*V*) was added to amend the water samples (to eliminate possible adsorption of PAHs on the walls of the sample containers) before passing through the cartridges. The flow rate was controlled at 6 mL/min with a vacuum. After the extraction process, the cartridges were dried with a N_2 stream (to eliminate evaporation of low weight PAHs and achieve high recoveries) and thereafter eluted three times with 3 mL of

DCM. The eluates were later combined and concentrated to 2 mL under a gentle N_2 stream. After exchanging the solvent to 10 mL hexane, the eluate was concentrated to approximately 0.5 mL. Prior to the instrumental analysis, the internal standards were added.

The SPM-loaded filters extraction was conducted as previously reported (Mai et al. 2002). In brief, after being freeze-dried and weighed, the SPM-loaded filters were shredded and the surrogate standards were spiked. Then the filters were Soxhlet extracted for 48 h with 250 mL DCM. After the DCM was concentrated to 2 ml, the extract solvent was replaced with hexane. Then, the extract was cleaned by passing through an alumina/silica gel column. The column was first eluted with 15 mL hexane and discarded the first fraction eluted from the column, while the second fraction eluted with DCM/hexane (30:70, *v*/*v*) was collected and concentrated to 0.5 mL. Prior to GC-MS analysis, the internal standards were added.

Instrumental analysis

The chromatographic analysis was performed on an Agilent 6890 gas chromatography and 5972B mass selective detector, equipped with a DB-5 capillary column (60 m × 0.25 mm × 0.25 μm). In total, 1.0 μL sample was injected by an auto sampler. The oven temperature program was: a 2-min hold at 80 °C, followed by an increase to 180 °C at 10 °C/min, an increase to 220 °C at 2 °C/min, and an increase to 290 °C at 8 °C/min (Xu et al. 2014).

Quality control and assurance

Procedural blank, spiked blank, and spiked samples were used for each set of samples for quality control. The recoveries of the surrogate standards were 62.8 ± 3.2% for naphthalene-d_8, 77.1 ± 5.6% for acenaphthene-d_{10}, 81.1 ± 11.2% for phenanthrene-d_{10}, 81.3 ± 10.3% for chrysene-d_{12}, and 75.5 ± 12.1% for perylene-d_{12}. The average recoveries of the 16 PAHs varied from 71.6 to 101% in spiked blanks and from 63.2 to 103% in spiked samples. Method detection limit was dervied with statistical analysis of repeatability by the low concentration standard addition experiments; the field blank and procedure blanks were deducted. The instrument detection limits were 1–5 ng/ml for 16 EPA PAHs. The procedural blank was used to assess the effect of the experimental procedure on the concentration of PAHs, while the spiked blank and spiked samples were used to monitor the recovery efficiency in the present study. The concentrations of PAHs were not corrected with blanks and recoveries because the average recovery values of the 16 PAHs obtained in the present study were within the analytically acceptable range (70–120%) (Okoli et al. 2016; Bispo et al. 2011; Fajgelj and Ambrus 2000).

Statistical analyses

Principal component analysis (PCA) is a useful tool of multivariate analysis that uses an orthogonal transformation to convert the original observations into a set of values called principal components. The number of original variables is reduced to the number of principal components without an obvious loss in the total variance. The principal component has the possible variance in turn. Grouping factors were selected when the components contributed more than 10% of the total variance, and each factor was associated with an emission source. The most representative PAH compounds in each factor were identified based on loading values. Factors were selected based on loading values greater than 0.5 (Ho et al. 2002; Singh et al. 2004). The software SPSS 20.0 was used for the PCA analysis. Other statistical analyses were performed with Origin 8.0.

Results and discussion

PAH concentrations in the dissolved form and SPM

ΣPAH in the dissolved form and SPM in the surface water from the main streams of the SHR, the SSHR, the NR, and their major tributaries are presented in Tables 1 and 2 respectively. Not all of the 16 priority PAHs were detected in all of the surface water samples. The high molecular weight PAHs of BbF, BkF, Ipy, BaP, BPE, and DBA were not detected in the dissolved form in surface water, mainly because they are hydrophobic and tend to associate with SPM or colloids. As shown in Table 1, PAH in the dissolved form from surface water ranged from 13.9 to 305.5 ng L^{-1}, and the average PAH in the dissolved form in the SHR, SSHR, NR, TSHR, TSSHR, and TNR were 33.7 ± 5.8, 51.9 ± 5.6, 34.1 ± 9.8, 65.1 ± 81.1, 92.1 ± 68.8, and 65.2 ± 17.9 ng L^{-1}, respectively. The PAH in the dissolved form from TSSHR was significantly higher than that from the other rivers in the Songhua River Basin, and the PAH in the dissolved form from SHR was the lowest. A large variability in samples collected from TSSHR and TSHR was observed because PAH from TSHR and TSSHR in different sample sites exhibited significant difference which have made the range of concentrations in TSHR and TSSHR get so large compared to the other rivers and tributaries. As shown in Fig. 1, the SSHR is the shortest and SHR is the longest among the three rivers; the number of sampling sites were 3 in TSSHR, 11 in TSHR, and 18 in TNR respectively. Most of the sampling sites in TSSHR and TSHR were near the villages or cities, which exposes the rivers to more contamination through pollutant chemicals discharge and disposal. The PAH in some sample sites are obviously higher due to the special nature of the sampling site, as indicated by the visible outliers shown in Fig. 2. Among the main streams, PAH in the dissolved form in the SHR was the lowest, while PAH in the

Table 1 Concentration of PAHs in surface water from the Songhua River basin (ng L^{-1})

	SHR		SSHR		NR		TSHR		TSSHR		TNR	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Nap	16.7–21.1	21.1 ± 3.4	29.7–34.4	32.5 ± 2.0	20.3–30.3	24.0 ± 3.3	11.5–91.7	32.4 ± 23.5	31.6–139.8	68.3 ± 61.9	24.3–76.0	51.8 ± 17.8
Acy	2.6–4.5	3.4 ± 0.7	3.8–4.3	4.0 ± 0.2	1.8–4.0	3.0 ± 0.9	1.5–144.5	15.9 ± 42.7	1.8–4.0	3.2 ± 1.3	2.2–4.7	3.5 ± 0.7
Ace	1.3–4.5	2.2 ± 1.3	1.4–2.0	1.5 ± 0.3	1.3–2.1	1.6 ± 0.3	1.3–40.4	5.3 ± 11.7	1.7–2.0	1.8 ± 0.2	1.4–2.7	1.9 ± 0.3
Fle	1.5–7.9	2.9 ± 2.8	1.6–2.7	2.2 ± 0.4	1.3–2.1	1.6 ± 0.3	1.5–26.1	4.5 ± 7	2.4–4.4	3.1 ± 1.1	1.0–2.1	1.5 ± 0.3
Phe	4.8–22.8	9.0 ± 7.7	4.9–10.0	8.3 ± 2.3	3.9–6.4	5.1 ± 1.0	1.7–16.7	7.1 ± 3.8	8.3–19.3	12.1 ± 6.2	3.4–5.6	4.6 ± 0.6
Ant	0.2–1.6	0.8 ± 0.5	0.4–1.1	0.6 ± 0.3	0.2–0.8	0.5 ± 0.2	nd-1.4	0.6 ± 0.4	0.4–1.8	0.9 ± 0.8	nd-0.9	0.3 ± 0.2
Fla	0.6–1.5	0.7 ± 0.3	0.4–1.2	0.9 ± 0.3	0.4–1.3	0.7 ± 0.3	0.5–1.0	0.7 ± 0.2	0.7–1.1	0.9 ± 0.2	0.3–1.0	0.6 ± 0.2
Pyr	0.6–1.2	0.7 ± 0.2	0.4–1.7	1.3 ± 0.6	0.4–1.0	0.6 ± 0.2	0.5–1.6	0.8 ± 0.3	1.1–1.6	1.4 ± 0.2	0.3–1.1	0.6 ± 0.2
BaA	nd-0.2	0.1 ± 0.1	nd-0.2	0.1 ± 0.1	nd-0.4	0.1 ± 0.2	nd-0.4	0.1 ± 0.1	0.06–0.1	0.1 ± 0.0	nd-0.3	0.1 ± 0.1
Chr	0.1–0.4	0.3 ± 0.1	0.1–0.3	0.3 ± 0.1	nd-0.3	0.2 ± 0.1	nd-0.8	0.3 ± 0.2	0.2–0.4	0.3 ± 0.1	0.1–1.2	0.2 ± 0.3
∑PAHs	25.4–33.5	33.7 ± 5.8	43.9–56.2	51.9 ± 5.6	13.9–42.6	34.1 ± 9.8	14.6–305.5	65.1 ± 81.1	51.3–171.7	92.2 ± 68.8	37.5–89.5	65.2 ± 17.9

BbF, BkF, BaP, Ipy, DBA, and BPE were not detected in surface water from the Songhua River Basin.

SSHR was the highest. This may be due to the different amount of runoff. The mean annual runoff in the SHR, NR, and SSHR were 76.2, 22.73, and 16.23 billion cubic meters, respectively. The results implied that the PAH concentrations were diluted more with more runoff. The same trend was observed in the tributaries of the Songhua River Basin. Most of the average PAH values in the tributaries were higher than that in the main streams of the SHR, NR, and SSHR (Fig. 3). Hence, the PAHs in the tributaries may have contributed to the main stream.

As shown in Table 2, the PAH in the SPM from the Songhua River Basin varied from 0.3 to 109.7 μg g^{-1}. The average PAH in the SPM from SHR, SSHR, NR, TSHR, TSSHR, and TNR were 2.9 ± 2.2, 18.3 ± 22.1, 12.4 ± 10.6, 13.5 ± 32.0, 0.9 ± 0.8, and 8.4 ± 6.8 μg g^{-1}, respectively. The trends observed in the SPM were as similar to those of the dissolved form. The average PAH in SPM in the TSSHR was significantly higher than that from the other rivers in the Songhua River Basin. Among the main streams, the average PAH in the SPM form the SHR was the lowest, while the average PAH from the SSHR was the highest. This observation may be due to the different amount of runoff. The PAH variations in the suspended particles from the tributary are affected by complex combination of series of factors: the runoff volume of the rivers, population density, distance of the sampling sites from the city and factories, and other possible emission sources. During the flood, some containers and cans from factories were poured into the rivers, which serve as input sources to the rivers.

The PAH concentrations at each sample site in the Songhua River Basin are presented in Fig. 2a–c. The results indicated that the higher concentration of PAHs was obviously related to urban sources contribution. The highest concentration of PAHs in the dissolved phase and in the suspended particle matter was observed at sampling sites 26 and 27, respectively, which are situated near the Mudanjiang City (Fig. 2a, b). Mudanjiang River is one of the biggest tributaries of SHR, and Mudanjiang City is the important regional central cities of northeast China, and with growing industrial and urban development in the past few years, sewage discharges, urban runoff, contamination emission of vehicular exhaust, and shipping activities were intense in Mudanjiang City. While higher concentration of PAHs in the dissolved phase was found at site S30, the sampling site 30 is situated in the Yinma River which is one of the biggest tributaries of SSHR and pass through six counties. Another study has reported that the deterioration of water quality of Yinma River had an evident influence on SSHR (Sun et al. 2011). Similarly, the higher PAH concentration in the suspended particle matter was observed at site 7 which is situated near the Songyuan City in SSHR. There are eight wharf around Songyuan City, and the Jilin oilfield which is the one of the four major production oil fields of China is located in Songyuan City. The urban and oilfield sources showed significant contribution to the PAHs at site 7.

Table 2 Concentration of PAHs in SPM from the Songhua River basin (μg g^{-1})

	SHR		SSHR		NR		TSHR		TSSHR		TNR	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Nap	nd-0.3	0.1 ± 0.1	nd −1.1	0.6 ± 0.5	nd −3.1	1.0 ± 1.1	nd −7.7	0.8 ± 2.3	nd	Nd	nd −2.4	0.5 ± 0.7
Acy	nd	nd	nd	nd	nd	nd	nd-0.7	0.1 ± 0.2	nd	Nd	nd −0.2	0.1 ± 0.1
Ace	nd	nd	nd	nd	0.1–0.6	0.2 ± 0.2	nd −0.6	0.1 ± 0.2	nd	Nd	nd −0.5	0.2 ± 0.1
Fle	nd −0.4	0.2 ± 0.2	0.2–0.9	0.4 ± 0.3	0.1–2.7	0.9 ± 1.0	0.1–2.2	0.4 ± 0.6	nd-0.1	0.1 ± 0.1	nd −1.8	0.5 ± 0.4
Phe	0.2–2.6	1.3 ± 0.9	1.4–15.9	6.9 ± 6.7	0.6–20.1	6.5 ± 6.5	0.6–23.0	4.2 ± 6.4	0.3–1.2	0.6 ± 0.5	0.2–11.3	4.7 ± 3.3
Ant	nd −0.3	0.1 ± 0.1	0.1–0.9	0.4 ± 0.3	nd −0.8	0.4 ± 0.3	nd −4.0	0.5 ± 1.1	nd −0.1	0.1 ± 0.1	nd −0.8	0.2 ± 0.2
Fla	nd −0.8	0.3 ± 0.3	0.2–1.7	1.1 ± 0.6	0.1–2.9	1.4 ± 1.1	0.1–15.6	1.7 ± 4.6	0.04–0.1	0.1 ± 0.1	nd −3.4	0.9 ± 0.9
Pyr	nd −1.1	0.3 ± 0.4	0.2–3.4	1.4 ± 1.3	nd −2.8	1.2 ± 1.0	nd −13.7	1.5 ± 4.0	nd −0.1	0.1 ± 0.1	nd −4.1	0.9 ± 1.1
BaA	nd −0.2	0.1 ± 0.1	0.1–0.7	0.3 ± 0.3	nd-0.3	0.1 ± 0.1	nd −7.1	0.7 ± 2.1	nd	Nd	nd −0.2	0.1 ± 0.1
Chr	nd −0.3	0.1 ± 0.1	0.1–1.6	0.5 ± 0.7	nd-0.5	0.2 ± 0.2	nd −7.4	0.8 ± 2.2	nd	Nd	nd −0.4	0.1 ± 0.1
BbFL	nd −0.3	0.1 ± 0.1	0.1–3.5	1.0 ± 1.6	nd-0.4	0.1 ± 0.1	nd −8.1	0.8 ± 2.4	nd	nd	nd-0.3	0.1 ± 0.1
BkFL	nd −0.2	0.1 ± 0.1	nd-0.8	0.2 ± 0.4	nd	nd	nd −5.1	0.5 ± 1.5	nd	Nd	nd −0.1	0.1 ± 0.1
BaP	nd	nd	0.1–8.2	2.1 ± 4.0	nd-0.2	0.1 ± 0.1	nd −2.8	0.3 ± 0.8	nd	Nd	nd-0.4	0.1 ± 0.1
Ipy	nd	nd	0.1–8.1	2.1 ± 4.0	nd	0.1 ± 0.1	nd −4.3	0.4 ± 1.3	nd	Nd	nd-0.3	0.1 ± 0.1
DBA	nd	nd	nd	nd	nd	nd	nd −2.7	0.3 ± 0.8	nd	Nd	nd-	nd
BPE	nd	nd	0.1–3.8	1.1 ± 1.8	nd-0.2	nd	nd −4.7	0.5 ± 1.4	nd	Nd	nd −1.2	0.1 ± 0.3
∑PAHs (μg g^{-1})	0.3–5.7	2.9 ± 2.2	2.8–50.7	18.3. ± 22.1	1.0–30.3	12.4 ± 10.6	0.8–109.7	13.5 ± 32.0	0.5–1.8	0.9 ± 0.8	0.3–25.4	8.4 ± 6.8

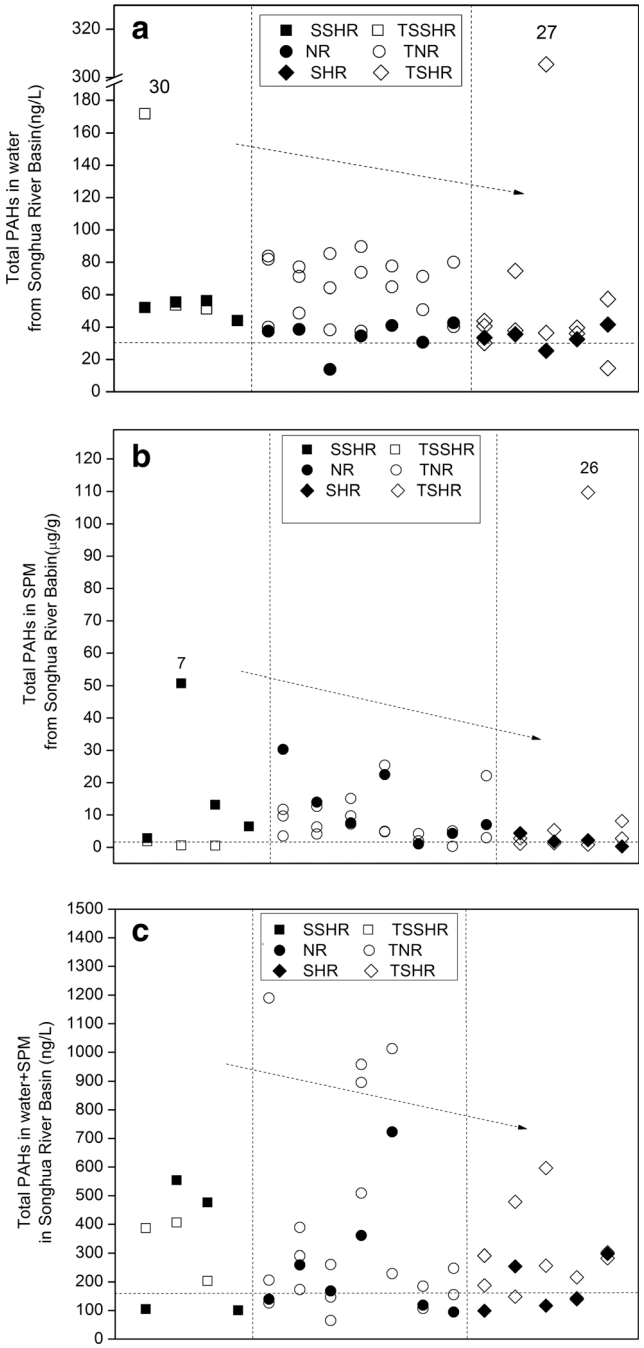

Fig. 2 Total PAHs in Songhua River Basin in water (**a**), SPM (**b**) and in water + SPM

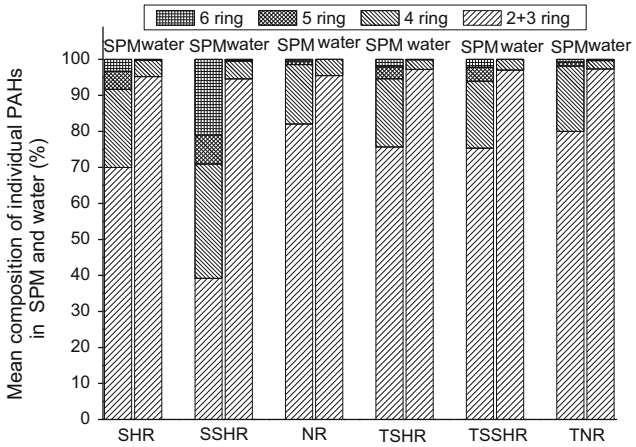

Fig. 3 The composition pattern of PAHs in water and in SPM

As discussed earlier, the amount of annual runoff maybe has a significant effect on the PAH in the rivers. The amount of annual runoff in the main streams was obviously higher than that in the tributaries in the Songhua River Basin; however, there were a complex set of factors causing unexpected results. In general, the PAHs in the tributaries maybe one of the main contributors to the main stream of the SHR.

Compared with PAHs pollution levels reported previously in the literature (Table 3), the PAH values in the Songhua River Basin were similar to those in the Moscow River and Mississippi River (Eremina et al. 2016; Zhang et al. 2007) and lower than in the Yangtze River (Yu et al. 2016), Tianjin River (Shi et al. 2005), Daliao River (Zheng et al. 2016), Pear River(Liu et al. 2014), Gaoping River (Doong and Lin 2004), Cauca River (Sarria-Villa et al. 2016), and Gomti River (Malik et al. 2011).The PAH concentrations in the Songhua River Basin are relatively low. There are two possible reasons. First, during the sampling time in 2010, there was heavy flooding in the Songhua River Basin; it was the most serious floods over the past 15 years. According to hydrology record, the flood increased the river discharge greatly to the Songhua River basin, and the PAHs have been diluted by the flood water (Song et al. 2015). The flooding also changed the PAH processes of dissolution, adsorption, and deposition in the water. The second reason is that the average population density is approximately 97 indiv km^{-2} throughout the river basin, and the population is mainly concentrated between Changchun City and Harbin City. The population density is much lower than the average population density (approximately 135 indiv km^{-2}) in China, so the anthropogenic contributions were likely relatively lower.

PAH composition profiles

The mean compositional profiles of the PAHs in the main streams of the SHR, SSHR, and NR and their major tributaries are shown in Fig. 3. The 2- and 3-ring PAHs were the most abundant PAHs in both the water and SPM. In the water samples, the mean percentage of low molecular weight PAHs (2- and 3-ring) was 96.2%, (range from 94.5 to 97.4%), and the proportion of 4-ring PAHs ranged from 2.3 to 4.9% of PAH, with a mean of 3.6%. Few 5- and 6-ring PAHs were detected in the surface water.

The proportion of PAHs in the SPM was also dominated by lower ring number PAHs except in SSHR. The percentage of 2- and 3-ring PAHs ranged from 39.2 to 82.1%, with a mean

Table 3 Comparison of PAHs concentrations in rivers worldwide

Locations	ΣPAHs Range in water (ng L^{-1})	ΣPAHs Range in SPM(μg g^{-1})	Reference
Yellow River, China	179–369 [a]	0.05–0.16	Li et al. 2006
Tianjin River, China	45.8–1270 [a]	0.94–64.2	Shi et al. 2005
Pearl River, China	849–1370 [a]		Liu et al. 2014
Yangtze River, China	128–302 [a]		Yu et al. 2016
Daliao River estuary, China	71.1–4250 [a]	1970–11,600 [d]	Zheng et al. 2016
Gaoping River, Taiwan	10.0–9400 [a]		Doong and Lin 2004
Mississippi river, USA	62.9–145 [a]		Zhang et al. 2007
Taizi River, China	367–5794.5 [a]		Song et al. 2013
Danube River, Hungary	25–1210 [a]		Nagy et al. 2013
Moscow River, Russia	50.6–120 [b]		Eremina et al. 2016
Cauca River, Colombia	52.1–12,888.2[c]		Sarria-Villa et al. 2016
Songhua River Basin	182–397 [a]	0.3–62.3	This study

[a] Sum of 16 PAHs
[b] Sum of seven PAHs
[c] Sum of 12 PAHs
[d] Unit, ng L^{-1}

value of 70.3%. The mean percentage of 4-ring PAHs was 20.9%, with a range from 16.5 to 31.7%. The 4-ring PAHs make up the largest percentage of the high-ring number PAHs (4-, 5-, and 6-ring). In SSHR, the proportion of higher ring number PAHs was higher in the SPM than in other rivers in the Songhua River Basin. As discussed above, there were visible outliers of higher concentration of PAHs both in the dissolved phase and in the suspended particle found, due to contributions of urban and oilfield sources. This observation was also the reason for the higher proportion of higher ring number PAHs in this SSHR.

The results, which the low molecular weight PAHs (2- and 3-ring) were dominant in the surface water, have been found in other studied area (Fernandes et al. 1997; Li et al. 2010; Song et al. 2013) indicating a relatively recent local source of PAHs in the study area. The observed trend is also a result of the solubility of PAHs. The solubility of PAHs has a negative trend with the molecular weight of PAHs. Low molecular weight PAHs are more likely to remain in solution than their higher molecular weight counterparts. Hence, high molecular weight PAHs are preferentially adsorbed onto SPM and fine particles and sink in the sediments due to the low aqueous solubility and hydrophobic nature which results in lower levels of higher molecular weight PAHs in the water samples (Zhu et al. 2004).

Identification of PAH sources by diagnostic ratios

The anthropogenic source of PAHs in the environment is typically generated via petrogenic process (petroleum oil and refined products) and pyrogenic process (combustion of organic matter, coal). Generally speaking, PAHs of petrogenic origin are abundant in 2- and 3-ring PAHs; however, PAHs from pyrogenic origin have higher molecular weight PAH compounds. Different PAH sources are marked with different ratios of some individual PAHs (Zhang and Tao 2008). Several ratios of specific individual PAHs are used to infer possible sources (Yunker et al. 2002, Ping et al. 2007; Wang et al. 2015a, 2015b; Parinos and Gogou 2016). In present study, the ratios of Fla/(Fla + Pyr) vs. Ant/(Ant + Phe) and Ipy/(Ipy + BPE) vs. BaA/(BaA + Chr) were used to identify the sources of PAHs in the Songhua River Basin. To avoid misdiagnosis of PAH origins caused by PAH partitioning between dissolved form and SPM, total PAH concentrations (dissolved + particle) were used to calculate the diagnostic ratios. The ratio of Fla/(Fla + Pyr) < 0.4 is characteristic of petroleum contamination, and ratios between 0.4 and 0.5 indicate that the PAHs derived from the petroleum combustion and the combustion of grass, wood, and coal result in a ratio >0.5. The ratio of Ant/(Phe + Ant) with 0.1 is usually used to distinguish petrogenic and pyrolytic origins. Petroleum products usually have low Ant/(Phe + Ant) (<0.1), while an Ant/(Phe + Ant) > 0.1 indicates that the origin is petrogenic (Yunker et al. 2002).

In the present study, the ratio of Ant/(Phe + Ant) at most sites was less than 0.1, while Fla/(Fla + Pyr) varied from 0.32 to 0.68(Fig. 4a), indicating the PAHs in the Songhua River Basin originated from combined sources, and the combustion of coal, petroleum, and biomass being the most important origins of PAHs in this region.

Ratios of BaA/(BaA + Chr) < 0.20 and Ipy/(Ipy + BPE) < 0.2 are characteristic of a petroleum source. The ratio

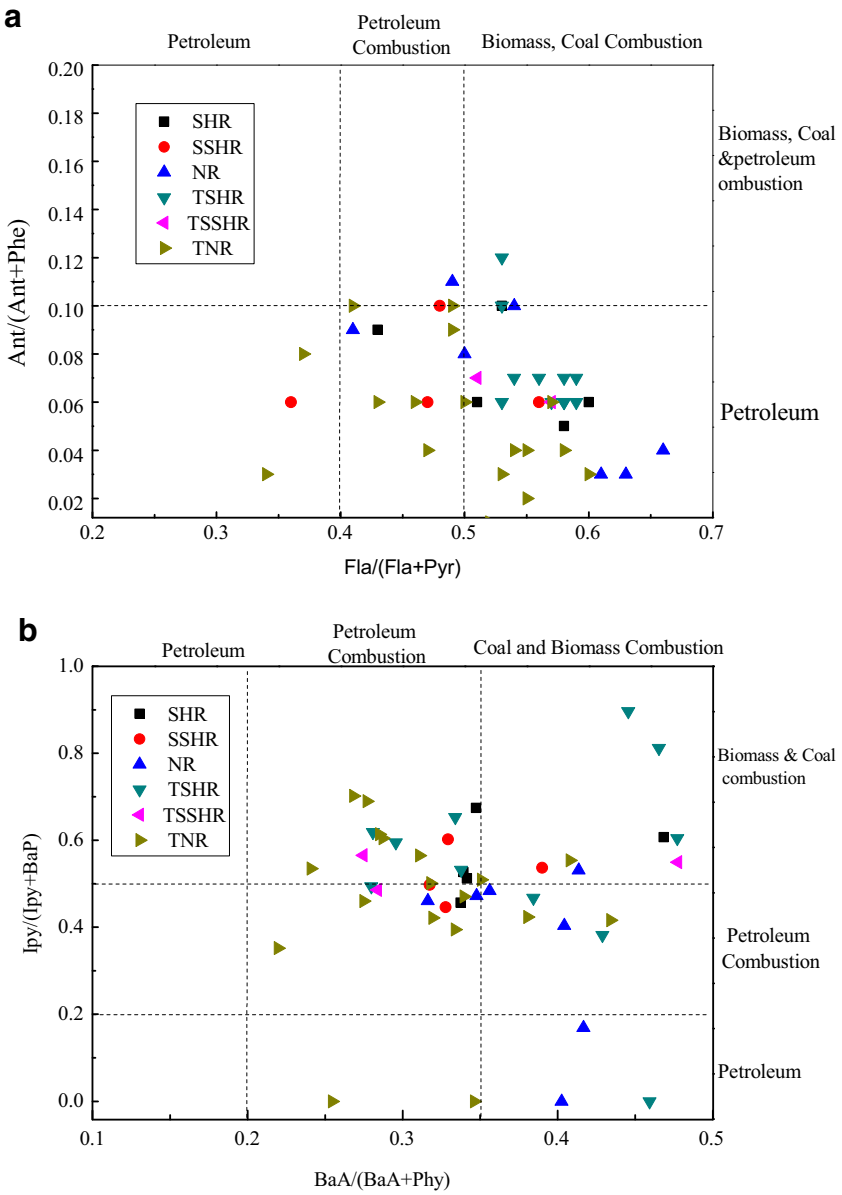

Fig. 4 Cross-plots for the isomeric ratios of: **a** Fla/(Fla + Pyr)vs. Ant/(Ant + Phe) and **b** Ipy/(Ipy + BaP) vs. BaA/(BaA + Chr) in Songhua River Basin

of BaA/(BaA + Chr) ranged from 0.20 to 0.35, and Ipy/(Ipy + BaP) from 0.20 to 0.50 indicate PAHs originated from petroleum combustion. BaA/(BaA + Chr) > 0.35 and Ipy/(Ipy + BPE) > 0.50 indicate PAHs derived from coal, wood, and grass combustion (Yunker et al. 2002). In Fig. 4b, the samples show evidence of a combination sources of biomass combustion, petroleum-derived pollution, and coal combustion.

The distribution of Fla/(Fla + Pyr) vs. Ant/(Ant + Phe), and Ipy/(Ipy + BPE)vs. BaA/(BaA + Chr) indicated that sources of the PAHs in of SHR, SSHR, NR, TSHR, TSSHR, and TNR were a combination of biomass combustion, petroleum-derived pollution, and coal combustion(Fig. 4).

In summary, the diagnostic ratios indicated that the PAHs in the Songhua River Basin originated from combined sources. Combustion of biomass, coal, and petroleum was the dominant source of PAHs in the Songhua River Basin. However, degradation of some PAHs is expected to take place during the river water that navigates its course downstream, which would lead to uncertainty about the trace sources. Having provided the qualitative identification with diagnostic ratios, PCA is necessary to provide the quantitative assessments.

Source identification of PAHs by PCA

Three principal components contributed more than 79.9% of the total variances (Fig. 5).

PC1 was characterized by high loadings of Fla, Pyr, BaA, Chr, BbF, BkF, and DBA and explained 40.6% of the variance. BkF are typical markers of gasoline and vehicle diesel

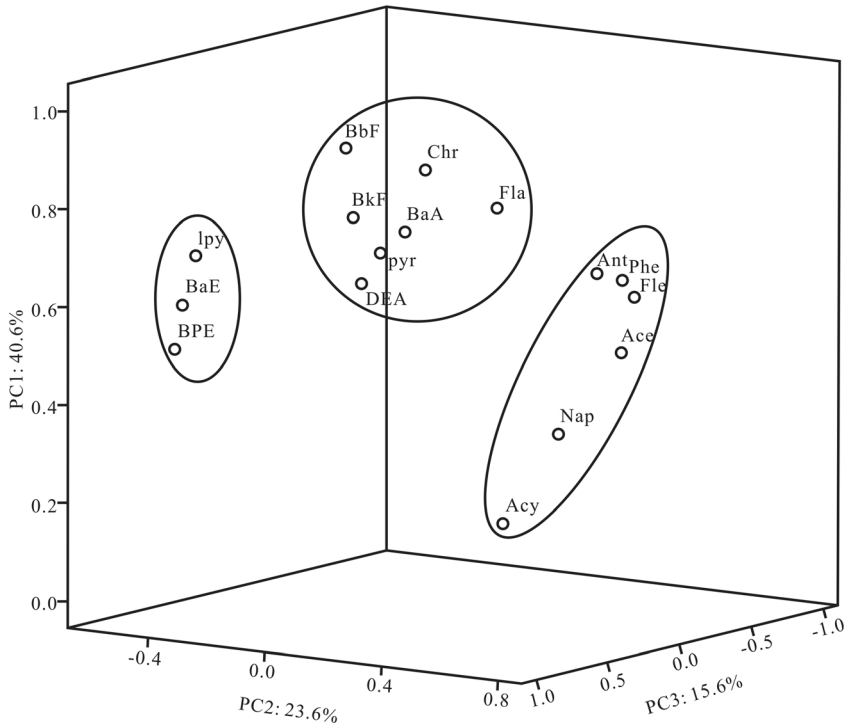

Fig. 5 Plots with PC1, PC2, and PC3 from principal component analysis for PAHs from the Songhua River Basin

emissions, while BbF and Chr are indicators of coal combustion. The high loadings for Fla, Pyr, and Chr indicated coal combustion (Harrison et al. 1996; Khalili et al. 1995; Simcik et al. 1999). PC1 represented combination of diesel vehicle emissions, gasoline emissions, coal combustion, and petroleum combustion.

PC2 (23.6% of the total variation) was characterized by lower molecular weight PAHs (Nap, Acy, Ace, Fle, Ant, and

Table 4 Mean values of $RQ_{(NCs)}$, RQ(MPCs), $RQ_{PAHs(NCs)}$, and $RQ_{PAHsMPCs)}$ of PAHs in the Songhua River basin, China

	Water (ng L^{-1})			$RQ_{(NCs)}$					$RQ_{(MPCs)}$						
	TEFs	NCs	MPCs	SHR	SSHR	NR	TSHR	TSSHR	TNR	SHR	SSHR	NR	TSHR	TSSHR	TNR
Nap	0.001	12.00	1200.00	0.00	0.10	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acy	0.001	0.70	70.00	0.00	0.10	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ace	0.001	0.70	70.00	0.00	0.10	0.30	0.10	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00
Fle	0.001	0.70	70.00	0.30	0.70	1.30	0.60	0.10	0.70	0.00	0.00	0.00	0.00	0.00	0.00
Phe	0.001	3.00	300.00	0.40	2.30	2.20	1.40	0.20	1.60	0.00	0.00	0.00	0.00	0.00	0.00
Ant	0.001	0.70	70.00	0.10	0.60	0.70	0.70	0.10	0.30	0.00	0.00	0.00	0.00	0.00	0.00
Fla	0.01	3.00	300.00	0.10	1.70	0.50	0.60	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00
Pyr	0.001	0.70	70.00	0.40	12.00	1.70	2.10	0.10	1.30	0.00	0.10	0.00	0.00	0.00	0.00
BaA	0.10	0.10	10.00	0.70	3.00	0.90	7.00	0.10	0.50	0.00	0.00	0.00	0.10	0.00	0.00
Chr	0.01	3.40	340.00	0.00	0.20	0.10	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BbF	0.10	0.10	10.00	0.90	10.00	1.00	8.00	0.20	0.60	0.00	0.10	0.00	0.10	0.00	0.00
BkF	0.10	0.40	40.00	0.10	0.50	0.10	1.30	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
BaP	1.00	0.50	50.00	0.00	4.20	0.10	0.60	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
DBA	1.00	0.50	50.00	0.10	4.20	0.10	0.80	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
IPY	0.10	0.40	40.00	0.10	0.10	0.10	0.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BPE	0.01	0.30	30.00	0.20	32.00	0.20	1.70	0.00	0.30	0.00	0.30	0.00	0.00	0.00	0.00
$RQ_{\sum PAHs}$				0.00	69.40	6.20	21.50	0.00	2.90	0.00	0.00	0.00	0.00	0.00	0.00

Phe), which are indicative of non-combustion fossil fuel processes (Dachs et al. 2002). As characterized by PC2, the PAHs may be due to the emissions from oilfield drilling platforms and motor vehicles including unburnt diesel oil and gasoline in the Songhua River Basin.

High loadings of BaP and BPE and IPY contributed more than 15.6% of the total variance for PC3 which are typical markers of diesel vehicles and gasoline (Harrison et al. 1996).

The diagnostic ratios and the PCA were consistent with respect to the source of PAH contamination. The area was exposed to PAHs originating from petrogenic and pyrogenic sources, and pyrogenic source had a greater impact.

Though alkylated PAHs and dibenzothiophenes would have given more information on the sources of PAHs and their risks, the present study focused on the 16 EPA priority PAHs; due to their prevalence and established toxicity profile, the present study focused on the 16 EPA PAHs. The study of alkylated dibenzothiophenes and other parent PAHs will be undertaken in the future to have a better understanding of the pollutant behavior in the environment.

Ecological risk assessment by RQ

The PAHs in river water can be absorbed by phytoplankton and zooplankton, accumulated in the body of aquatic organisms, and enters into the food web, resulting in a potential risk to the river ecosystems. Ecological risk assessment of PAHs is important to identify the possible dangers to the aquatic ecosystem (Wu et al. 2011a, 2011b).

When assessing the potential risk of PAHs in the aquatic ecosystem from the Songhua River Basin, the concentrations of PAHs in the water were compared to their corresponding quality values, and reference values described in previous literatures were used for the assessment. The ecosystem risks of 16 individual PAHs were characterized by the risk quotients RQ_{NCs} and RQ_{MPCs} (Kalf et al. 1997; Cao et al. 2010; Dushyant et al. 2016). RQ_{NCs} and RQ_{MPCs} were calculated as follows:

$$RQ_{NCs} = \frac{CPAHs}{CQV(NCs)}$$

$$RQ_{MPCs} = \frac{CPAHs}{CQV(MPCs)}$$

where C_{PAHs} is the concentration of a specific individual PAH in the medium, $C_{QV(NCs)}$ is the quality values of the negligible concentrations (NCs) and $C_{QV(MPCs)}$ is the maximum permissible concentrations (MPCs) in the medium. $RQ_{(NCs)} < 1.0$ indicates that a specific PAH is risk free and the risk can be of negligible, while $RQ_{(MPCs)} < 1.0$ and $RQ_{(NCs)} > 1.0$ indicate concentration level of the specific PAH poses a moderate risk. To prevent further contamination, some control action should be taken. $RQ_{(MPCs)} > 1.0$ indicates that the pollution with a specific PAH is severe; the ecosystem risk of the PAH is high risk, and urgent and effective control methods and remedial measure should be taken immediately.

The average values of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in different media from different sites are listed in Table 4. The average values presented $RQ_{(NCs)} > 1.0$ and $RQ_{(MPCs)} < 1.0$ for Phe, Fla, Pyr, BaA, BbF, BaP, DBA, and BPE in the SHR; for Phe, Fla, Pyr, BaA, BbF, BaP, DBA, and BPE in the SSHR; for Fle, Phe, Pyr, and BbF in the NR; and for Phe BaA, BbF, BkF, and BPE in the TSHR, which indicated that these PAHs presented a medium level of ecosystem risk at these sites. However, no ecosystem risk was identified for Nap, Acy, Ace, Ant, Chr, and Ipy at any of the sampling sites. No values of $RQ_{(MPCs)} > 1.0$ were found, which indicated no severe ecosystem risk of individual PAHs was at any of the sites in Songhua River Basin. In general, high molecular weight PAHs are more mutagenic and carcinogenic. The ecosystem risk is mainly due to 3- and 4-ring PAHs; the moderate molecular weight PAHs posed a much greater ecosystem risk in the Songhua River Basin.

To assess the ecosystem risk more accurately and comprehensively, the ecosystem risk posed by the combination of all 16 PAHs was characterized based on the risk quotients $RQ_{PAHs(NCs)}$ and $RQ_{PAHs(MPCs)}$. When the values of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of the individual PAHs were greater than 1, they were combined to calculate $RQ_{PAHs(NCs)}$ and $RQ_{PAHs(MPCs)}$ of PAHs. $RQ_{PAHs(NCs)}$ and $RQ_{PAHs(MPCs)}$ were calculated as follows:

$$RQ\sum PAHs(NCs) = \sum_{i=1}^{16} RQNCs(RQ(NCs) \geq 1)$$

$$RQ\sum PAHs(MPCs) = \sum_{i=1}^{16} RQMPCs(RQ(MPCs) \geq 1)$$

The values of $RQ_{PAHs(NCs)}$ and $RQ_{PAHsMPCs}$ reflect the ecosystem risk levels of the PAHs. $RQ_{PAHs(NCs)} = 0$ indicates that PAHs in a level of risk free, while $RQ_{PAHs(MPCs)} = 0$ and range of $RQ_{PAHs(NCs)}$ from 1 to 800 suggest that PAHs in a level of low risk, $RQ_{PAHs(NCs)\,\square} \geq 800$ and $RQ_{PAHs(MPCs)} = 0$ indicate the PAHs in a level of moderate $risk_1$, the $RQ_{PAHs(MPCs)} \geq 1$ and $RQ_{PAHs(NCs)\,\square} < 800$ indicate the PAHs pose a moderate $risk_2$, $RQ_{PAHs(NCs)\,\square} \geq 800$ and $RQ_{PAHs(MPCs)} \geq 1$ indicate the ecosystem risk of the PAHs is high risk.

As shown in Table 4, $RQ_{PAHs(NCs)}$ in SSHR, NR, TSHR, and TNR was less than 800 but greater than 1.0, while $RQ_{PAHs(MPCs)}$ was 0, which indicated that

the contamination of PAH in the aquatic environment of the SSHR, NR, TSHR, and TNR showed low ecosystem risk. There was no risk in the SHR and TSSHR; the PAH contamination in these rivers was negligible. $RQ_{PAHs(MPCs)}$ was always less than 1.0, and $RQ_{PAHs(NCs)}$ was always less than 800, which indicated that there was no moderate- or high-risk PAH contamination in the aquatic environment in the entire Songhua River Basin.

Conclusion

This study focused on assessing the concentration, source, and ecological risk in the main streams of the Songhua River Basin in Northeast China. Both the water and SPM contained mostly low molecular weight PAHs. The average PAH in the tributaries of the TSHR, TSSHR, and TNR was higher than in the main streams of the SHR, SSHR, and NR. Compared with PAH river pollution levels reported in the literature, the PAH concentration in the Songhua River Basin was lower than other rivers around the world. The diagnostic ratios and PCA confirmed that the PAHs in the Songhua River Basin came from combined petrogenic and pyrogenic sources, and the pyrogenic source made a greater contribution. The ecosystem risk assessment indicated the PAH in the aquatic environment of the Songhua River Basin posed a low ecosystem risk, while some individual PAHs presented moderate risks. The flood events had a significant impact on the concentrations of PAHs in the rivers of the Songhua River Basin. It is suggested that researchers should pay close attention to the effect of these unpredictable events on the quality of rivers in the area in the future research.

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