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ORIGINAL PAPER

Temporal-spatial variation, source forensics of PAHs and their derivatives in sediment from Songhua River, Northeastern China

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Abstract The distribution patterns and health risk assessment of nitrated polycyclic aromatic hydrocarbons (NPAHs), hydroxy polycyclic aromatic hydrocarbons (OH-PAHs), and regular 16 priority polycyclic aromatic hydrocarbons (PAHs) in sediment from the Songhua River in northeastern China were investigated in this research. During dry seasons, concentrations of 16 USEPA priority PAHs, OH-PAHs, and NPAHs were extremely high, with average values of 1220 ± 288, 317 ± 641, 2.54 ± 3.98, and 12.2 ± 22.1 ng/g (dry weight, dw). The dry period level was confirmed to be 4 times greater than the wet period concentration. Modeling with positive matrix factorization (PMF) and estimation of diagnostic isomeric ratios were applied for identifying sources, according to the positive matrix factorization model: vehicle emissions (38.1%), biomass burning (25%), petroleum source (23.4%), and diesel engines source (13.5%) in wet season as well as wood combustion (44.1%), vehicle source (40.2%), coke oven (10.8%), and biomass burning (4.9%) in the dry season. The greatest seasonal variability was attributed to high molecular weight compounds (HMW PAHs). BaP was

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confirmed to be 81% carcinogenic in this study, which offers convincing proof of the escalating health issues.

Keywords PAHs · OH-PAHs · NPAHs · Sediment · Environmental · Risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs), described as a group of aromatic hydrocarbons with two or even more fused benzene rings, which are among the most important classes of organic hydrophobic pollutants. PAHs were seen to be the major components accountable for the impacts on organisms due to their carcinogenesis, teratogenicity and toxicity (Hong et al., 2016). Population growth and higher energy demand have been associated with rapid urbanization and industrialization leading to increased discharged of PAHs into the environment (Balgobin and Singh, 2019). Sediment is a vast sink that tends to absorb many types of pollutants. PAHs are easily gathered in sediments and are likely to harm human health through the food chain (Nam, Li et al., 2021). Polycyclic aromatic hydrocarbons are introduced in coastal areas through polluted water, industrial processes, vehicle exhausts, and fossil fuel spills (Moghaddam, Hashemi et al., 2021). These NPAHs have been identified as having more harmful effects than their PAHs and therefore have received increasing more attention in recent years (Kong et al., 2021). The atmospheric transformation leads to produce NPAHs that are released from combustion sources directly to the environment (Yadav & Devi, 2021). PAHs were biodegraded, thermally degraded, as well as photochemically oxidized, which all lead to the formation of NPAHs (Gbeddy, Goonetilleke et al., 2020). Nitro PAHs in sediments from various locations worldwide have been reported in the scientific literature: Hiroshima Bay, Japan (sea sediments), Lake Michigan, Elba River, China, Japan and Barcelona sediments, Sweden and Denmark (Bandowe & Meusel, 2017). Furthermore, PAHs are less volatile than their parent OH-PAHs, which are commonly found in particles (Barrado et al., 2012). Importantly, OH-PAHs, such as 1-hydroxyl-pyrene, could be used as biomarkers to determine human PAH exposure and possible toxicity (Wang et al., 2012). Several pieces of research have shown the OH-PAHs concentrations in occupational groups, such as coke and road pavements (Li et al., 2010). OH-PAHs are the most abundant PAH metabolites in the human body (Motorykin et al., 2015). Furthermore, hydroxy PAHs are reacted to form glucuronate and sulfate conjugates, which help in excretion via urine or feces (Campo, Rossella et al., 2008). As a result, if we wanted to determine accumulated exposures and hazards from PAHs toxicity, we need to calculate the profiles of a broad variety of OH-PAHs. Furthermore, PAHs contaminated sediments can have a direct effect on benthic ecosystems and are a constant source of harmful contaminants in aquatic environments (Gong et al., 2018). The basic goals of this study were to detect PAHs concentrations in sediment, as well as their hydroxylation and nitration compounds (OH-PAHs and NPAHs), and to determine the adverse effect of combustion sources on such concentrations. A detailed investigation into their occurrence in the Songhua River was conducted. As far as we are concerned would be necessary to guarantee the safety of water quality and the aquatic ecosystem.

Materials and methods

Sample collection

A total of 46 surface sediment samples were measured for both dry and wet periods. Figure 1 displays the specific details on the sampling sites. The climate is cold in this area and six months, starting from the middle of October to the middle of April of the next year, are heating season, and the other six months, starting from the middle of April to the middle of October, are non-heating season. The study site represents the various industries and human activities in the region. The main sections and divisions in Songhua River, Nen, Second Songhua, and Mudan were divided into three sections of Songhua River. Samples were taken from several locations along the river, including downstream of the river, (S1, S7, S9, S10, S12, S13, S14, S15, S16, S21, S23), middle of the river (S2, S8, S18), and upstream of the river (S3, S4, S5, S6, S11, S19, S20, S17, S22).

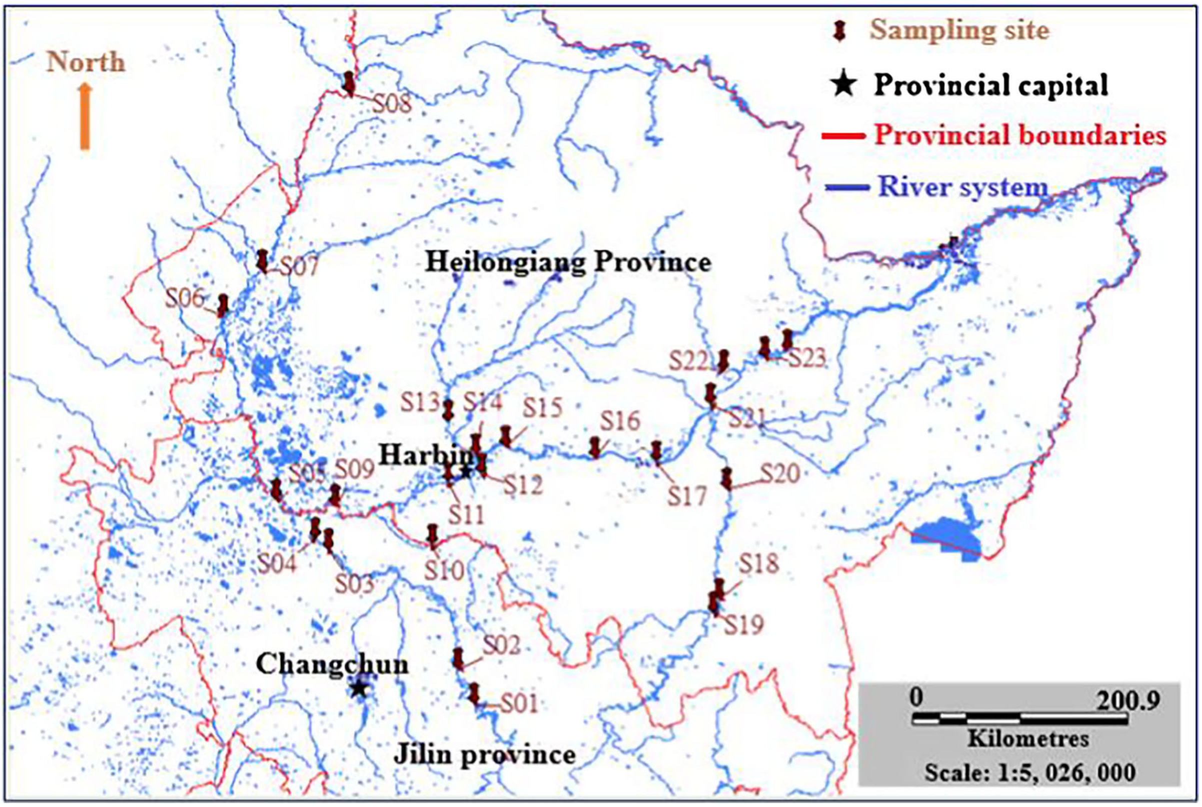


Fig. 1 Sampling sites from Songhua River

Analytical method

Ultrasonic extraction had been used. The sediment samples were freeze-dried and homogenized, briefly 3–5 g of dry sample added with 25 mL of MeOH-DCM (1:1 v/v) mixture solvent had been ultrasonically extracted for 20 min and centrifuged at 4000 rpm for 15 min. The supernatant was selected, and the extraction was performed three times. Agilent 7890A-7000B gas chromatography-tandem triple-quadrupole mass spectrometry applied to an EI ion source (GC-EI-MS/MS) was used to detect PAHs. Agilent 19091 J-433E (30 m × 250 µm × 0.25 µm) HP-5 MS chromatographic column was employed in GC, and (MRM) chromatogram. The injection pulse pressure was 40 psi until 0.8 min, one microliter of the aliquot was injected in with pulsed split less mode at 1 mL/min, 20 mL/min after 3 min, 3 mL/min for the septum purge, and 50 mL/min for the purge flow to split vent at 1.2 min, and the inlet temperature was 280 °C. The optimized oven temperature was programmed as follows: initial temperature set at 80 °C for 3 min, ramping at 8 °C/min to 180 °C and holding for 10 min, then ramping at 15 °C/min to 300 °C and finally holding for 6.5 min. After this, the post-run temperature was 310 °C for 1 min. Ultra-high purity helium was used for carrier gas, and the nitrogen collision gas rate was 1.5 mL/min. All of the transfer variables including collision energy as well as the retention time in Table S1, 2.

Quality assurance/quality control (QA/QC)

All of the data was established including quality assurance (QA) as well as quality control (QC). A procedural blank, a matrix spike (20 ng/g dry weight with sediment samples), and a matrix spike extra were checked to verify for contaminants, peak identification, and measurement in each batch of 12 samples analyzed. The average recoveries of the target compounds ranged from 68.4 to 116.7%. Limits of quantification (LOQ) were determined using a signal to noise (S/N) of 10 (Table S3), and all the data over the LOQ would be calculated in the result. A sequence of injections of objective compounds at different concentrations with an unchanging level of internal standard (100 ng/mL) was attained to figure out the linear range of the system. If each of the sample's extracts reaching the range, it would be diluted appropriately to get the reaction within the calibration range.

Positive matrix factorization model and statistical analysis

The values were presented using several Statistical Software Sciences (SPSS) versions 22 by standard and stepwise modes, and the T-test one-sample analysis was evaluated. The US EPA PMF v.5 models had also been used to quantify the source of the substance. PMF (Positive Matrix Factorization) is a mathematical receptor model which could be used to analyze data from different environmental media such as sediments, surface water, and atmospheric (Balgobin & Ramroop Singh, 2019). The PMF tool decomposes a matrix of spectated sample data into two matrices: factor contributions and factor profiles (Liu et al., 2018). In PMF, the factor analysis model is represented by the following matrix relationship:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{X_{\mathrm{ij}} - \sum_{k=1}^{p} g_{\mathrm{ik}} f_{\mathrm{kj}}}{U_{\mathrm{ij}}}\right)^{2} \quad (1)$$

U_{ji} is the uncertainty estimate of source j measured in sample i, p is the number of factors, g_{ik} is mass contributed by each factor to each sample, and f_{kj} is a species profile of each source.

In the present study, values of uncertainty (U_{nc}) matrix were calculated based on the method detection limits of the PAHs using Eqs. (2) and (3) in the PMF user guide:

$$U_{\mathrm{nc}} = \frac{5}{6} \times \mathrm{MDL} \quad (2)$$

$$U_{\mathrm{nc}} = \sqrt{(\text{Error fractions} \times \text{Concentration error} \times \text{Concentration})^{2} + (0.5 \times \mathrm{MDL})^{2}} \quad (3)$$

Potential cancer risk assessment

The potential cancer risk for PAHs was calculated as per Eq. (4) by multiplying the concentration of each compound by its corresponding TEF value (Bertrend et al., 2015; Ashayeri et al., 2018). The total carcinogenic potency of $\sum$16 PAHs, for each season, was assessed by summing the BaPeq of all compounds, with more details found in the literature (Brewster et al., 2018; Mohammed et al., 2016).

$$\sum \mathrm{BaP}_{\mathrm{eq}} = \sum \mathrm{PAH}_{i} \times \mathrm{TEF}_{i} \quad (4)$$

Results and discussion

Total concentrations of PAHs and associated OH-PAHs, NPAHs

The average level of NPAHs, OH-PAHs, and PAHs, in dry and wet seasons from sediments, is displayed in Table 1. A one-sample t-test was used to explain differences in both the wet and dry periods. The research revealed that all 33 compounds exposure levels and values were statistically and relatively different ($p > 0.05$). The mean concentrations of $\sum$**16** PAHs were considerably high in the dry season accounting for 1220 ± 2880 ng/g. Equally, the $\sum$**5** OH-PAHs and $\sum$**12** NPAHs average concentration were in the dry season accounting for 9.87 ± 26.4 ng/g and 36.9 ± 106 ng/g (Table 1).On the other hands, many other investigators found out that the level of NPAHs and PAHs was higher during dry seasons (Kong et al., 2021). This could clarify when, during floods, the dilution effect of sedimentary particle deposition in catchment areas nearly doubled(Kelly, Bian et al., 2017).

The results of various research are displayed in Table 2, including the present work. The average values of PAHs in this study 317 ng/g in the wet season were lower than a wet season in another region, for instance, 13 river South China, 573 ng/g (Gong et al., 2018), Changing Lake, China 241 ng/g (Hussain et al., 2016), Nanjing, China, 2169 ng/g (Zhao, Qin et al., 2017), Chaohu, China, 1467 ng/g (Qin et al., 2014), Yangtze River, 1335 ng/g (Feng et al., 2007), Tiaozi River, Northeast China, 2215 ng/g (Sun et al., 2018), Yangtze estuary, China, 1310 ng/g (Chen et al., 2018), Pearl River Estuary, China, 520 ng/g (Niu et al., 2020), Gomti River, India, 687 ng/g (Malik et al., 2011), Langkawi Island, Malaysia, 1523 ng/g (Nasher, Heng et al. 2013), coastal Caribbean island, 481 ng/g (Balgobin & Ramroop Singh, 2019), Kharg,

Table 1 Annual average concentrations of ∑16 PAHs, ∑OH-PAHs and ∑NPAHs

Variable	Wet season			Dry season		
	Mean	STD	Median	Mean	STD	Median
∑16 PAHs	317	641	112	1220	2880	927
∑5 OH- PAHs	2.54	3.98	1.23	9.87	26.4	1.41
∑12 NPAHs	12.2	22.1	0.17	36.9	106	0.22
LMW PAHs	94.8	17.2	64.9	302	45.8	74.6
HMW PAHs	222	13.8	48	926	60.2	56.2
LMW/HMW PAHs	0.42	1.25	0.35	0.32	0.76	0.86
$\sum PAH_{carc}$	132	7.37	21.6	545	29.8	19.3
BaPEQ16PAH	28.8	4.11	0.11	36.5	5.22	0.57

Concentrations of sediment in both seasons are expressed in ng/g dw

Table 2 Comparison of mean/median sediment concentrations of PAHs (values are expressed in ng/g dw)

Countries	Sites	Seasons		PAHs tested	References
		Dry season	Wet season		
This study	Songhua River, North China	1220	317	∑16 PAHs	This study
China	13 river South China	361	573.4	∑16 PAHs	Cui et al. (2021)
China	Huangpu River, China	107	183.5	∑16 PAHs	Motorykin et al. (2015)
China	Changdang Lake, China	295	240.9	∑14 PAHs	Kong et al. (2021)
China	Qinhuai River, Nanjing, China	1084	2169	∑16 PAHs	Kumar et al. (2014)
China	Lake Chaohu, China	1266	1467	∑16 PAHs	Li et al. (2010)
China	Yangtze River, China	1294	1334	∑11 PAHs	Liu et al. (2021)
China	Tiaozi River, Northeast China	1105	2214	∑9 PAHs	Liu et al. (2018)
China	Yangtze Estuary, China	129	308	∑16 PAHs	Nam et al. (2021)
China	Yangtze estuary, China	152,403	1310	∑16 PAHs	Kelly et al. (2017)
China	Luanhe River, China	478	187	∑16 PAHs	Nasher et al. (2013)
China	Pearl River Estuary, China	660	520	∑16 PAHs	Liu et al. (2020)
India	Gomti River, India	1118	687	∑16 PAHs	Malik et al. (2011)
Malaysia	Langkawi Island, Malaysia	1010	1523	∑16 PAHs	Masood et al. (2018)
Spain	coastal Caribbean Island	410	481	∑16 PAHs	Dong et al. (2021)
Kenya	River Nzoia, Kakamega-Kenya	67.5	51.3	∑16 PAHs	Mohammed et al. (2016)
Iran	Kharg, Lark, Persian Gulf, Iran	248	335	∑30 PAHs	Mihankhah et al. (2020)

Lark, Gulf, Iran, 335 ng/g (Jafarabadi et al., 2018). The sediment concentration of PAHs was relatively high in other cities in China that characterized by the dry season, Lake Chaohu, China, 1266 ng/g (Qin et al., 2014), Yangtze River, China, 1295 ng/g (Feng et al., 2007), and Yangtze estuary, China, 152,403 ng/g (Chen et al., 2018). Examples of places with lower than a dry season in this study comparing with worldwide: Selangor River, west Malaysia, 499 ng/g (Masood et al., 2018), Kharg, Lark, Persian Gulf, Iran, 248 ng/g (Jafarabadi et al., 2018), River Nzoia, Kakamega-Kenya, 67.5 ng/g (Basweti et al., 2018), coastal Caribbean island, 410 ng/g (Balgobin & Ramroop Singh, 2019), Langkawi Island, Malaysia, 1010 ng/g (Nasher, Heng et al., 2013), Gomti River, India, 1119 ng/g (Malik et al., 2011). It has to be noted that all the above values of sediment concentration represent mean/median concentrations, not maximum or minimum values; wherein part of studies a range of average values of difference research were presented.

Variations in concentrations of individual NPAHs, OH-PAHs, and PAHs are highlighted in Table 3. FLT, PHE, PYR, BbF, CRY, and InP were the most prevalent PAHs within wet periods, and FLT, PYR, PHE, BbF, InP, and BaA have been the most abundant PAHs during the dry season. Less exposed with ACY, ACE, ANT, Daha, and BKF had been inconstant as well as the concentration with wet and dry season was no substantial variations. This indicates that the latter five compounds were less influenced by sediment conditions or were less directly affected by the state of balance between sediment and water (Cui, Fu et al., 2016). In the dry season, FLT and PYR showed greater variations in seasons compared to the wet period. Effective carbon combustion behaviors of FLT as well as PYR are already reported (Buha-Marković, Marinković et al., 2020). The significant increase in these two compounds in the dry season was thus recognized to a source that was further confirmed by PMF modeling. Conversely, FLT, PHE, and PYR also showed relatively high accumulation rates, with two sampling times equivalent these were typical diesel combustion indicators (Dong et al., 2021). The concentration of individual OH-PAHs and NPAHs congeners is illustrated. The most abundant congeners were -HP, 9,10-DNAN, 2-NAN, 9-NPH, and 9-NAN during the wet periods, and 9,10-DNAN, 2-NAN, 9-NPH, 9-NAN, 2-NBP, and 1-HP during the dry periods, In contrast with PAHs in sediments, the accumulation of detected OH-PAHs and NPAHs was lower, proposing that most NPAHs and OH-PAHs also migrate small distances in the ambiance and accumulate in the coastal fast after discharge (Yujie & Yang, 2021).

High molecular weight PAHs versus low molecular weight PAHs

High molecular PAH's, representing 43.73%, 24.51%, and 7.15% in the dry season and 41.15%, 22.75%, and 6.2% in the wet season, defined by the PAH's, 5 OH-PAHs and 12 NPAH's which are considered more harmful than low molecular PAHs, as shown in Fig. 2. LMW PAHs, in comparison, represent 6.27%, 23.61%, and 29% for the dry season, in wet seasons, including ACE, FLU, PHE, ANT, 5-NAR, 9-NAN, 9-NPH, 2-NDB, 3-NPH, 2-NAN, and 9,10- DNAN. The high and low LMW and HMW PAHs percentages in wet and dry seasons could explain that two sources make persistent contributions from two sources. These two sources were recognized as such a source that further confirmed by PMF modeling gas demonstrated

Table 3 Annual average concentrations of individual PAHs and calculated BaPeq (ng/g dw)

Compound names	Symbols	Average conc.(wet)	Average conc.(dry)	BaPeq (wet)	BaPeq (dry)	TEF
Naphthalene	Nap	19.93	40.85	0.019	0.040	0.001
Acenaphthylene	ACY	2.583	15.09	0.002	0.015	0.001
Acenaphthene	ACE	4.496	20.10	0.004	0.020	0.001
Fluorene	FLU	12.23	43.60	0.012	0.043	0.001
Phenanthrene	PHE	48.72	140.5	0.048	0.140	0.001
Anthracene	ANT	6.865	42.34	0.068	0.423	0.01
Fluoranthene	FLT	50.34	224.9	0.050	0.224	0.001
Pyrene	PYR	39.25	156.8	0.039	0.156	0.001
Benz [a]anthracene	BaA	19.72	84.11	1.972	8.411	0.1
Chrysene	CRY	21.22	71.85	0.212	0.718	0.01
Benz [b]fluoranthene	BbF	26.37	102.4	2.637	10.24	0.1
Benz [k]fluoranthene	BkF	7.951	30.56	0.795	3.056	0.1
Benzo [a]pyrene	BaP	18.22	80.98	18.22	80.98	1
Indeno [1,2,3-cd]pyrene	InP	19.59	87.30	1.959	8.730	0.1
Dibenz [a,h]anthracene	DahA	3.662	15.04	18.31	75.23	5
Benzo [ghi]perylene	BghiP	16.00	72.90	0.16	0.729	0.01

TEF from (Barhoumi et al., 2014)

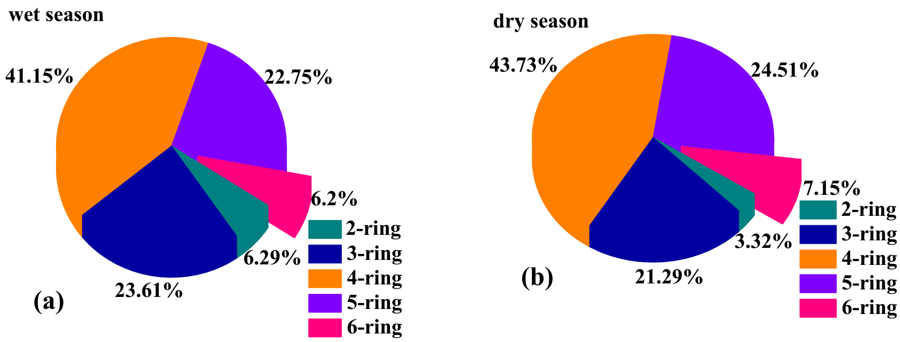


Fig. 2 The percentages of HMW and LMW PAHs from surface sediments in wet and dry seasons, from Songhua River in North of China

in Fig. 2. The mean ratios of LMW/HMW were <1 for the dry and wet seasons (Table 1). It could be likened to octanol-water partition coefficients with LMW as well as HMW PAHs and they are combining to sediment (Reininghaus et al., 2020). Besides, the percentages of LMW/HMW were <1 also signifies that the sources of PAHs during such two seasons are controlled by high-temperature fossil fuel (coal, oil) combustion (Wang et al., 2020a, 2020b). LMW 2 to 3 ring PAHs have greater solubility in the dissolved phase, whereas HMW 4 to 6 ring PAHs pollution more intensely with suspended particulate matter and marine sediment (Niu et al., 2021). The expected levels of NPAHs, OH-PAHs, and PAHs during the dry period were indeed higher than in the wet period, and the levels of HMW are most prominent than LMW.

Source identification

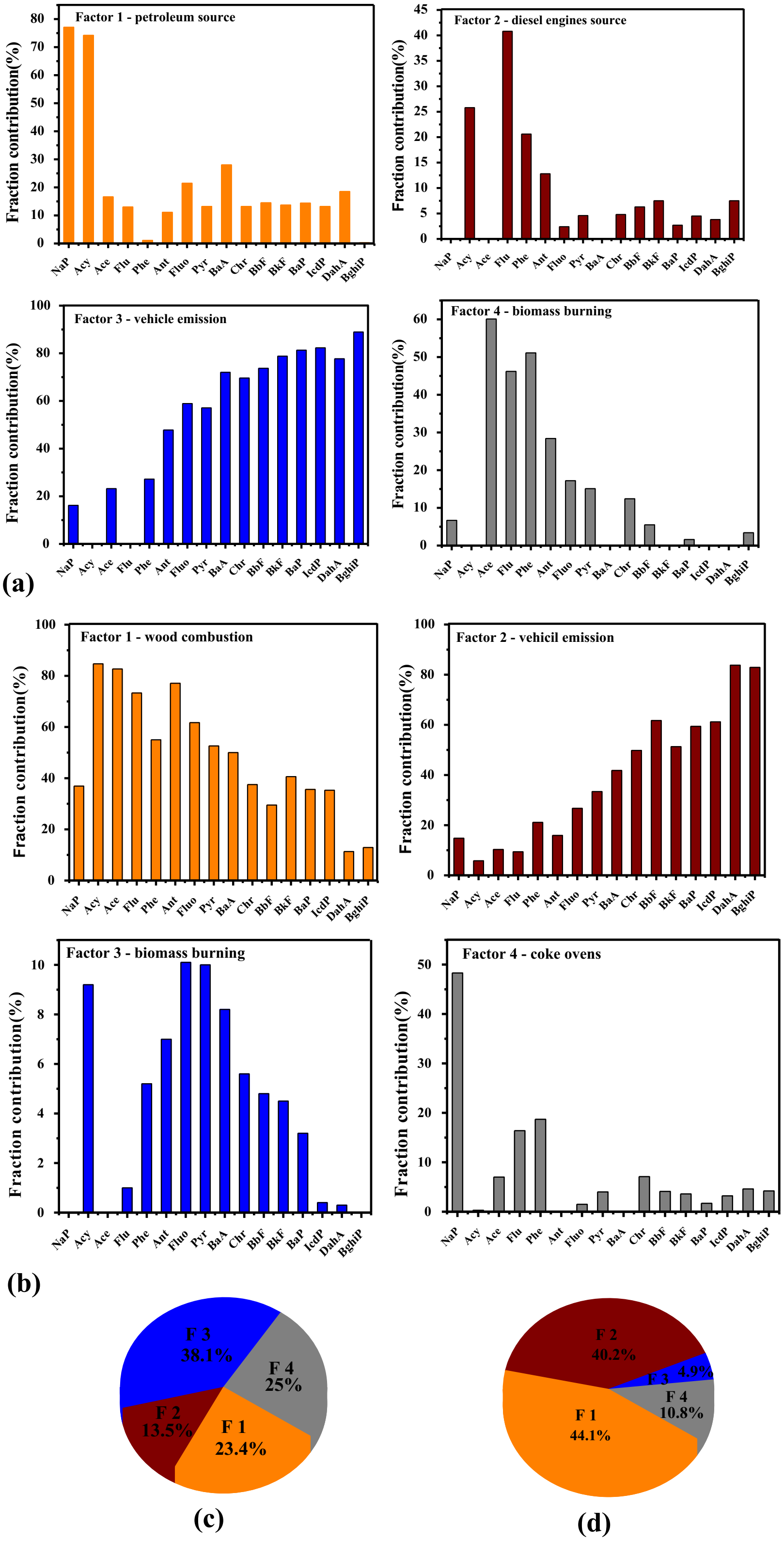
PMF model

The positive matrix factorization (PMF) model had been used to describe PAHs source contribution for both wet and dry periods (Fig. 3a, b). A high correlation between measured and modeled PAHs concentration verified the option of the selected factor ($r^2 = 0.99$). Four sources were determined with average contribution of 23.4%, 13.5%, 38.1% and 25% for wet season and 44.1%, 40.2%, 4.9% and 10.8% for dry season (Fig. 3c, d). During the wet period, Factor 1 was mainly loaded by Nap, Acy, BaA, Fluo, and Ace, which signified an oil source because the predominance of NaP and Ace, has been stated to be identifiers for petroleum sources (Shen et al., 2021). Factor 2 could represent the contribution from diesel engines, which were found to be heavily loaded by Flu, Acy, Phe, and Ant, (Liu et al., 2021). BghiP, IcdP, BaP, BKF, and DahA were the largest contributors to Factor 3, where the majority of substances are being used as effective tracers of vehicle emissions (Zhao et al,. 2020). The fourth factor recognized source was categorized by high levels of Ace, Phe, Flu, and Ant, among these PAHs, Ace, and Flu were identified as coal and biomass burning (Mihankhah, Saeedi et al., 2020). In the dry period Factor, 1 was loaded by Acy, Ace, Ant, and Flu, prevailing by Acy and Ace were used as an indicator to recognize wood combustion (Liu et al., 2020). Factor 2 was identified for vehicle source, which displayed higher loaded by DahA, BghiP, BbF, and IcdP (Zhao et al., 2020). Thirdly, biomass burning was characterized by the highest Pyr, Fluo, Acy, BaA, and Chr (Mihankhah, Saeedi et al., 2020). The fourth factor recognized source was categorized by high levels of Nap, Phe, Flu, Ace, and Chr, and the contribution signified cooking oven dust was reported to be major sources (Wang et al., 2020a, 2020b).

Diagnostic isomeric ratios

Positive matrix factorization indicates the changeable scale of source impacts while computing diagnostic isomeric ratios, another perfect method for source recognition. The InPy/(InPy + BghiP) and BaA/228 ratios have been utilized to determine the current contribution of various types of combustion, such as vehicle exhaust, gas, and wood combustion (Wang et al., 2010). As shown in Fig. 4 a, b, the rations ranged between 0.0046 to 0.804, 0.00153 to 3.145 and 0.448 to 0.645, 0.33 to 0.790, for both wet and dry seasons, suggesting pyrogenic sources (biomass burning and coal combustion), combustion of coal, grass, and wood, and during these periods, petrogenic characterize the outcomes of liquid fossil fuel burning (Cui

Fig. 3 Source composition profiles using PMF model and contributions of each source to the PAHs during **a**, **c** wet season and **b**, **d** dry season



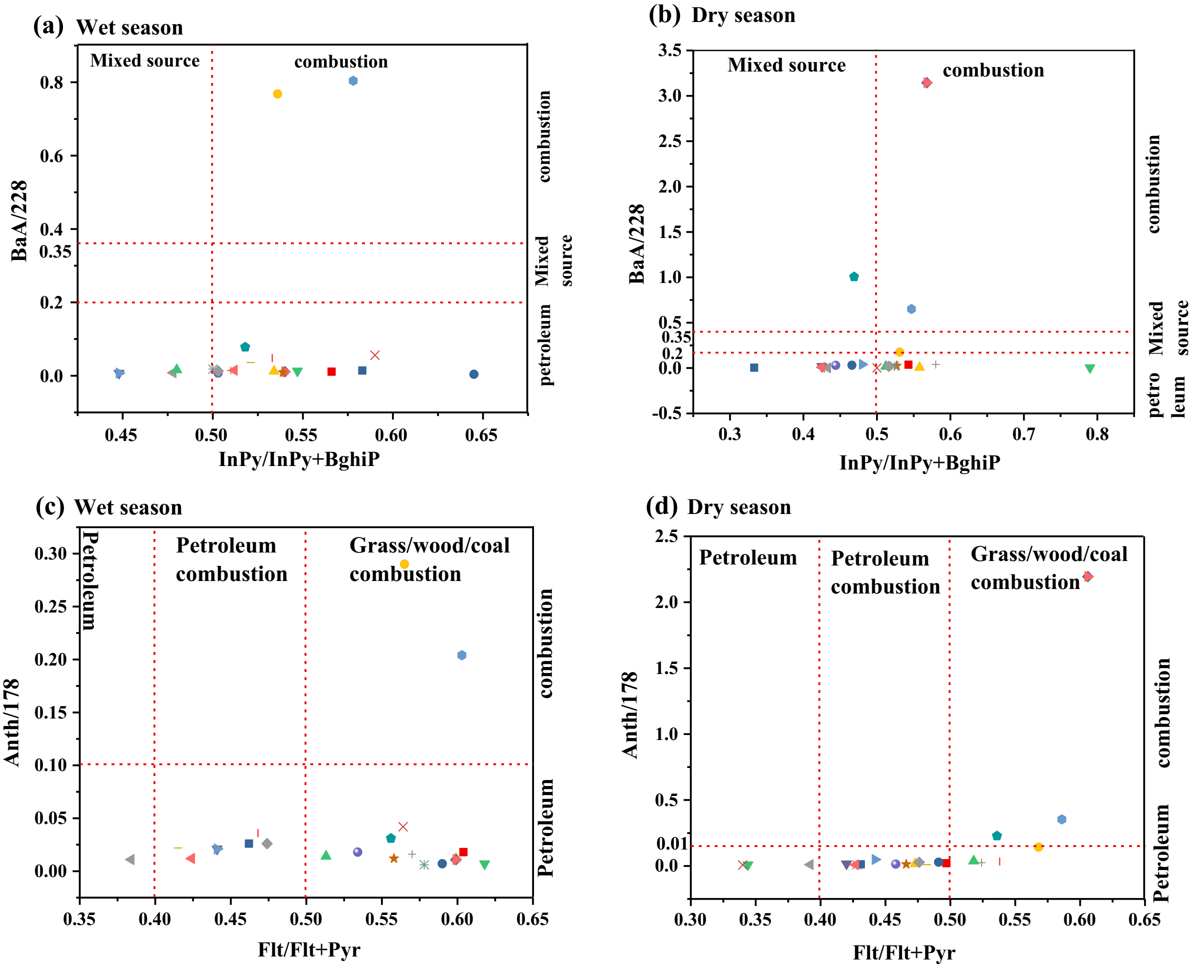


Fig. 4 PAHs cross-plots for the ratios of **a**, **b** BaA/228 versus InPy/ (InPy + BghiP) and **c**, **d** Ant/178 versus Flt/ (Flt + Pyr), ratios in the wet and dry season cores from the Songhua River North China

et al., 2021). Cross-plotting of Anth/178 and Flt/Flt + PYR ratio (Fig. 4c, d), as previously suggested, provided four groups: ranged from 0.0066 to 0.290, 0.0083 to 2.195 and 0.343 to 0.61835, 0.3407 to 0.6066, which was shown that the main sources were petroleum, diesel, pyrogenic process (coal and biomass burning sources). Petroleum combustion (both unburned and incomplete combustion) had a major impact in both wet and dry periods.

Carcinogenic potency of the sediments

During the dry periods, the total average carcinogenic potency (BaPEQ) of 16 PAHs (Toxic-equivalent concentrations) was extremely high, accounting for 545 ± 29 ng/g (Table 1). The overall carcinogenic potency of 16 PAHs was poor during the wet season, accounting for 132 ± 7.3 ng/g, which was close to previous studies' results (Adeniji et al., 2019). The carcinogenic potencies were 4 times greater in the dry period than in the wet period according to statistics. BaP was classified as carcinogenic in either research, followed by D(ah)A, and then, a group of compounds linked to combustion sources (BbF, BkF, InP, and BaA), which is in partial agreement with recently published studies(Baran et al., 2017; Bertrand et al., 2015; Kumar et al., 2014). In the dry period, BaP and DahA contributed 81% and 75% of the total carcinogenicity, due to its higher TEF values of 5.0 and 1.0 (Table 3). The result for carcinogenic PAHs observed in this research was higher than those obtained in Estuary, Argentina. (Oliva et al., 2015), sediments from Taiwan's Kaohsiung Harbor (Chen et al., 2013), and Taihu Lake in China (Qiao et al., 2006). Based on a body of evidence, the International Agency for Research on Cancer recently upgraded BaP to Sect. 1 (carcinogenic to humans) and DahA to Sect. 2A (known human carcinogen), while BbF, BkF, InP, and BaA are all assigned as possibly carcinogenic compounds to humans (group B2) (Nganje et al., 2011; Ramírez et al., 2011). We suggest further studies in the research area since the IARC recently replaced the category of BaP carcinogenic to humans, which contributed to 81% carcinogenicity during this study. This gives proof about the increasing health concerns.

Conclusions

The levels of NPAHs, OH-PAHs, and PAHs were estimated for both wet and dry periods. The four sources identified were vehicle emissions, biomass burning, petroleum source, diesel engines, with contributions of 38.1%, 25%, 23.4%, and 13.5% in the wet period as well as wood combustion, vehicle source, coke oven, and biomass burning, with contributions of 44.1%, 40.2%, 10.8% and 4.9% in a dry period. High molecular weight (4 to 6 rings) had the most seasonal variability rather than low molecular weight. During the two measurement seasons, the much more prevalent PAHs' congeners were FLT, PYR, PHE, BbF, InP, as well as BaA, compared to less abundant compounds such as ACY, ACE, ANT, DahA, BKF, 4-NBP, 2,2'-DBP, and 2-NDB. PAHs' exposure was assessed through the relative potency factor approach (RPF). The expected carcinogenic potencies in the dry period were four times higher than in the wet period, according to the RPF process. BaP has been confirmed to be 81% carcinogenic in this study, which corresponds to the International Agency for Cancer Research (IAC) and provides strong evidence of increased health risks.

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Authors' contributions RM, collected data, analyzed and drafted the manuscript; ZZ, supervised the work and approved the final version for publication, validation; YH and CJ both worked on data analysis and 3.5 part of the manuscript; ZH and WW worked on instrumental analysis; YL: supervision, the project administration and reviewed the manuscript.

Availability of data and materials The data collected are property of our research center but will be made available by the corresponding author when requested.

Declarations

Conflict of interest We firmly believe that the present work has not been influenced by any of the financial and personal relationships with anyone or with industries. We declare that there is no conflict of interest.

Consent for publication This manuscript was approved for publication by all the authors.

Ethical approval Participation of human subjects did not occur in this study.

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