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RESEARCH ARTICLE

Distribution, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in surface water in the coal mining area of northern Shaanxi, China

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Abstract

This study investigated the spatial distribution, pollution source, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in the Kuye River, which is a typical river in the mining area of China, 16 priority PAHs were quantitatively detected at 59 sampling sites by high-performance liquid chromatography-diode array detector-fluorescence detector. The results showed that the ∑PAHs concentrations in the Kuye River were in the range of 50.06–278.16 ng/L. The PAHs monomer concentrations were in the range 0–121.22 ng/L, of which chrysene had the highest average concentration (36.58 ng/L), followed by benzo[a]anthracene and phenanthrene. In addition, the 4-ring PAHs showed the highest relative abundance in the 59 samples, ranging from 38.59 to 70.85%. Moreover, the highest concentrations of PAHs were mainly observed in coal mining, industrial, and densely populated areas. On the other hand, according to the diagnostic ratios and positive matrix factorization (PMF) analysis, it can be concluded that coking/petroleum sources, coal combustion, vehicle emission, and fuel-wood combustion contributed to the PAHs concentrations in the Kuye River by 37.91%, 36.31%, 13.93%, and 11.85%, respectively. In addition, the results of the ecological risk assessment indicated that benzo[a]anthracene had a high ecological risk. Among the 59 sampling sites, only 12 belong to low ecological risk areas, and others were at medium to high ecological risks. The current study provides data support and a theoretical basis to effectively manage pollution sources and ecological environment treatment in mining areas.

Keywords Mining area river · Polycyclic aromatic hydrocarbons (PAHs) · Concentration distribution · Source apportionment · PMF model · Ecological risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have potential toxic, mutagenic, and carcinogenic characteristics to the environment and human beings (Tong et al. 2018; Chen et al. 2020), with semi-volatility and continuous degradation proprieties. In addition, PAHs can be transported over a long distance through the air, surface water, sediment, soil, biota, and other environmental compartments (Khanal et al. 2018; Liu et al. 2021a, b). Therefore, PAHs have attracted increasingly more attention from researchers in recent years. Scholars have conducted a lot of research on PAHs in the environment, pointing out that PAHs in the natural environment are mainly derived from human activities (e.g., industrial production, agricultural waste, automobile exhaust, coal combustion, and petrochemical product emission) and reach the surrounding environmental media, more particularly water bodies, through atmospheric dry and wet deposition, industrial sewage discharge, and surface runoff (Montuori et al. 2016; Zhang et al. 2022a, b). The maximum threshold concentration of PAHs in the water environment was fixed by the United States Environmental Protection Agency (USEPA) and the Canadian Council of Ministers of the Environment (CCME) (Meng et al. 2019).

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In recent years, China's total energy consumption and coal mining activities have significantly increased, resulting in a significant increase in PAHs emissions. Therefore, it is necessary to monitor and assess the PAHs pollution levels in coal mining areas and energy and chemical industry areas.

In recent years, the impacts of exposure to PAHs on the ecological environment have generated considerable concern in coal mining areas. Several researchers have studied the abundance, distribution, source, and health risks of ambient PM_{10}-bounded PAHs in coal mining cities (Zheng et al. 2019). In addition, numerous studies were carried out on PAHs in coal waste material, mine water, underground sludge, and groundwater in coal mining areas to investigate the contamination levels, distributions, and potential sources of PAHs, as well as their associated ecological risks (Ribeiro et al. 2012; Shao et al. 2014; Hao et al. 2018; Chen et al. 2019; Wu et al. 2021; Jiang et al. 2022), whereas other studies have investigated the concentrations, spatiotemporal variations, and origins of PAHs in soils and sediments in the vicinity of coal mines, highlighting the great effects of human activities on PAHs (Orecchio et al. 2015; Ugwu et al. 2016; Liu et al. 2017; Zhang et al. 2022a, b). However, a few studies have investigated PAHs in the surface water of mining areas.

The northern Shaanxi mining area is China's national energy and chemical industry base and one of the seven largest coalfields worldwide. However, with the rapid industrialization of the region, the Kuye River, as the main river in this mining area, is becoming increasingly polluted by PAHs from mining production activities, including coal mining, transportation, coal washing, combustion power generation, and coal coking. Surface water is not only an important source of water in the lives of surrounding residents but also an important irrigation water source for farmlands. To date, there is little information available on the content and spatial distribution of PAHs in surface water in mining areas. To better understand the effects of coal industries on the levels and distributions of PAHs in surface water, northern Shaanxi, which is a typical coal mining area, was selected in this study to assess the contents and spatial distributions of PAHs in the Kuye River. In addition, diagnostic ratios and the positive matrix factorization (PMF) model were used to analyze the sources of PAHs in the study area. Finally, the ecological risks of PAHs were evaluated to provide a basis for the protection, development, and utilization of water resources in the study area and similar areas.

Materials and methods

Study area

The Yulin region in northern Shaanxi is an important coal production area and a national energy and chemical industry base in China. It is located in the border zone between the Loess Plateau and the Mu Us Desert. The region has a typical semi-arid inland climate area with poor water resources (Dong et al. 2020). In recent years, the coal industry in Yulin has developed rapidly. In 2021, coal mining volume exceeded 550 million tons, which stimulated the development of related industries. Kuye River as the main river in the northern Shaanxi mining area is the first-class tributary of the Yellow River, and numerous coals are being mined in the upper reaches, whereas the middle reaches consist of Ningtiaota Industrial Park, as well as energy and chemical production activities, such as thermal power generation, coking, and coal products manufacturing. The downstream consists mainly of rural residential areas. PAHs generated by human activities, such as coal production and processing emissions in the region, are accumulated in the Kuye River (Liu et al. 2019a, b). Moreover, the significant decrease in the natural runoff of the Kuye River, the high regional evaporation rates, the increase in the industrial water consumption, and the irrigation water return flows have affected the PAHs concentrations and compositions in the study area (Wu et al. 2020; Han et al. 2019).

Water sampling

In total, 59 sampling sites in the Shaanxi section of the Kuye River and the mainstream of the Yellow River were selected for water sampling, including 57 sampling sites in the Kuye River and 2 sampling sites in the mainstream of the Yellow River (Fig. 1). In this study, the water samples were collected in the wet season (October 2021), characterized by high precipitation amount and surface runoff, promoting the pollutant entry from industrial and agricultural activities and traffic into the surface water. The sampling sites are located in the coal mining, Lantan, coking, and other mining active industrial areas in the upper and middle reaches of the Shaanxi section of the Kuye River, as well as the rural residential and agricultural areas in the lower reaches. The sampling was carried out by collecting a 2-L water sample at 0.5-m depth from each sampling site using the JK-8008 water sampler (stainless steel, JKD, China). The water samples were sealed in brown glass bottles and stored.

Chemicals and instruments

In this study, the solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) were used to quantitatively detect 16 PAHs types at 59 sampling sites of the typical river in the northern Shaanxi mining area—Kuye River.

The instruments and equipment used in this study were Agilent1200 high-performance liquid chromatography-diode array detector-fluorescence detector (HPLC-DAD-FLD,

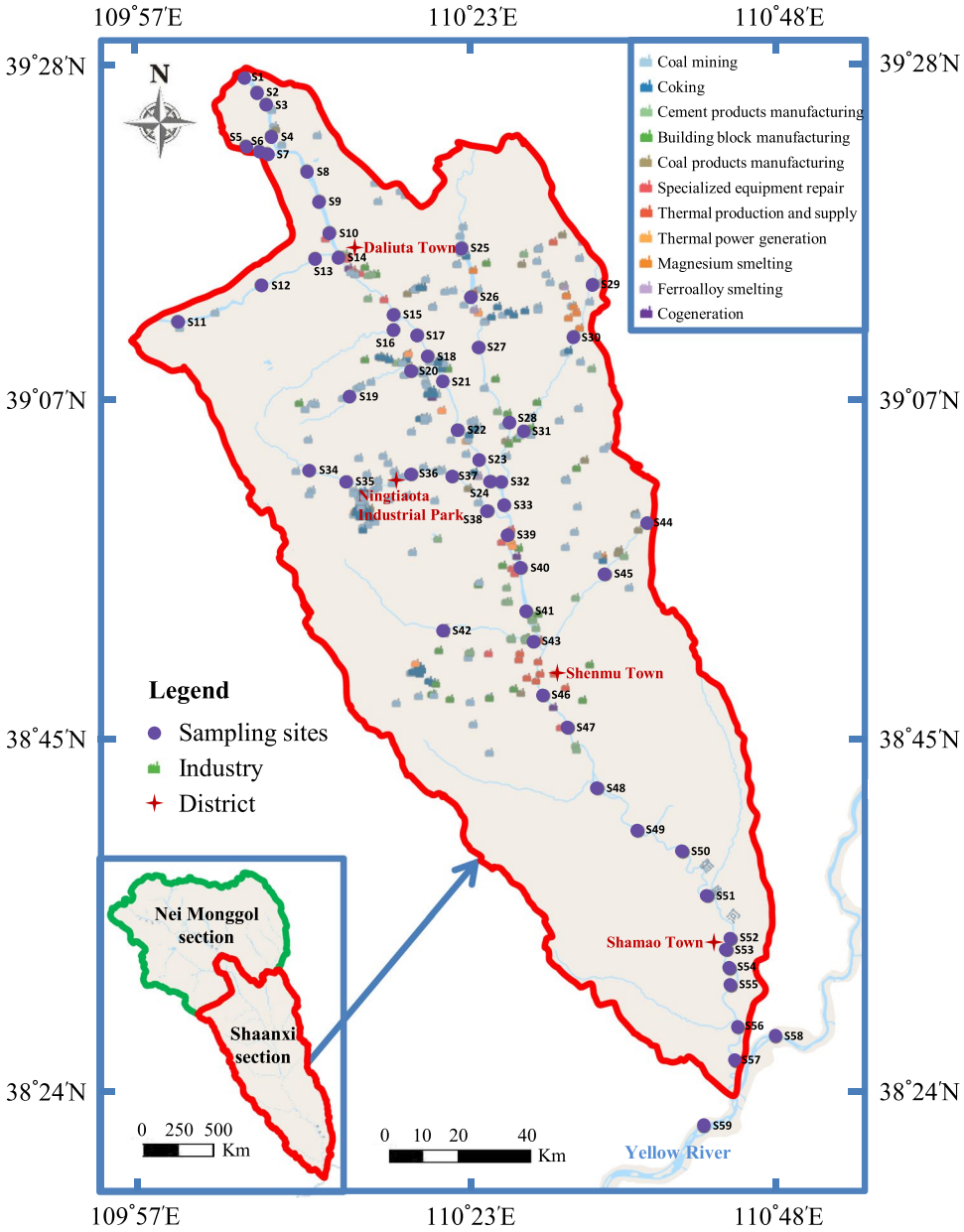

Fig. 1 Study area and the sampling sites in Kuye River Basin, China

Agilent, USA), solid-phase extraction device (Mediwax, USA), rotary evaporator (N-1000, Eyela, Japan), and nitrogen blower (TTL-DCII, Tongtailian, China), whereas the analytical reagents were liquid chromatography pure reagents, including acetonitrile, methanol, dichloromethane, and decafluorobiphenyl with 99% purity, which obtained from the Aladdin Holdings Group Co., Ltd. (Beijing, China). The standard mixture solution for PAHs contained 16 components, namely naphthalene (Nap), acenaphthylene (Acy), fluorene (Flu), benzo[g,h,i]perylene (BghiP), acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), indeno[1,2,3-cd]pyrene (InP), fluoranthene (Fla), pyrene (Pyr), chrysene (Chry), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), and dibenzo[a,h]anthracene (DahA), and was obtained from AccuStandard, Inc. (New Haven, CT, USA).

Pretreatment method and instrument analysis

The 1 L collected water samples were first passed through a 0.45-μm glass fiber filter membrane (surface waterman, UK) and then were enriched by a solid-phase extraction device. C_{18} column (Supelco, 1000 mg/6mL) was used in the solid-phase extraction. Before the water samples were enriched, the C_{18} column was pre-washed with 10 mL dichloromethane and then activated using 10 mL methanol and 10 mL water twice respectively. After sample enrichment, the C_{18} column was washed with 10 mL water and blown with

high-purity nitrogen for 10 min, followed by dichloromethane elution and dilution to 0.5 mL using acetonitrile after concentration.

The PAHs concentrations in water samples were determined using a high-performance liquid chromatography-diode array detector-fluorescence detector. The diode array detector was used in this study at a wavelength of 238 nm since the acenaphthylene concentrations cannot be determined using the fluorescence detector. The concentrations of the remaining 15 PAHs monomers were determined using the fluorescence detector using multiple wavelength gradients (Jin et al. 2022). The chromatography column was a specific column for polycyclic aromatic hydrocarbons (5 μm × 250 mm, waters). The acetonitrile-water mobile phase was used, with a flow rate of 1.2 mL/min. The elution was performed by increasing the acetonitrile gradient from 65 to 100% at 2.5%/min until reaching the peak capacity.

Quality assurance and quality control

The multi-point calibration external standard curve method of high-performance liquid chromatography was used to determine the concentrations of PAHs in the samples. The linear coefficient of marking (R^2) values varied from 0.9937 to 0.9990. The accuracy of the experimental process was ensured using experimental blanks, parallel samples, and matrix labeling (Zhang et al. 2007). On the other hand, the relative standard deviation of the 16 PAHs monomer concentrations in water samples ranged from 0.6 to 2.4%. The detection limit and spiked recovery ranges were 0.4~1.5 ng/L and 79.6~101.7%, respectively. In addition, 10% double parallel determinations and 2 experimental blanks for each batch of samples were carried out, and the determination results of blank experiments were lower than the detection limit, thus meeting the quality control requirements.

PMF model

The PMF receptor model (EPA PMF5.0) of the US Environmental Protection Agency was used to quantitatively assess the PAHs source compositions and their contributions to the pollution of the Kuye River in the study area (Liu et al. 2019a, b; Ren et al. 2021). The input data were the PAHs concentrations and its corresponding uncertainty at various points.

When concentration x_{ik} was lower than the method detection limit (MDL) and σ_{ik} is uncertainty and calculated with Eq. (1):

$$\sigma_{ik} = 5/6 \times \mathrm{MDL} \tag{1}$$

When concentration was higher than the detection limit, the uncertainty is calculated with Eq. (2):

$$\sigma_{ik} = \sqrt{\left(\mathrm{EF} \times \mathrm{x_{ik}}\right)^2 + (0.5 \times \mathrm{MDL})^2} \tag{2}$$

Ecological risk assessment

The Kalf risk quotient method was used in this study to assess the ecological risk of PAHs in the Kuye River. A risk quotient value greater than 1 suggests an ecological risk of PAHs. The higher the value, the greater the risk (Li et al. 2021; Wang et al. 2010).

The risk quotient of PAHs monomer was calculated using Eqs. (3) and (4):

$$\mathrm{RQ_{MPCs}} = \mathrm{C_{PAHs}}/\mathrm{C_{QV(MPCs)}} \tag{3}$$

$$\mathrm{RQ_{NCs}} = \mathrm{C_{PAHs}}/\mathrm{C_{QV(NCs)}} \tag{4}$$

where $\mathrm{RQ_{MPCs}}$ and $\mathrm{RQ_{NCs}}$ are the risk quotient of the highest and lowest allowable concentrations of PAHs, respectively; $C_{\mathrm{QV(MPCs)}}$ and $C_{\mathrm{QV(NCs)}}$ are the maximum and minimum risk standard concentrations of PAHs monomers, respectively; C_{PAHs} is the measured concentration of each monomer.

The maximum and minimum ecological risk quotient values of ΣPAHs at each sampling site were calculated using Eqs. (5) and (6):

$$\mathrm{RQ_{\sum PAHs(MPCs)}} = \sum_{\mathrm{i=1}}^{16} \mathrm{RQ_{i(MPCs)}} \left(\mathrm{RQ_{i(MPCs)}} \geq 1\right) \tag{5}$$

$$\mathrm{RQ_{\sum PAHs(NCs)}} = \sum_{\mathrm{i=1}}^{16} \mathrm{RQ_{i(NCs)}} \left(\mathrm{RQ_{i(NCs)}} \geq 1\right) \tag{6}$$

The ecological risk quotient classification of ΣPAHs is shown in Table S2 of the Supplemental material.

Data processing and analysis

The PAHs concentration data were corrected for recovery. The undetected concentrations in water samples were assumed to be equal to 0. Data calculations and descriptive statistics were performed using Excel 2019. In addition, PMF 5.0 software was used to perform the positive definite matrix factorization analysis. The spatial distribution maps of PAHs concentrations in the study area and other related plots were generated using ArcGIS 10.1 and Origin 8.0, respectively.

Results and analysis

Occurrence of PAHs in river water

The observed concentrations of PAHs in the study area and their national standard values for surface water are reported

in Table S1 of the Supplemental material. In total, 16 PAHs monomers were detected in most samples, with variation coefficients greater than 0.4, suggesting significant spatial differences of 16 monomers concentrations. In addition, the results showed mostly higher mean values than median values, indicating positive skew distributions. This finding suggests significant impacts of human activities on the accumulations of PAHs in river water in the study area. The concentration range of ΣPAHs was 50.06~278.16 ng/L, with mean and median values of 128.22 ng/L and 116.34 ng/L, respectively. Chry showed the highest concentration, with a mean value of 36.58 ng/L and a median value of 23.59 ng/L, followed by BaA and Phe. The detection rates of all PAHs monomers were above 70%, of which 12 monomers were 100%, and BbF and BkF revealed detection rates of 77.97% and 76.27%, respectively. The relatively low detection rates of BbF and BkF were related to the fact that these two components are high molecular weight monomers characterized by high hydrophobicity (Liang et al. 2020; Liu et al. 2018). Moreover, BbF and BkF showed the highest variation coefficients of 1.39 and 1.08, respectively, suggesting significant spatial differences.

In order to further assess the 16 PAHs monomers concentrations in the river water of the study area, the concentrations of each monomer at 59 sampling sites were compared with national standards (detailed data listed in Table S1). However, China's Environmental Quality Standards for Surface Water (GB3838-2002, 2002) reported only the BaP concentration standard. The National Recommended Water Quality Criteria of the USEPA (USEPA 2015) and the Canadian Environmental Quality Guidelines (CCME 2015) highlighted stricter concentration limits of all PAHs monomers in water. Therefore, the stricter threshold in USEPA and CCME water quality criteria were used in this study to assess the concentrations of PAHs. The maximum detectable concentration of the BaP monomer at all the sampling sites was 13.35 ng/L, significantly exceeding the Chinese standard. The concentrations of BaA, InP, BbF, BaP, and DahA exceeded the USEPA threshold values at 100%, 93.2%, 50.8%, 91.5%, and 93.2% sampling sites (Fig. 2). These monomers have potential carcinogenicity. Indeed, the BaP monomer can cause lung and gastric cancers and teratogenesis, as well as endangering the immune and reproductive systems (Taghvaee et al. 2018). In addition, the concentrations of ΣPAHs at all 59 sampling sites were higher than those reported in the USEPA safety guidelines for exposure of aquatic organisms to PAHs in surface water, thus suggesting that PAHs in the river water in the study area may affect human health through biological enrichment (Wang et al. 2018). Therefore, the human exposure risk to PAHs in the study area cannot be ignored.

Spatial distribution characteristics of PAHs

The spatial distribution of ΣPAHs at 59 sampling sites in the Kuye River is shown in Fig. 3. The highest ΣPAHs concentrations ranged from 227.74 to 278.16 ng/L and were observed at sampling sites S36~S40, near Ningtiaota Industrial Park. The highest proportions were attributed to Chry and BaA, with concentrations of 86.91~121.22 ng/L and 45.68~58.10 ng/L, respectively, whereas S53, S54, S57, and S45~S48, in the densely populated residential areas (Shamao and Shenmu Town), revealed the second-highest ΣPAHs concentrations range content of 153.95~207.16

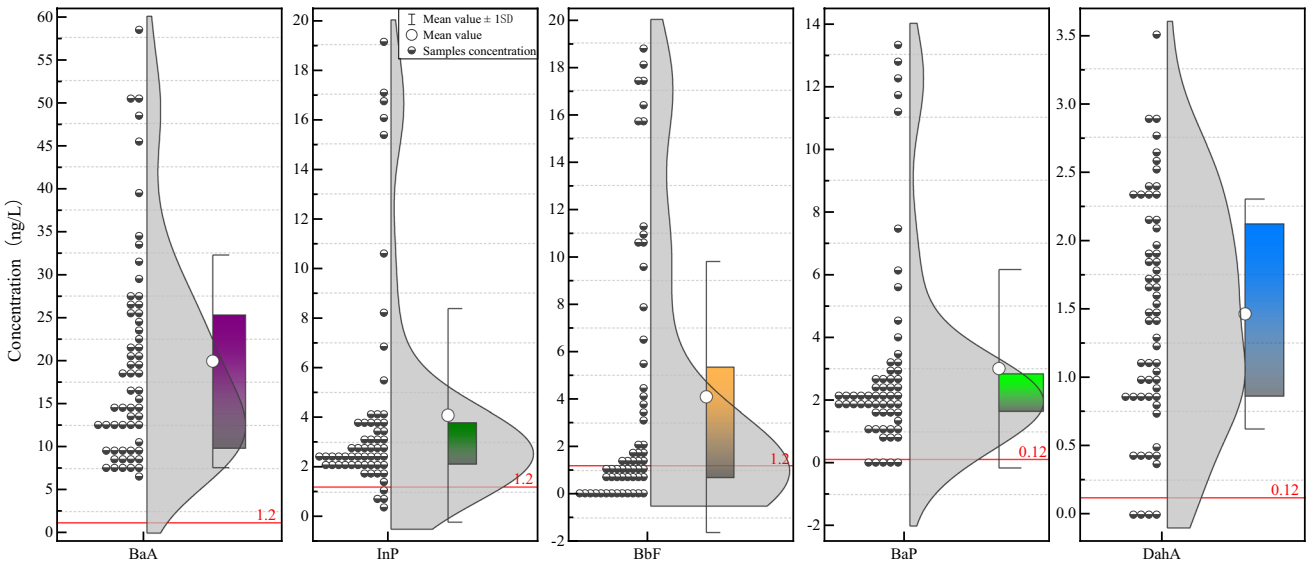

Fig. 2 PAHs monomer concentrations at the 59 sampling sites in the study area. Red lines indicate the USEPA threshold values

ng/L. In addition, ΣPAHs concentrations at the sampling sites S13 and S14 of Daliuta Town were 142.16 and 153.96 ng/L, respectively, whereas the ΣPAHs concentrations at the sampling sites S5, S6, S7, S19, and S20 were relatively low, which were located in remote areas, far away from areas with industrial and human activities. On the other hand, the sampling site S59, located downstream of the Kuye River entrance into Yellow River, showed ΣPAHs concentration (87.09 ng/L), indicating that the PAHs pollution in the Kuye River did not significantly affect the water quality at the main stream of the Yellow River.

The obtained results showed 5 PAHs monomers exceeding the USEPA threshold concentrations at multiple sampling sites in the Kuye River, namely BaA, InP, BbF, BaP, and DahA (Fig. 2). The spatial distributions of these 5 monomers are shown in Fig. 3. Among them, BaA

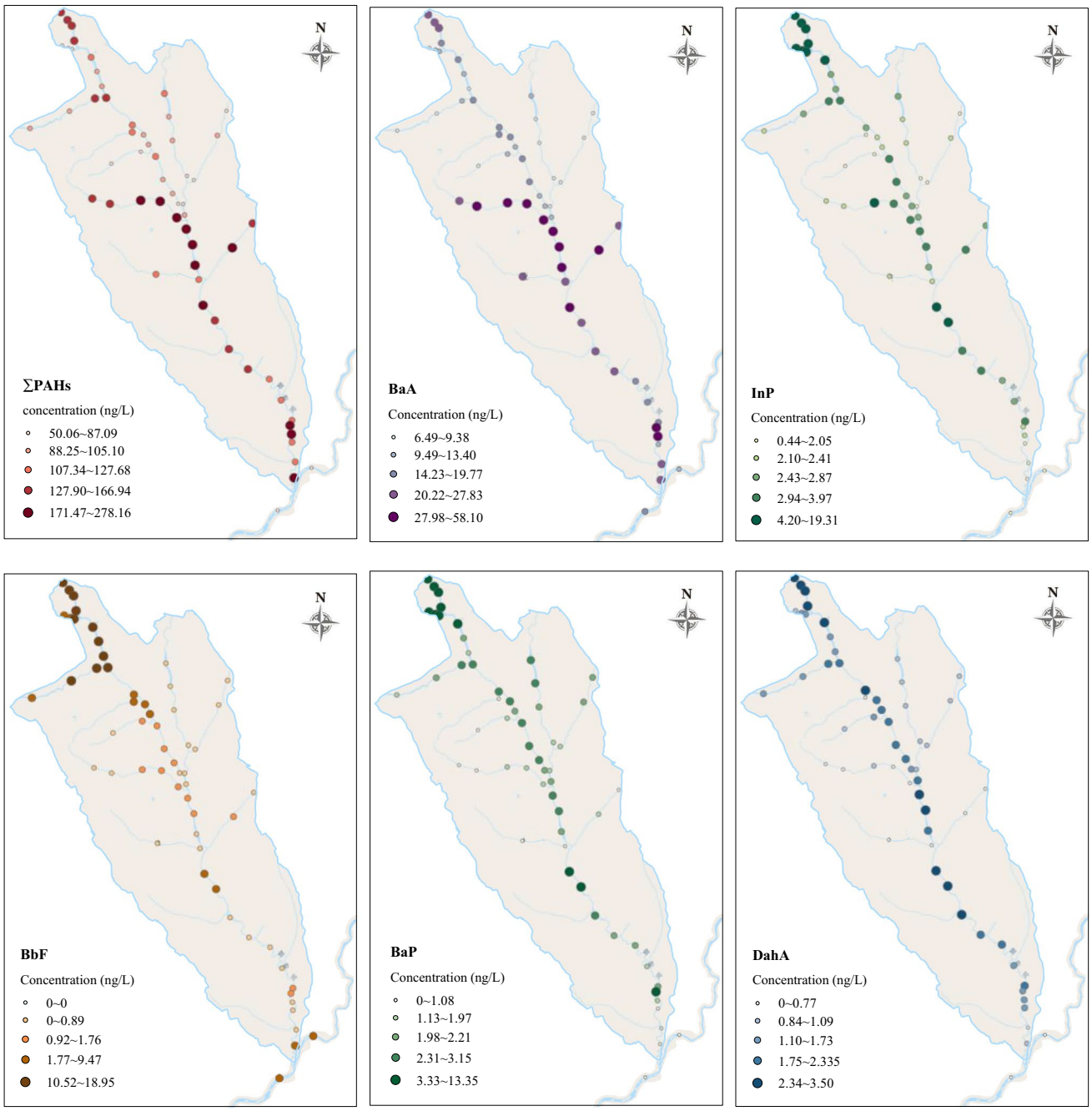

Fig. 3 ΣPAHs and 5 PAHs monomers concentration distributions of water samples in study area. The bubble size and color depth in the figure represent the concentration

showed the highest concentration in Ningtiaota Industrial Park, followed by Shamao Town, whereas InP and BaP showed similar distribution characteristics, except for the upstream area, where Shenmu Town showed high concentrations. The BbF concentration in the area above Daliuta Town was significantly higher than that in other areas, while DahA high concentrations were widely distributed and revealed slight spatial differences. The spatial distributions of the remaining 11 monomers are shown in Fig. S1 of the Supplemental material.

According to these results, the high-value point of each monomer concentration and ΣPAHs were similar; these were mainly distributed near mining active industrial areas and towns. In fact, Lantan production, thermal power generation, coking, and coal products manufacturing accounted for a large proportion of production structures in Ningtiaota Industrial Park. PAHs, generated from coal combustion, entered the rover water through atmospheric dry and wet deposition and surface runoff. In addition, industrial wastewater from coal mining, coal chemical industry, magnesium aluminum industry around Daliuta and Shenmu Town, tail gas emission from coal-heavy truck transportation vehicles, and agricultural production, living, and vehicle exhaust emissions in densely populated residential areas may have also contributed to the increase in the concentrations of PAHs in the river water. Mining production and coal-fired industries, as pillar industries in the local area, had a significant impact on the spatial distribution of PAHs, which requires particular attention.

Component characteristics

The 16 PAHs monomers were classified in this study according to their ring numbers. Figure 4 shows the ternary composition diagram of PAHs in the Kuye River. The results revealed large relative abundances of 4-ring PAHs, namely Fla, Pyr, Chry, and BaA, at the 59 sampling sites, ranging from 38.59 to 70.85%, with an average value of 51.41%. The 2- and 3-ring PAHs were the second most abundant PAHs in the study area, accounting for 9.44~50.79%, with an average value of 33.22%, whereas the relative abundances of the 5- and 6-ring PAHs were low, mostly below 20%. Indeed, 5- and 6-ring high molecular weight PAHs are generally carcinogenic, with toxicity equivalent factors often higher than those of 2–4 rings. In addition, the results showed relative abundances close to 50% for only the high ring PAHs in the upstream (S1–S8 sampling sites), while medium and low ring PAHs, with low toxicity equivalent factors, were mainly observed at the remaining sampling sites, suggesting low toxicity risk.

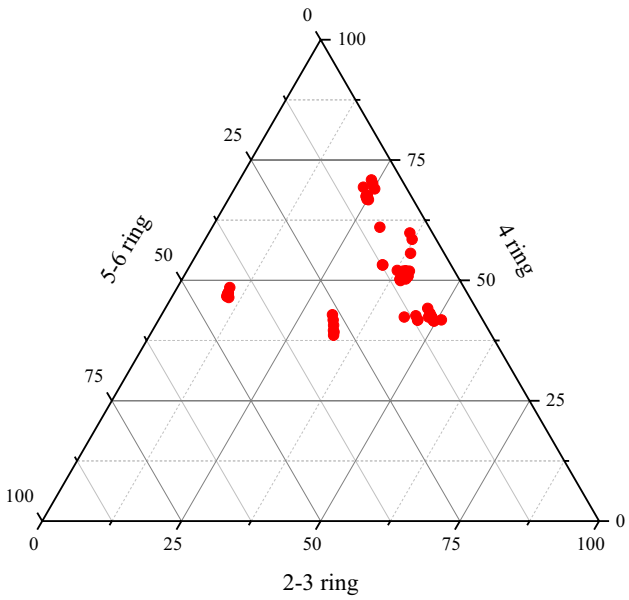

Fig. 4 Ternary composition diagram of PAHs in the surface water of Kuye River

Comparison with other water bodies

Compared with other surface water in similar regions worldwide (Table 1), the concentrations of ΣPAHs in the Kuye River (50.06–278.16 ng/L) were much higher than those observed in the surface water of the Fengfeng coal mining area (Hao et al. 2018), Huainan mining area (Chen et al. 2005), and Jianghan oilfield river (Li et al. 2020). In addition, the concentrations of ΣPAHs in the Kuye River were slightly similar to those observed in the surface water of the Shilong coal mining area (Yang et al. 2007) and Amu Darya Basin (Jin et al. 2022) and significantly lower than those observed in the Heshan coalfield river (Huang et al. 2016), Shaying River (Du et al. 2020), and Fenhe Basin (Zhao et al. 2017). Therefore, the concentrations of ΣPAHs in the study area were at moderate levels compared to those revealed in previous related studies.

Discussion

Source identifications of PAHs using diagnostic ratios

The identification of PAHs sources in the natural environment is relatively complex since PAHs monomers can be derived from several anthropogenic sources, including oil, oil combustion, and coal and biomass combustion. Indeed, the isomer ratios of PAHs, showing stable chemical proprieties, can be used to determine their related

Table 1 Concentrations of PAHs and their associated ecological risk values in surface water of mining areas in China and other countries

Region	Water body	Number PAHs	Range ΣPAHs/(ng/L)	Mean ΣPAHs/(ng/L)	References	Ecological risk assessment	
						High-risk monomers	Risk quotient of ΣPAHs
Coal mining area	Kuye River, China	16	50.06–278.16	128.22	This study	BaA	$RQ_{\sum PAHs(MPCs)}$=1.99 $RQ_{\sum PAHs(NCs)}$=328.82
Coal mining area	Heshan coalfield river in Guangxi, China	16	199.45–1350.84	426.98	Huang et al. (2016)	BaA, BbF	$RQ_{\sum PAHs(MPCs)}$=2.87 $RQ_{\sum PAHs(NCs)}$=608.90
Coal mining area	Shaying River, China	16	356.60–2275.04	1051.23	Du et al. (2020)	BghiP, InP, Pyr, BaA, BbF, BaP	$RQ_{\sum PAHs(MPCs)}$=29.88 $RQ_{\sum PAHs(NCs)}$=3277.70
Coal mining area	Fenhe Basin, China	15	530–16002	2738	Zhao et al. (2017)	Acy, Flu, Ace, Phe, BaA, BbF, BkF	$RQ_{\sum PAHs(MPCs)}$=32.97 $RQ_{\sum PAHs(NCs)}$=3580.65
Coal mining area	Surface water of Shilong coal mining area, China	14	68–380	—	Yang et al. (2007)	—	—
Coal mining area	Surface water of Fengfeng coal mining area, China	16	1.35–2.92	2.14	Hao et al. (2018)	No	$RQ_{\sum PAHs(MPCs)}$=0 $RQ_{\sum PAHs(NCs)}$=3.10
Coal mining area	Surface water of Huainan mining area, China	5	—	23.70	Chen et al. (2005)	No	$RQ_{\sum PAHs(MPCs)}$=0 $RQ_{\sum PAHs(NCs)}$=46.39
Oilfield area	Jianghan oilfield river, China	7	ND–14.12	4.04	Li et al. (2020)	No	$RQ_{\sum PAHs(MPCs)}$=0 $RQ_{\sum PAHs(NCs)}$=3.26
Coking area	Surface water around coking plant in Tangshan, China	16	282–1269	757	Xing et al. (2021)	Ant, BaA, BbF	$RQ_{\sum PAHs(MPCs)}$=6.06 $RQ_{\sum PAHs(NCs)}$=1048.44
Industrial area	Amu Darya Basin, Uzbekistan	16	3.19–779	98.4	Jin et al. (2022)	BbF	$RQ_{\sum PAHs(MPCs)}$=1.57 $RQ_{\sum PAHs(NCs)}$=361.97
Industrial area	Ganges River, India	16	0.05–65.90	31.89	Sharma et al. (2018)	—	—
Industrial area	Daliao River Estuary, China	16	71.12–4255.43	748.76	Zheng et al. (2016)	Pyr	$RQ_{\sum PAHs(MPCs)}$=3.07 $RQ_{\sum PAHs(NCs)}$=673.87
Industrial area	Yongding River, China	15	53.53–506.53	124.43	Wang et al. (2018)	No	$RQ_{\sum PAHs(MPCs)}$=0 $RQ_{\sum PAHs(NCs)}$=156.31

"—" denotes "no data", *ND* not detected

anthropogenic sources and transport, based on the distinct composition characteristics of PAHs from different sources (Tu et al. 2018). In this study, PAHs isomer ratios, namely Fla/(Fla+Pyr) and Ant/(Ant+Phe), were used to identify the pollution sources, as shown in Fig. 5. It is generally believed that when Fla/(Fla+Pyr) is greater than 0.5, PAHs pollution mainly comes from the combustion of biomass and coal. A Fla/(Fla+Pyr) ratio between 0.4 and 0.5 indicate the combustion of petroleum, whereas a Fla/(Fla+Pyr) ratio of less than 0.4 suggests leakage of petroleum. In addition, Ant/(Ant+Phe) ratios of greater than 0.1 and less than 0.1 suggest combustion sources and leakage of petroleum, respectively (Wu et al. 2011; Maioli et al. 2011).

According to the results obtained (Fig. 5), Fla/(Fla+Pyr) and Ant/(Ant+Phe) ratios of 7% sampling sites of Kuye River suggested leakage of petroleum. Indeed, these sampling sites were adjacent to the coal mine and were vulnerable to be impacted by the leakage of machine petroleum in mining. In addition, about 38% of the sampling sites showed mixed pollution sources of petroleum leakage, combustion of biomass and coal, and combustion of petroleum. PAHs pollution in other regions was mainly caused by combustion, of which 16% of sampling sites revealed a petroleum

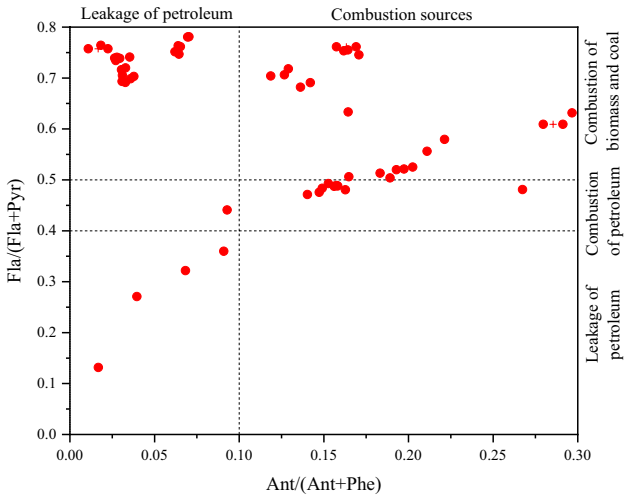

Fig. 5 PAHs source identifications by diagnostic ratios

combustion source. In fact, most of these sample sites were close to the main channel of coal transportation. In addition, frequent traffic congestion on national highways caused a large amount of exhaust from motor vehicles. The remaining 39% of samples suggested combustion sources of biomass and coal. It should be noted that the observed Chry, BaA, and Phe concentrations in the Kuye River were relatively high, which is described in the "Occurrence of PAHs in river water" section. Chry is a gasoline combustion and coal combustion characteristic compound, while BaA and Phe are specific characteristic compounds of coal combustion (Qu et al. 2020; Zhang et al. 2022a, b). The relatively high concentrations of these three compounds suggested a more coal combustion source in the study area, with significant pollution from heavy-truck vehicle exhaust, which conformed to the characteristics of the research area as a national energy and chemical industry base and one of the seven largest coalfields in the world. The PAHs diagnostic ratios allowed the identification of the pollution sources in the study area, providing a basis for quantitative analysis of PAHs sources.

Source apportionment of PAHs using PMF model

The PMF model was used to further quantitatively assess the PAHs source compositions and their contributions to the pollution of the Kuye River in the study area. The error factor (EF) ranged from 0.05 to 0.3. In this study, the EF value was assumed to be 0.2. Different factor numbers from 3 to 6 were sequential operations. In addition, the smaller dQ(Robust) value, the larger R^2, and the clearly interpretable factors in this region were considered in this study. The final factor number was 4, and the optimal number of model iterations and dQ(Robust) were the third time, −0.29, respectively, with a monomer R^2 range of 0.45–0.99, suggesting good operation results of the model. The final source profiles obtained are shown in Fig. S2 of the Supplemental material.

It can be seen from Fig. S2 that the main identified components of factor 1 were InP, BbF, and BaP. These PAHs compounds are common characteristic emission monomers of gasoline and diesel engine emissions (Riaz et al. 2019; Ili et al. 2021). This factor was related to the vehicle emission source due to the presence of many national roads in the region, which are the main transportation routes for coal and heavy traffic. On the other hand, the main load monomers of factor 2 were Phe, Chry, and BaA, which were characteristic emissions of coal combustion (Cao et al. 2020; Huang et al. 2016), thereby, this factor was related to the coal combustion source. Coal mining, as pillar industries in the local area, has also driven the development of the coal chemical industry and some related industries in the study area, such as cogeneration, thermal power generation, and metal smelting. As a combustion energy, coal is widely used in this region. Moreover, the study area is rich in coal, and coal combustion is the main heat source for residents in this area. The main load monomer of factor 3 was Ant, which was generally used as an identification component of fuel-wood combustion source (Hellén et al. 2008); therefore, this factor was related to the fuel-wood combustion source. The study area contains a high proportion of the rural population. In fact, biomass (e.g., wood and straw) are one of the living fuels in rural areas. On the other hand, factor 4 revealed higher loads on Nap, Acy, Flu, and Ace, all of which were 2~3 ring PAHs, and these low rings' PAHs were related to coking emission sources (Liu et al. 2021a, b). Also, Nap, Acy, and Flu are indicators of petrochemical leakage (Miao et al. 2018; Qiao et al. 2021). So they are identified as coking/petroleum sources. There are several coking companies in the study area, so PAHs in coking waste gas and fly ash can enter the water through dry and wet depositions. The coal mining industry in the study area is mainly mechanical mining, and certain petroleum substances will leak during mechanical mining. In addition, industrial wastewater discharged by coal chemical enterprises will also cause petroleum pollution.

According to the average contribution rate of each pollution source, calculated using PMF5.0, coking/petroleum sources revealed the highest contribution (37.91%) to PAHs in the Kuye River, followed, respectively, by coal combustion sources (36.31%), vehicle emission sources (13.93%), and fuel-wood combustion sources (11.85%). Indeed, the coal industry is the pillar industry in Yulin, where there are hundreds of coal mines, coal chemical companies, and thermal power plants, which is consistent with source apportionment results. The PAHs in the study area were mainly derived from coal-related activities.

In order to comprehensively assess the spatial impact of different pollution sources on the river water of the study

area, the contribution rates of each pollution source to PAHs concentration at the 59 sampling sites were calculated using the PMF method (Fig. 6). The highest contribution rates of coal combustion and coking/petroleum sources to the PAHs concentrations in the river water were 92% and 87%, respectively, and were mainly observed near the mining activity area, indicating that the coal industry had a great impact on the quality of the surrounding waters. On the other hand, a small number of sampling sites located at the coal transportation hub were greatly affected by vehicle emission sources, while sporadically distributed sampling sites were greatly affected by fuel-wood combustion sources. In addition, vehicle emission and fuel-wood combustion sources showed contribution rates of less than 40% at most other sampling sites, suggesting insignificant impacts of these sources on water PAHs pollution in the study area.

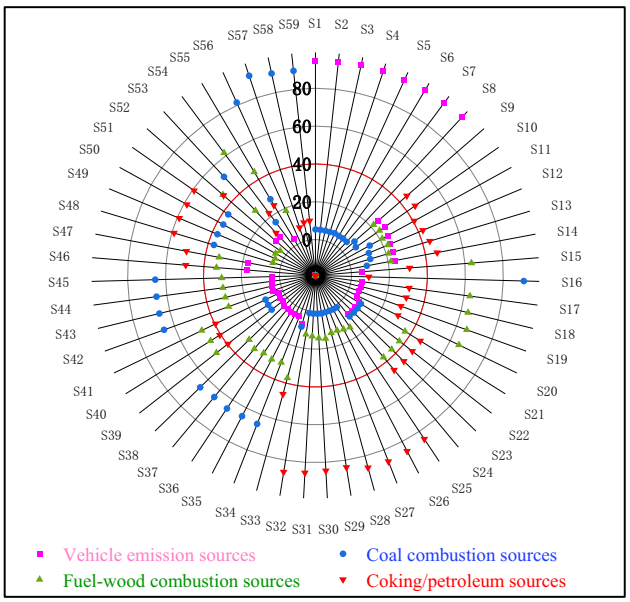

Fig. 6 Contribution rations of each pollution source to 59 receptor samples

Ecological risk assessment of PAHs in the Kuye River

The calculated risk quotient of PAHs monomer (Fig. 7a) showed that the RQ_{MPCs} and RQ_{NCs} values of Nap were less than 1, suggesting a low-risk level, whereas RQ_{MPCs} and RQ_{NCs} values of BaA were 1.99 and 199.28, respectively, significantly higher than those of the other monomers, suggesting a high-risk level, which indicating that BaA significantly affected the ecological environment of the Kuye River in the study area. Therefore, prompt actions should be taken to reduce the concentration of this monomer. On the other hand, RQ_{MPCs} values of other monomers were all less than 1, and RQ_{NCs} values were all greater than 1, suggesting medium risks. Therefore, surveillance of these monomers should be strengthened in the Kuye River to prevent subsequent increases in their concentrations.

The results of the ecological risk quotient of ΣPAHs at each sampling site (Fig. 7b) showed that the $RQ_{\sum PAHs(MPCs)}$ values of S5, S6, S11, S19, and S25–32 were equal to 0, while those of $RQ_{\sum PAHs(NCs)}$ were less than 800, indicating low ecological risk at these sampling sites. On the other hand, $RQ_{\sum PAHs(MPCs)}$ and $RQ_{\sum PAHs(NCs)}$ values of the

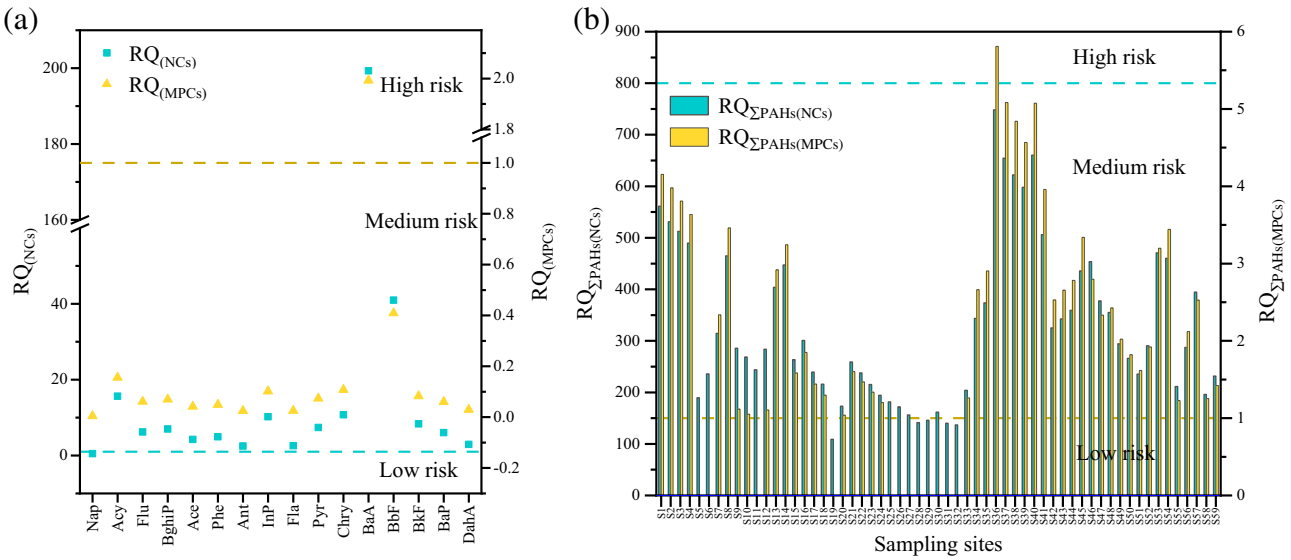

Fig. 7 PAHs ecological risk in the study area. **a** Ecological risk quotient of PAHs monomer. **b** ΣPAHs ecological risk quotient of 59 sampling sites

remaining sampling sites were greater than 1 and less than 800, respectively, indicating medium- to high-risk levels. Among them, $RQ_{\sum PAHs(NCs)}$ value at S36 was 748.40, which was close to the high ecological risk threshold. This sampling site is located in the Ningtiaota Industrial Park, and the PAHs produced during industrial production process exposed the surrounding waters to a high ecological risk. Therefore, it is urgent to formulate a prevention and control plan in the study region.

By considering the concentrations of PAHs in other surface water of mining areas in the Kalf risk quotient method, the high-risk monomers and ecological risk quotient of ΣPAHs were obtained for each water body (Table 1). Compared with other surface water, the ecological risk of ΣPAHs in the Kuye River was at a moderate level. In addition, as can be seen from Table 1, BaA and BbF in rivers exhibited high-risk levels in many mining areas. Therefore, it is important to develop effective measures in future related studies on the ecological environment in mining areas to control the sources of these two monomers.

The detected PAHs in the surface water of the Kuye River presented certain ecological risks. Indeed, PAHs pollution may become increasingly serious in the future due to the continuous development of coal industries, thereby further affecting negatively the ecological environment and endangering human health. Therefore, researchers should monitor surface water regularly and collect soil, air, and groundwater PAHs samples in the study area to improve the accuracy of source distribution analysis in future research, thereby contributing to the assessment of pollution control plans for ensuring sustainable development of coal industries.

Conclusions

In this study, the statistical analysis and PMF model were used to analyze the characteristic of PAHs in surface water in the Kuye River, northern Shaanxi mining area, China. The results showed a ΣPAHs concentration range of 50.06–278.16 ng/L, with an average value of 128.22 ng/L, indicating an average pollution level compared to other rivers in mining areas. In addition, the middle ring PAHs accounted for a large proportion. There were substantial spatial variations in the concentrations of PAHs in the study area. Moreover, the high-value point of each monomer concentration and ΣPAHs were similar, particularly near active mining areas and towns. The PMF model results showed that coking/petroleum and coal combustion were the major sources contributing to the increase in the concentrations of PAHs in the Kuye River, with average contribution rates of 37.91 and 36.31%, respectively, followed by vehicle emission (13.93%) and fuel-wood combustion (11.85%). The ecological risk assessment results showed a high BaA-related ecological risk, affecting seriously the ecological environment of the Kuye River. On the other hand, the ecological risk of ΣPAHs in the Ningtiaota Industrial Park was close to the high ecological risk threshold. This work should be valuable for revealing the fates of PAHs and also provide support for the control and management of persistent organic pollutants in mining area river.

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Data availability Not applicable

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Declarations

Ethical approval Not applicable

Consent to participate Not applicable

Consent for publication The authors confirm that the work described has not been published before; it is not under consideration for publication elsewhere; and this publication has been approved by all co-authors; its publication has been approved by the responsible authorities at the institution where the work is carried out.

Competing interests The authors declare no competing interests.

References

Canadian Council of Ministers of the Environment (CCME) (2015) Canadian environmental quality guidelines. http://st-ts.ccme.ca/en/index.html

Cao Y, Xin M, Wang B, Lin C, Liu X, He M, Lei K, Xu L, Zhang X, Lu S (2020) Spatiotemporal distribution, source, and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in the urbanized semi-enclosed Jiaozhou Bay China. Sci Total Environ 717:137224

Chen J (2005) Distribution and occurrence of polycyclic aromatic hydrocarbons in Huainan mining area and its environmental impact. China University of Geosciences (in Chinese)

Chen D, Feng Q, Liang H, Gao B, Alam E (2019) Distribution characteristics and ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in underground coal mining environment of Xuzhou. Hum Ecol Risk Assess 25(6):1564–1578

Chen J, Fan B, Li J, Wang X, Li W, Cui L, Liu Z (2020) Development of human health ambient water quality criteria of 12 polycyclic aromatic hydrocarbons (PAH) and risk assessment in China. Chemosphere 252(4):126590

Dong Y, Li L, Wu H, Wu X, Jia G (2020) Applied on potassium permanganate pre-oxidation technology based on water quality change of water source. Water Wastewater Eng 46(9):60–64

Du S, Ding T, Dong H, Liu X, Zhang Y, Zeng H, He L (2020) Pollution and ecological risk assessment of polycyclic aromatic hydrocarbons in the water environment of Shaying River Basin China. J Agro-Environ Sci 39(3):601–611

Han J, Liang Y, Zhao B, Wang Y, Xing F, Qin L (2019) Polycyclic aromatic hydrocarbon (PAHs) geographical distribution in China and their source, risk assessment analysis. Environ Pollut 251:312–327

Hao C, Huang Y, Ma D, Fan X, He P, Sun W (2018) Environmental behaviors of PAHs in Ordovician limestone water of Fengfeng coal mining area in China. Environ Monit Assess 190(12):701–713

Hellén H, Hakola H, Haaparanta S, Pietarila H, Kauhaniemi M (2008) Influence of residential wood combustion on local air quality. Sci Total Environ 393(2-3):283–290

Huang H, Xing X, Zhang Z, Qi S, Yang D, Yuen DA, Sandy EH, Zhou AG, Li X (2016) Polycyclic aromatic hydrocarbons (PAHs) in multimedia environment of Heshan coal district, Guangxi: distribution, source diagnosis and health risk assessment. Environ Geochem Health 38(5):1169–1181

Ili P, Nii T, Farooqi ZUR (2021) Polycyclic aromatic hydrocarbons contamination of soil in an industrial zone and evaluation of pollution sources. Pol J Environ Stud 30(1):155–162

Jiang C, Zhao D, Chen X, Zheng L, Li C, Ren M (2022) Distribution, source and ecological risk assessment of polycyclic aromatic hydrocarbons in groundwater in a coal mining area. China Ecol Indic 136:108683

Jin M, Wu J, Zhan S, Shaniyazov S (2022) Distribution, sources and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in waters of Amu Darya Basin. Uzbekistan J Lake Sci 34(3):855–867

Khanal R, Furumai H, Nakajima F, Yoshimura C (2018) Carcinogenic profile, toxicity and source apportionment of polycyclic aromatic hydrocarbons accumulated from urban road dust in Tokyo. Japan Ecotoxicol Environ Saf 165:440–449

Li S, Tan G, Li Z, Peng Z, Wang S (2020) Study on distribution characteristics and risk assessment of PAHs in water environment of Jianghan oilfield. Res Environ Eng 34(4):580–585

Li Y, Liu M, Hou L, Li X, Yin G, Sun P, Yang J, Wei X, He Y, Zheng D (2021) Geographical distribution of polycyclic aromatic hydrocarbons in estuarine sediments over China: human impacts and source apportionment. Sci Total Environ 768:145279

Liang M, Liang H, Rao Z, Xu D (2020) Occurrence of polycyclic aromatic hydrocarbons in groundwater from rural areas in eastern China: spatial distribution, source apportionment and health cancer risk assessment. Chemosphere 259:127534

Liu X, Bai Z, Yu Q, Cao Y, Zhou W (2017) Polycyclic aromatic hydrocarbons in the soil profiles (0-100 cm) from the industrial district of a large open-pit coal mine. China RSC Adv 7(45):28029–28037

Liu H, Yu X, Liu Z, Sun Y (2018) Occurrence, characteristics and sources of polycyclic aromatic hydrocarbons in arable soils of Beijing. China Ecotoxicol Environ Saf 159:120–126

Liu J, Liu YJ, Liu Z, Zhang A, Liu Y (2019a) Source apportionment of soil PAHs and human health exposure risks quantification from sources: the Yulin National Energy and Chemical Industry Base, China as case study. Environ Geochem Health 41(2):617–632

Liu Y, Gao P, Su J, da Silva EB, de Oliveira LM, Townsend T, Xiang P, Ma LQ (2019b) PAHs in urban soils of two Florida cities: background concentrations, distribution, and sources. Chemosphere 214:220–227

Liu C, Huang Z, Qadeer A, Liu Y, Qiao X, Zheng B, Zhao G, Zhao X (2021a) The sediment-water diffusion and risk assessment of PAHs in different types of drinking water sources in the Yangtze River Delta. China J Cleaner Prod 309:127456

Liu J, Zhang A, Liu Y, Liu Z, Liu Y, Wu X (2021b) Analysis of the mechanism for enhanced pyrene biodegradation based on the interactions between iron-ions and Rhodococcus ruber strain L9. Ecotoxicol Environ Saf 225:112789

Maioli OLG, Rodrigues KC, Knoppers BA, Azevedo DA (2011) Distribution and sources of aliphatic and polycyclic aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems. Cont Shelf Res 31(10):1116–1127

Meng Y, Liu X, Lu S, Zhang T, Jin B, Wang Q, Tang Z, Liu Y, Guo X, Zhou J, Xi B (2019) A review on occurrence and risk of polycyclic aromatic hydrocarbons (PAHs) in lakes of China. Sci Total Environ 651:2497–2506

Miao Y, Kong X, Li C (2018) Distribution, sources, and toxicity assessment of polycyclic aromatic hydrocarbons in surface soils of a heavy industrial city, Liuzhou. China Environ Monit Assess 190(3):164

Ministry of environmental protection of the People's Republic of China (2002) Environmental Quality Standards for Surface Water (GB3838-2002)

Montuori P, Aurino S, Garzonio F, Sarnacchiaro P, Nardone A, Triassi M (2016) Distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in water and sediments from Tiber River and estuary. Italy Sci Total Environ 566-567:1254–1267

Orecchio S, Bianchini F, Bonsignore R, Blandino P, Barreca S, Amorello D (2015) Profiles and sources of PAHs in sediments from an open-pit mining area in the Peruvian Andes. Polycycl Aromat Compd 36(4):429–451

Qiao X, Zheng B, Li X, Zhao X, Dionysiou DD, Liu Y (2021) Influencing factors and health risk assessment of polycyclic aromatic hydrocarbons in groundwater in China. J Hazard Mater 402:123419

Qu Y, Gong Y, Ma J, Wei H, Liu Q, Liu L, Wu H, Yang S, Chen Y (2020) Potential sources, influencing factors, and health risks of polycyclic aromatic hydrocarbons (PAHs) in the surface soil of urban parks in Beijing. China Environ Pollut 260:114016

Ren C, Zhang Q, Wang H, Wang Y (2021) Characteristics and source apportionment of polycyclic aromatic hydrocarbons of groundwater in Hutuo River alluvial-pluvial fan, China, based on PMF model. Environ Sci Pollut Res 28:9647–9656

Riaz R, Ali U, Li J, Zhang G, Alam K, Sweetman AJ, Jones KC, Malik RN (2019) Assessing the level and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in soil and sediments along Jhelum riverine system of lesser Himalayan region of Pakistan. Chemosphere 216:640–652

Ribeiro J, Silva T, Filho JGM, Flores D (2012) Polycyclic aromatic hydrocarbons (PAHs) in burning and non-burning coal waste piles. J Hazard Mater 199-200:105–110

Shao Y, Wang Y, Xu X, Wu X, Jiang Z, He S, Qian K (2014) Occurrence and source apportionment of PAHs in highly vulnerable karst system. Sci Total Environ 490:153–160

Sharma BM, Melymuk L, Bharat GK, Přibylová P, Sáňka O, Klánová J, Nizzetto L (2018) Spatial gradients of polycyclic aromatic hydrocarbons (PAHs) in air, atmospheric deposition, and surface water of the Ganges River basin. Sci Total Environ 627:1495–1504

Taghvaee S, Sowlat MH, Hassanvand MS, Yunesian M, Naddafi K, Sioutas C (2018) Source-specific lung cancer risk assessment of ambient PM (2.5)-bound polycyclic aromatic hydrocarbons (PAHs) in central Tehran. Environ Int 120:321–332

Tong R, Yang X, Su H, Pan Y, Zhang Q, Wang J, Long M (2018) Levels, sources and probabilistic health risks of polycyclic aromatic hydrocarbons in the agricultural soils from sites neighboring suburban industries in Shanghai. Sci Total Environ 616-617:1365–1373

Tu YT, Ou JH, Tsang DCW, Dong CD, Chen CW, Kao CM (2018) Source identification and ecological impact evaluation of PAHs in urban river sediments: a case study in Taiwan. Chemosphere 194:666–674

Ugwu KE, Ukoha PO (2016) Analysis and sources of polycyclic aromatic hydrocarbons in soil and plant samples of a coal mining area in Nigeria. Bull Environ Contam Toxicol 96(3):383–387

USEPA (2015) National Recommended Water Quality Criteria. United States Environmental Protection Agency, Washington, DC

Wang J, Chen S, Xia T (2010) Environmental risk assessment of heavy metals in Bohai Sea. North China Procedia Environ Sci 2:1632–1642

Wang Y, Zhang S, Cui W, Meng X, Tang X (2018) Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface water from the Yongding River basin, China: seasonal distribution, source apportionment, and potential risk assessment. Sci Total Environ 618:419–429

Wu YL, Wang HX, Li YY, Hong HS (2011) Occurrence of polycyclic aromatic hydrocarbons (PAHs) in seawater from the Western Taiwan Strait. China Mar Pollut Bull 63(52):459–463

Wu X, Lenon GP, Dong Y (2020) The calculation of riverine ecological instream flows and runoff profit-loss analysis in a coal mining area of northern China. River Res Appl 36(5):760–768

Wu X, Gao X, Tan T, Li C, Yan R, Chi Z, Feng Y, Gong P, Fang J, Zhang X, Aihemaiti K, Xu D (2021) Sources and pollution path identification of PAHs in karst aquifers: an example from Liulin karst water system, northern China. J Contam Hydrol 241:103810

Xing S, Li L, Fu G, Feng H, Hao Z, Zhang X, Chen B (2021) Characteristics and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in surface water in coking areas, Tangshan City. China Acta Sci Circumst 41(9):3586–3597

Yang C, Zhong N, Chen D, Wang J, Peng X (2007) Composition and distribution characteristics of polycyclic aromatic hydrocarbons in waters samples from a coal-mining area, Henan. China J Saf Environ 7(1):75–78

Zhang S, Zhang Q, Darisaw S, Ehie O, Wang G (2007) Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana. USA Chemosphere 66(6):1057–1069

Zhang K, Chang S, Fu Q, Fan Y, Wang E, Sun X, Wang S (2022a) Pollution characteristics and risks of polycyclic aromatic hydrocarbons in underground and surface drinking water sources in northeast Inner Mongolia. Environ Sci 43(6):3005–3015

Zhang Y, Cheng D, Lei Y, Song J, Xia J (2022b) Spatiotemporal distribution of polycyclic aromatic hydrocarbons in sediments of a typical river located in the Loess Plateau, China: influence of human activities and land-use changes. J Hazard Mater 424:127744

Zhao Y, Dang J, Wang F (2017) Spatial variety and ecological risk of polycyclic aromatic hydrocarbons (PAHs) in water and surface sediments of Fenhe River Basin. China Asian J Ecotoxicol 12(3):579–596

Zheng B, Wang L, Lei K, Nan B (2016) Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area. China Chemosphere 149:91–100

Zheng L, Ou J, Liu M, Chen Y, Tang Q, Hu Y (2019) Seasonal and spatial variations of PM_{10}-bounded PAHs in a coal mining city, China: distributions, sources, and health risks. Ecotoxicol Environ Saf 169:470–478