Pol. J. Environ. Stud. Vol. 32, No. 1 (2023), 773-787
DOI: *10.15244/pjoes/155966* ONLINE PUBLICATION DATE: 2022-12-19

Original Research

Source Analysis of Black Carbon with Polycyclic Aromatic Hydrocarbons and Heavy Metals in Sediments and Soils and its Heath Risk Assessment from Chan & Ba River Drainage Basin of China

Tantan Tan[1], Zhihai Tan[1,2]*, Maolin Gu[1], Longjiang Mao[1], Yubo Yuan[1], Qiujing Lei[1], Dongxue Li[1]

[1]School of Environment and Chemistry Engineering, Xi'an Polytechnic University, China
[2]State Key Laboratory of Loess and Quaternary Geology, Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, China

Received: 26 June 2022
Accepted: 21 October 2022

Abstract

Potential risks to people's health should receive much more attention with an increasing compound pollution in urban river ecological landscape. In this paper, the concentrations of 8 heavy metals (HMs, V, Cr, Mn, Co, Ni, Zn, As and Pb), black carbon (BC, char and soot) and polycyclic aromatic hydrocarbons (PAHs) were determined in soils and river sediments collected from 72 sampling sites along the Chan-Ba River, and also were evaluated, concerning source analysis and health risks. The results indicate that the concentrations of BC and PAHs varied seasonally, and the concentration of HMs showed little seasonal variation. The concentration of BC was higher in winter than in summer, while that of PAHs was higher in summer than in winter. These pollutants were spatial heterogeneity. The concentrations of these pollutants in the middle reaches of the Ba River were much higher than those in the upper and lower reaches. These changes are attributed to the spatial-temporal distribution of local pollutant emissions and the characteristics of regional pollutant transportation and deposition. Source and cluster analysis revealed that BC, HMs and PAHs were pyrogenic (including coal and biomass combustions, vehicular emissions). The evaluation of health risk of PAHs and HMs revealed that the cancer risk for adults and children was higher than the 10^{-6} and lower than 10^{-4} implying low to moderate risk, and it is noted that there are higher potential risks of Phe and Flu at the middle reaches in summer and As at the lower reaches in Autumn. Therefore, pollution prevention and monitoring,

*e-mail: tonishtan@163.com

classification management and control mechanisms in designated river basins are necessary to ensure the quality and safety of the ecological environment in the Chan & Ba River basin.

Keywords: sediment, Polycyclic aromatic hydrocarbons (PAHs), Heavy metals (HMs), Black carbon (BC), source

Introduction

With the development of urban industrialization, the ecological landscape of urban river watersheds will be faced with the risks of extensive combined pollution [1]. The river ecological landscape not only improve the urban environment, but also provide water resources, thereby playing an important part in urban development. Sediments from urban rivers are of great significance in river ecosystem. On the one hand, sediments will provide habitats and food sources for various organisms, while on the other hand, sediments function as a primary carrier and reservoir for the migration, transformation and accumulation of pollutants in the environment [2]. Black carbon (BC, char and soot) produced through incomplete combustion of fossil fuels and vegetation is ubiquitously present in soils and sediments, with complex environmental behaviors and environmental effects [3]. BC is considered to be an important factor affecting the migration and transformation of pollutants such as PAHs and HMs in sediments has been attributed its high specific surface area and microporosity [4-5]. This causes a decrease in their mobility and bioavailability, and weakens their ecotoxicological risk. Polycyclic aromatic hydrocarbons (PAHs) are generated from incomplete combustion of energy materials (biomass burning, coal combustion, heating, industrial activities, vehicle emissions, etc.) [6]. PAHs exhibit semi-volatility, long-term persistence and bioaccumulation of persistent organic pollutants and widely occur in a variety of environmental media [7-8]. Research has indicated that the environmental behavior and bioavailability of PAHs are strongly affected by BC [9]. HM produced by industrial coal combustion and traffic emissions settles in sediments and soils in the form of particulate matter by adsorption and condensation [10].

River sediments and soils are challenging concerning environmental problems in urban watersheds [11]. In urbanized areas, most contaminations from internal combustion engines, coal power stations, slash-and-burn agricultural practices, smoke out of industrial and domestic activities (e.g., cooking) can enter river sediments and soils through atmospheric sedimentation (both wet and dry deposition) [12]. Moreover, package and waste from street vendors and food due to inadequate environmental management (weak legislation, enforcement and management), alteration of industrial structure and urban planning are increasing and contaminating the surrounding environment [13-14]. Toxic composite pollutants originating from different emission sources can accumulate in river sediments and soils, producing potential threats to aquatic organisms, ecological and human health through migration and transformation of hydrodynamic mechanisms and food chains [15-16]. Therefore, the potential risk to the residents exposed to PAHs, BC and HMs from river sediments and soils should receive much more attention.

In recent decades, regional pollution exhibits regional heterogeneity and complexity over time [17]. Numerous studies have studied respectively the levels, spatial and temporal variations, sources and ecological risks of individual pollutants (BC or HMs or PAHs) in river sediments and the surrounding soils [18-19]. Moreover, a few publications have reported the correlation of PAHs and HMs, HMs and BC, PAHs and BC [20-21]. But there are limited studies on the environmental/ geographical distribution patterns and interrelation among the three pollutants of BC, HMs and PAHs in soils and river sediments. Therefore, we investigated the sources of pollution and potential relationships among these three pollutants more intuitively in order to understand the compound pollution characteristics and potential pollution sources of urban watersheds.

Chan-Ba River Basin at the east of Xi'an in China is one of the important areas of water conservation, and also an important area for urban ecological environment development across this region. However, the compound pollution has been further aggravated and expanded over the years. This undoubtedly increases the potential risk to the health of the residents here [22-23]. In order to understand the impact of urbanization process on the pollution pattern of river ecological landscape, the study on the pollution characteristics of the Chan & Ba River Basin was taken as an example to provide a basis for the sustainable development and pollution prevention. Therefore, this study focused on investigating the correlations among BC, HMs, and PAHs in river sediments and soils, assessing their potential impacts on environmental safety, and exploring changes in pollution patterns.

Materials and Methods

Study Area and Samples

The study area (109°00′~109°47′E, 33°50′~34°27′N) includes Ba River and Chan River, which are the tributaries of Wei River (it is the largest tributary of Yellow River) (Fig. 1). The river originates in the eastern part of the Zhongnan Mountains of the Qinling Mountains, with a total length of 109 kilometers and a drainage area of 2051 square kilometers. The study

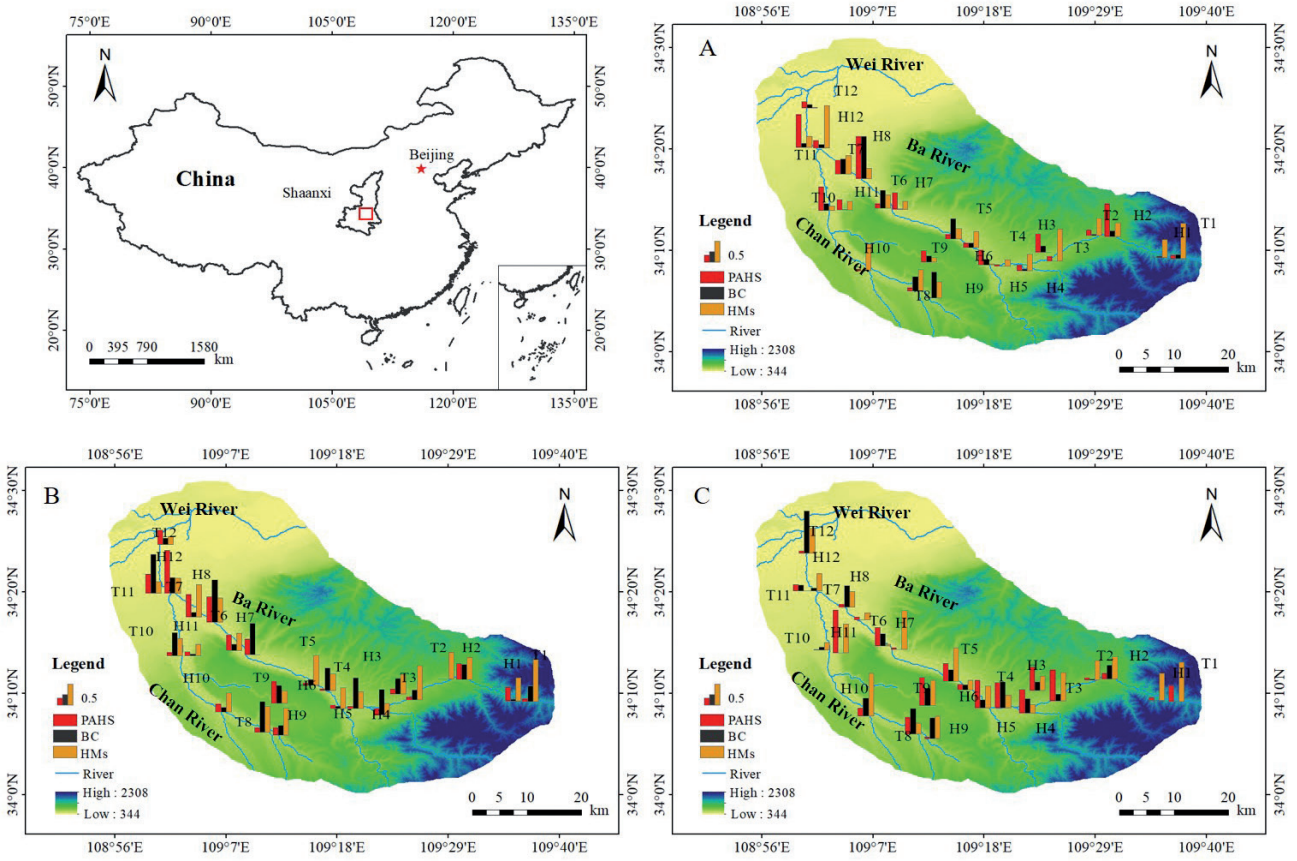

Fig. 1 Study area and sampling sites A: in autumn, B: in winter, C: in summer of Chan & Ba River drainage basin, Xi'an, China.

area lies in the semi-arid and semi-humid monsoon zone. The annual average temperature and average precipitation are 13.3ºC and 720mm, respectively, with 79.3% of precipitation occurring between July and October. This area occupies a very important position in the allocation of water resources in Xi'an.

In this study, a total of 72 samples (Fig. 1) were collected from river sediments (sample points H1-H12) and topsoil in surrounding areas (sample points T1-T12) in October of 2018, January and July of 2019, respectively. Each sample is sealed and delivered to the laboratory for low temperature storage and testing.

Methods

Concentrations of BC were determined with a Model 2001 Thermal/Optical Carbon Analyzer (Atm AA Inc., Calabasas, CA) using IMPROVE thermal/optical reflectance method after acid pretreatment (HCl 10% and HF 48%) to remove carbonates and the mineral fractions. For this process, mostly volatilized carbon evolves in a pure He atmosphere while the temperature is heated stepwise to 120, 250, 450 and 550 °C to produce OC1, OC2, OC3, and OC4 thermal carbon fractions. Then, 2% O_2/98% atmosphere is introduced after OC4 peak returns to baseline, and oxidized carbon evolves at 550, 700 and 800 °C to produce EC1, EC2, and EC3 fractions. The POC nearly evolves as part of EC1 fraction. Char and soot contents were calculated as described by LI [24]. In terms of quality control, standard samples (glucose) were selected before analysis and blank samples, and two duplicate samples every 12 samples.

HMs contents were analyzed using PW2403 X-ray fluorescence spectrometer (Philips, HOL). After natural airing, the collected samples are sieved through 200 meshes, 0.6 g soil samples are weighed and 6 g lithium tetraborate is added, stirred evenly, and the content of HMs is measured after melting the samples (about 20 min). Before sample analysis, PAHs correction was used to ensure the stability of XRF. The quality control included the determination of Chinese National Standard material and blank samples (boric acid tablets). The results showed that the difference between standard material and reference values was less than 0.4%. One duplicate sample was prepared for every 12 samples. No target element is detected in the blank, and the RSD of duplicate samples is less than 10%.

The concentrated extracts were analyzed for 16 EPA priority PAHs by GC/MS (Agilent 6890 GC-5975 MS). Soil samples were Ultrasonic-extracted with acetone-dichloromethane (1:1, v/v). The extract was concentrated to 5 ml by nitrogen, then 30 ml of dichloromethane and n-hexane mixture (1:1, v/v) Elute,

blow nitrogen to 1 ml, and transfer it to a 1.5 ml injection bottle for testing. The GC equipped with HP-5MS silica capillary column chromatography (30 m × 0.25 mm × 0.25 μm)) and helium as the carrier gas. The oven temperature was held at 100ºC for 1min, heated to 240ºC at a rate of 5ºC /min and held for 20 min, and then heated to 280ºC at a rate of 10ºC /min and held for 20min. The injection volume was 1.0 μL in split less mode.

During the test, take 2 samples from each batch of analytical samples and add standard samples with known concentration to control the recovery rate. Set 1 duplicate sample every 12 samples to confirm the reproducibility of test results, and set 1 blank sample for each batch of analytical samples to ensure the cleanliness of reagents and containers. The recovery of soil samples was 71.67-122.36%.

Health Risk Assessment

Health risk assessment (HRA) model and Increment lifetime cancer risk (ILCRs) model were employed to evaluate the health risks of HMs and PAHs. HMs and PAHs may enter human body in three ways, such as direct intake, respiration and skin contact. The calculation method and parameter significance of acceptable daily intake of pollutants as described in Mihankhah et al. and Zou et al. [25-26].

CR risk classification standard described in Men et al. [27]: low risk ($CR<10^{-6}$); moderate risk ($10^{-6}<CR<10^{-4}$); High risk ($CR>10^{-4}$). For HI, <1 is acceptable; >1 is high risk.

Relative standard deviations and relative average deviations were calculated using Excel 2007. One-way analysis of variance (ANOVA) was conducted using Origin 2009b, and the means considered significantly different for p-value was less than 0.05. Correlation analysis, principal component analysis (PCA) and multiple linear regression (MLR) were performed using SPSS 25.0 (SPSS Inc., USA).

Results

Seasonal variation of total concentration of BC in river sediments and soils ranged from 4.10~8.50 mg/g and 6.41~9.72 mg/g, respectively. Generally, the concentration of BC in soils over the heating periods was significantly higher than that of the non-heating periods. The highest contents of BC ranged from 0.89 to 3.33 mg/g and 2.12 to 4.55 mg/g, respectively, in middle reaches of Ba River, and the lowest value of that in outer suburbs ranged from 0.32 to 1.48 mg/g and 0.33 to 1.88 mg/g in upper reaches of Ba River.

Seasonal variation of the concentrations of PAHs (∑PAHs) are 3649.09~8659.4 ng/g in river sediments and 4745.33~8649.63 ng/g in soils at the study region. Specifically, the total contents of ΣPAHs in the river sediments of the upper, middle and lower reaches of Ba River and Chan River are 215.88~1228.77 ng/g, 182.40~1150.19 ng/g, 280.19~1562.45 ng/g and 213.33~1153.69 ng/g, respectively, while in soils ranging from 151.07 to 993.886 ng/g, 227.68 to 1035.98 ng/g, 344.29 to 848.46 ng/g and 164.17 to 1478.88 ng/g, respectively. 3- and 4-ring are most abundant in river sediments and soils across this area. Together, they represent from 7 to 83% and from 1 to 90 % of the ΣPAH. The abundance of 3-ring compounds was 46% and 52%, meanwhile 4 rings was 31 to 32 %.

The total concentration of HMs (∑HMs) in river sediments and soils collected from different periods range from 14.22 to 15.34 mg/g and 12.34 to 13.14 mg/g, respectively. The highest contents of HMs in river sediments and soils were obtained in autumn and winter, respectively, and the lowest value of that appeared in summer. The ∑HMs in the river sediments of the upper, middle and lower reaches of Ba River and Chan River are 4.71~5.47 mg/g, 4.54~4.62 mg/g, 1.04~1.67 mg/g and 3.40~3.91 mg/g, in soil ranging from 3.32 to 3.38 mg/g, 3.98 to 4.49mg/g, 1.92 to 2.05 mg/g and 3.04 to 3.36 mg/g, respectively. In the two sampling environments, Mn contributes the most and Co contributes the least.

Discussion

The Distribution of BC, PAHs and HMs

Generally, river sedimentary pollutants primarily from long-term transportation, migration and deposition of river and groundwater pollutants as well as the surrounding soils washed by rainwater, while surface soil pollutants primarily from the process of atmospheric deposition [28]. The concentrations of BC, PAHs, HMs in the study area are shown in Fig. 2. The results indicate that the contents of eight HMs in river sediments (43.96±0.49 mg/g) were significantly higher than those in soils (38.45±0.34 mg/g), while the contents of BC and PAHs in soils (25.16±1.42 mg/g, 21334.8±1698.12 ng/g) were higher than those in river sediments (16.91±2.02 mg/g, 19820.9±2143.31 ng/g), which are primarily attributed to the hydrodynamic transportation and the conditions of pollutants deposition [29]. According to the data in southwestern Nigeria and Daye Lake, the changes in the average concentrations of HMs and PAHs in soils and river sediments are primarily attributed to the differences in the hydrodynamic transportation and the conditions with the low water solubility and water velocity [29-30]. Seasonally, the BC concentrations were obviously higher in winter (18.21±0.44 mg/g) than in summer (10.73±0.41 mg/g), while the concentrations of ∑PAHs were higher in summer (17309±372.29 ng/g) than those in autumn (8394.42 ± 190.06 ng/g). The BC and PAHs contents have obvious seasonal variation, but not in HMs concentration. Therefore, it may be closely related to the changes in meteorological conditions and the spatio-temporal distribution of pollutant emissions [31].

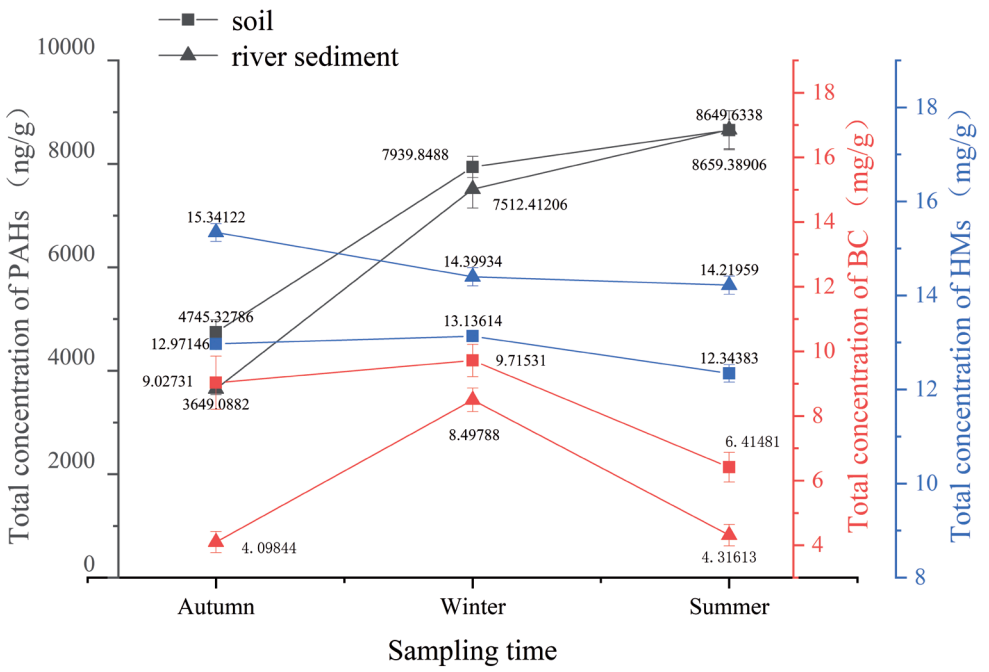

Fig. 2 Total concentrations of PAHs, HMs and BC in soils and river sediments from Chan & Ba River drainage basin (The error bars mean±SD).

Specifically, ∑PAHs in river sediments and soils were at a higher level in summer, because of particle size and meteorological conditions in the study site [32]. For instance, under the influence of increased atmospheric turbulent activity and precipitation in summer, PAH emissions from the surrounding areas (the northeast industrial zone) were transported and then deposited in river sediments and soils in the study area with wet and dry deposition. Previous studies have shown that the high PAHs levels in summer at the Seine Estuary were caused by atmospheric deposition, and surface runoff from significant precipitation or dredging activity [33]. Besides, LMW-PAHs compounds in the asphalt of urban asphalt roads can be highly volatile due to persistently hot weather in summer, and eventually settle into soil and groundwater for its low polarity and high hydrophobicity [30]. It is noted that the component of LMW-PAHs in the study area can be a potential source of soil and groundwater pollution.

The high level of BC concentration in winter in the study area may be related to the large amount of coal biomass combustion for heating in winter. (Fig. 2 and Fig. 4). For instance, the contribution of fossil fuel combustion to BC in the winter of 2008-2009 and 2015-2016 in Xi'an was 77% ±4% and 72% ±5%, respectively, which can undoubtedly explain the reason

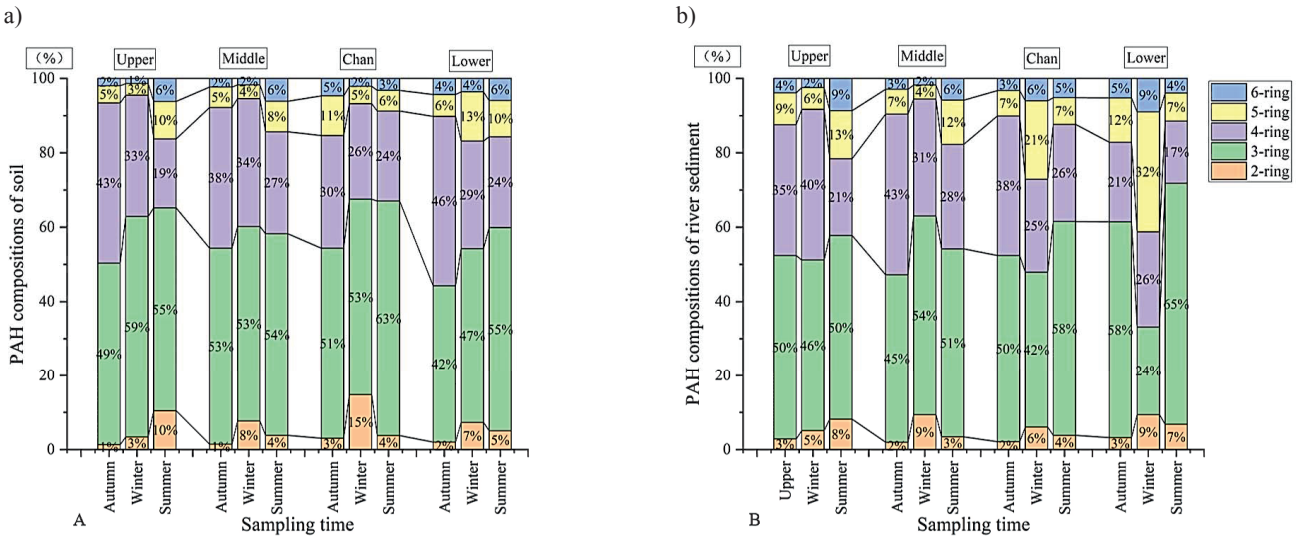

Fig. 3 The composition pattern of PAHs by ring-size from Chan & Ba River drainage basin a) in soils and b) in river sediments.

for the increase in BC concentration [34]. The Coal-fired Power Station in Baqiao District, Xi'an, located in the northeast of the study area, is the largest thermal power generation heating plant in Shaanxi Province and undertake half of the heating supply for the urban of Xi'an [35]. Hence, the typical northern winter energy consumption characteristics may be one of the reasons to explain the increase of BC levels in winter. Additionally, another reason for high BC concentrations lies in the increase of private cars and vehicles for transporting goods across the area. So, high BC concentration in winter of Xi'an was primarily affected by emissions from coal burning and vehicles exhaust [36].

Seasonal variations in HMs are not significant, and the content of eight HMs (V, Cr, Mn, Co, Ni, Zn, As, Pb) is slightly higher than the soil background value in Shaanxi province [37]. However, it is below the limit of the standard content of inorganic pollutants in the soil environmental quality standard (GB15618 - 2018) [38]. This change indicates that the emission of HMs pollution in this area is stable every year, mainly from the pollution sources in the surrounding area. In terms of industrial distribution, there is a close exposure to the northeast industrial zone (represented by Baqiao Thermal Power Plant) in this area [39]. The slightly higher content of Zn and Pb in the upstream sediments of this region is primarily due to the HMs emission from the northeast industrialzone, which is transported to the study area in the northeast monsoon, and the influence of the valley topography of this region, which eventually leads to the deposition of high contents of Zn and Pb here [40].

Regionally, the total concentrations of PAHs, BC and HMs in the middle reaches of the Ba river (13822.4 ng/g, 18.32 mg/g and 26.48 mg/g) were much higher than those in the lower reaches (5675.71 ng/g, 5.63 mg/g and 9.67 mg/g) (Fig. 1 and Fig. 5). Clearly, high contents of PAHs, BC and HMs in river sediments and soils in the study region are primarily attributed to the industrial pollutants emission from major industries such as the Textile City Industrial Zone and the Baqiao Thermal Power Plant [41]. Furthermore, the lower of Ba River is within ecological areas with less industrial distribution, where the Chan-Ba National Wetland Park is located. The wetland system turns out to be an efficient factor to the removal of pollutants [42].

Collectedly, seasonal and regional heterogeneity of these pollutants and variations in the concentrations of PAHs, BC and HMs in river sediments and soils across the basin rely not only on differences in the spatial and temporal distribution of industrial emissions, but on the hydrodynamic transportation and deposition of pollutants, as well as meteorological and topographic conditions.

Sources of BC, PAHs and HMs

Presently, Molecular diagnostic ratios (MDRs) and Principal component analysis (PCA) have been widely used to determine the source of contaminants in the environment due to the flexibility and simplicity of the desired sample volume [43-45]. In the study, we used MDRs and PCA to comprehensively determine their possible sources from PAHs, HMs, and BC.

Generally, BC is primarily derived from incomplete combustion of fossil fuels and biomass combustion [46]. The sources of PAHs in sediments or soils are pyrogenic and petrogenic [43, 45]. Since the Quaternary, there has been no historical data record of volcanic eruption and geological movement [47]. Therefore, the sources of PAHs in the study area are pyrogenic sources. Additionally, there are two sources of HM pollution in the soil environment are rock genesis (weathering from soil matrix) and anthropogenic input (sedimentation

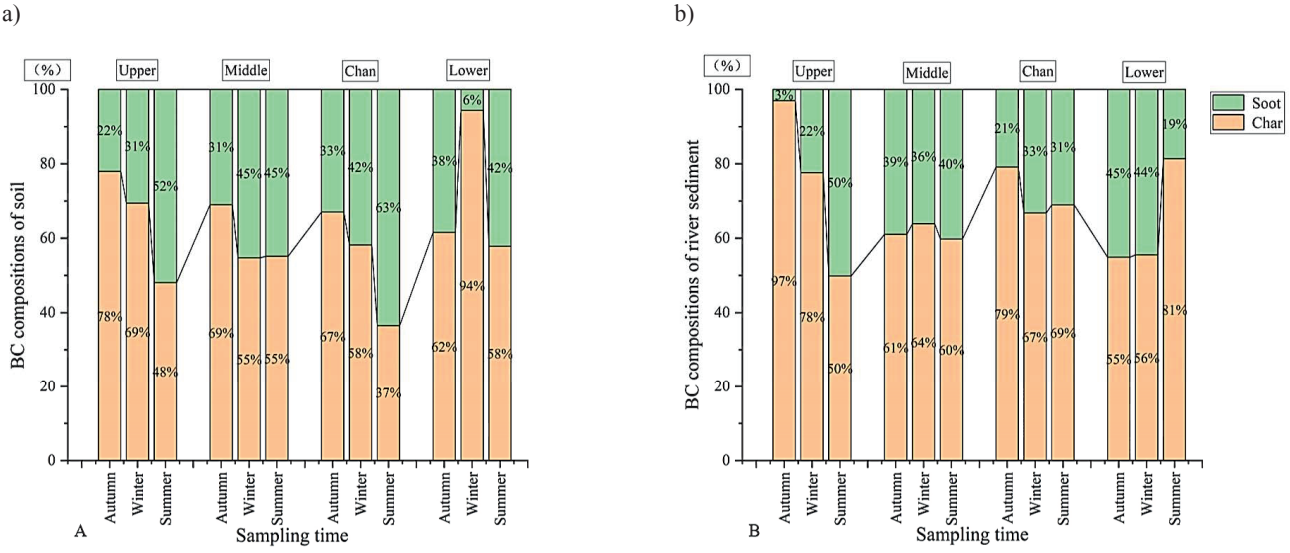

Fig. 4 The composition pattern of BC from Chan & Ba River drainage basin a) in soils and b) in river sediments.

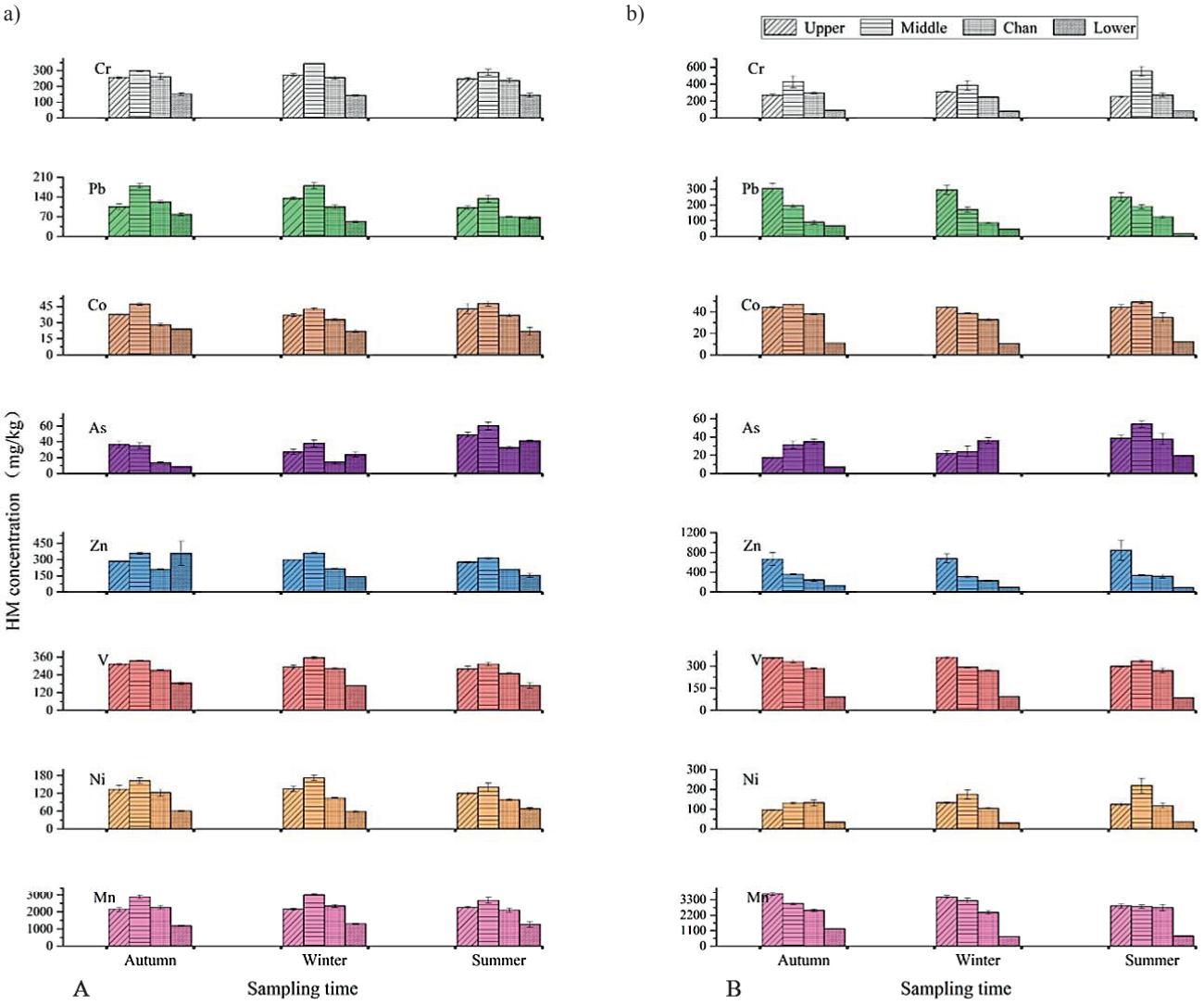

Fig. 5 The concentration of heavy metals from Chan & Ba River drainage basin (The error bars mean± SD) a) in soils and b) in river sediments.

through atmospheric migration, industrial emissions, coal and fossil fuel combustion, etc.) [48].

The number of aromatic rings contained in PAHs is determined by the type of fuel and the combustion conditions [49]. For instance, 2- and 3-ring PAHs are mostly released from and petroleum products [50-51]; 3- and 4-ring PAHs from biomass burning and coal combustion and 4-, 5- and 6-ring PAHs from coal combustion and vehicle emissions [45,52];. In this study, 3- and 4-ring PAHs predominate at sampling points in all seasons, followed by 5-ring (Fig. 3), indicating a mix of biomass, coal combustion and vehicle emissions sources. Moreover, the proportion of 5- and 6-ring PAHs in the lower reaches of the Ba River in winter in soils and river sediments was 17% and 41%, respectively, which was higher than the samples in the rest of the season. This suggests an increase in the contribution of motor vehicle emissions in the lower reaches of the Ba River.

Previous studies have suggested that the value of BbF/BkF>1 indicate diesel vehicle emissions and coal combustions, whereas BaP/(BaP + Chr) <0.5 indicate coal combustion [52]. Flu/(Flu + Pyr) and IcdP/(IcdP + BghiP) less than 0.5 indicated coal combustion, high than 0.5 showed liquid fossil fuel combustion [53]. When Ant/(Ant + Phe) high than 0.1 indicated high temperature combustion [54]. According to the sediment samples collected from the study area. (Fig. 6a), both Flu/(Flu + Pyr) and BaP/(BaP + Chr) values were less than 0.5, while the value of IcdP/(IcdP + BghiP) >0.5. Ant/(Ant + Phe) higher than 0.1 and BbF/BkF higher than 1 in this study. Hence the results suggest the possible sources of PAHs in the study area was from coal combustion and motor vehicle emissions.

The statistical software SPSS 25.0 was applied to the principal component analysis of PAHs, HMs and BC in river sediments and soil samples [55]. In Kaiser-Meyer-Olkin (KMO) test, KMO reached 0.8, indicating that the

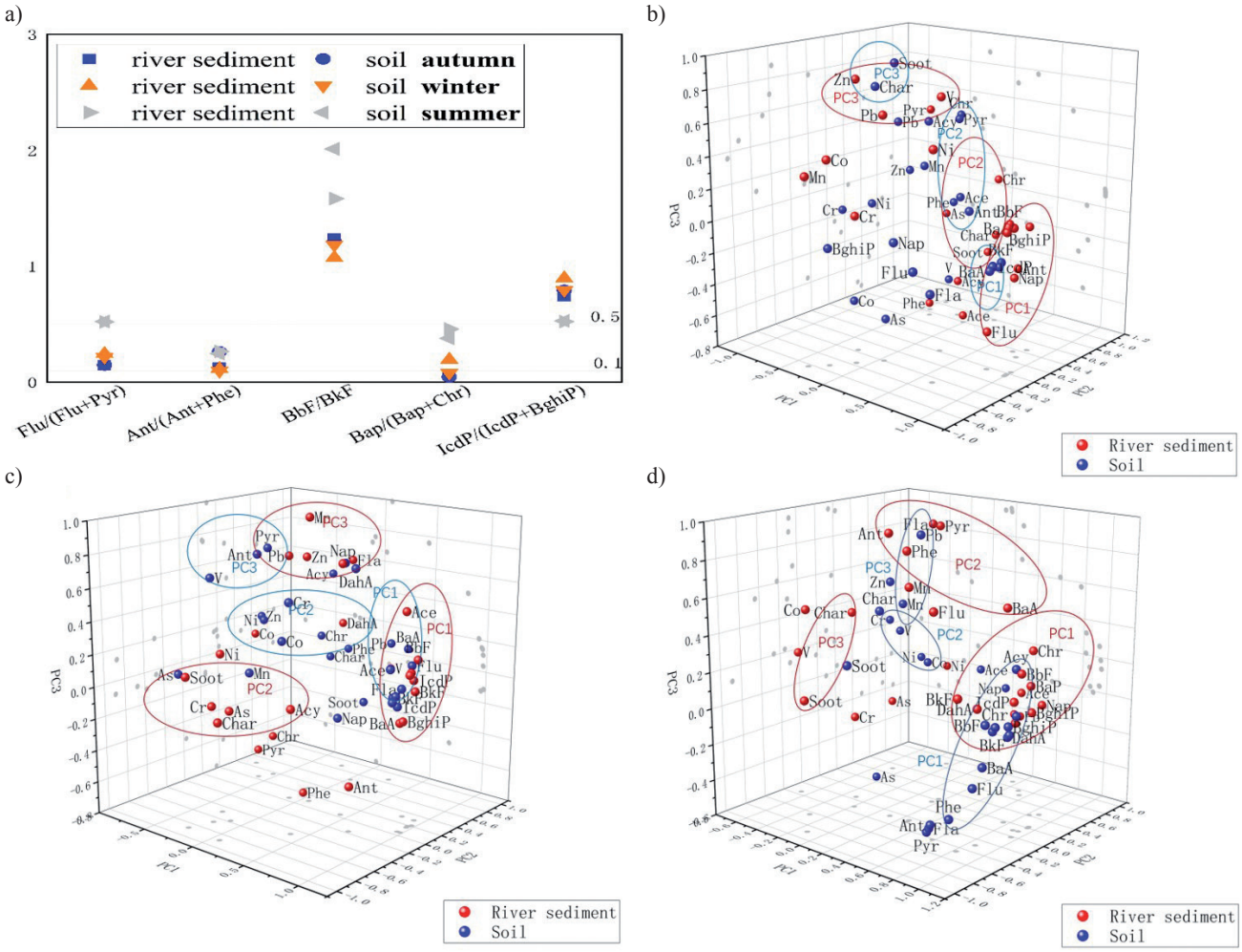

Fig. 6 a) MDR of PAHs and results of the PCA analysis in soils and river sediments from Chan & Ba River drainage basin; b) in winter, c) in autumn and d) in summer.

variables are recognized. In this study, three principal component factors were extracted for pollutants (PAHs, HMs and BC) in winter, autumn and summer.

In summer (non-heating period of every year), the PCA analysis results of soils and river sediments were similar in the study area (Fig. 6d). PC1 contributes 42.6% of the total variance, which is composed of Acy, Chr, HMW-PAHs and Zn. It was suggested that HMW-PAHs (Chr, BbF and BkF) were used to indicate motor vehicle emissions [56]. Thus, PC1 could be defined as emissions from vehicles because it aggregated mainly PAHs of high molecular weight, except for Acy. PC2 contributes 25.7% of the total variance and is composed of Phe, Ant, Fla and Pyr. It was suggested that Phe, Ant, Fla and Pyr was used to indicate coal combustion source [57]. Thus, PC2 showed coal combustion source. PC3 contributes 14.0% of the total variance and is composed of char and soot. It was suggested that Char and soot were used to indicate biomass combustion [58]. Recent studies have reported that BC primarily stems from motor vehicle emission and biomass burning in summer in Puding, Guizhou, China. [59]. Therefore, PC3 was identified as a mixed source of vehicle emission and biomass combustion.

However, in autumn and winter (heating period of every year), the PCA analysis results of soils and river sediments differ slightly in pollutant sources in the study area (Fig. 6b,c). In river sediments, PC1 contributes 38.3%-41.4% of the total variance, which is composed of Flu, Ant, Fla, BaA, 5- and 6- ring of high molecular weight PAHs. It was suggested that Flu, Ant, Fla and BaA were related with coal combustion [57], whereas 5- and 6- ring PAHs was applied to indicate automobile emissions [19]. Therefore, PC1 was identified as a mixed source of coal combustion and motor vehicle emissions [60-61]. PC2 contributes 19.0%-26.8% of the total variance, with high loads on Chr, char, soot, Cr, Ni and As. It was suggested that char and soot in sediments originate from incomplete combustion of biomass and fossil fuels, respectively [24]. By 2012, there have been 72 coal-fired power plants in Shaanxi Province, accounting for about 94.1% of total power generation in Shaanxi Province [62]. Therefore, PC2 was identified as coal and biomass combustion sources.

PC3 contributes 18.3%-19.3% of the total variance and is composed of Zn and Pb, which indicate that industrial coal combustion and transportation activities, respectively [63], thus PC3 was identified as the vehicle emission and coal combustion source.

For soils, PC1 contributes 31,3%-34.5% of the total variance. High factor loads of Flu, Fla, BaA, BbF, BkF, BaP, IcdP and DahA are obviously observed. It was suggested that Flu and Fla were linked with coal combustion [64], and BbF, BkF, IcdP and DahA was employed to indicate vehicle emission [65]. Thus, PC1 was identified as a mixed source of coal combustion and vehicle emission. PC2 contributes 17.6%-25.3% of the total variance and is composed of Phe and Chr, which were related to coal combustion [66]. It was identified as the coal combustion source. PC3 contributes 15.6% of the total variance and is composed of char and soot. Char and soot indicate that biomass and fossil fuels combustion [67], thus PC3 was identified as the biomass and coal combustion source. Briefly, PAHs, BC and HMs in soils and river sediments of this study area are pyrogenic sources, including vehicle emissions, coal and biomass combustion.

Health Risk Assessment (HRA) of HMs and PAHs

To measure the health risk to the resident around Chan-Ba River Basin, HRA and ILCRs were evaluated for different age groups. In our study, only Cr, Co, Ni and As were separately assessed for carcinogenic risk. According to the evaluation results the CR varied from 5.54×10^{-9}-5.17×10^{-4} for adults and 2.61×10^{-9}-3.14×10^{-4} for children (Table 1). And the values of cancer risk for adults and children were lower than 10^{-4} indicating low to moderate level. Specially, none of the CR of Co was higher than 10^{-6}, indicating Co has negligible risk for adults and children. The CR of Cr, As and Ni are all greater than 10^{-4} and has a moderate risk. Furthermore, the higher carcinogenic risk of Ni and Cr in the middle reaches of the Ba River (the mean CR were 3.14×10^{-4}-5.17×10^{-4} and 2.19×10^{-4}-4.06×10^{-4}, respectively). Whereas, the carcinogenic risk of As in the lower reaches of the Ba River were higher (the mean CR was 8.23×10^{-5}-1.87×10^{-4}).

The non-carcinogenic risk values of HMs varied from 4.4×10^{-3}-1.21 for adults and 1.31×10^{-9}-2.13 for children (Table 2), indicating low to high risk level. It was noted that the HI of Cr for children is greater than 1, which has a high risk of non-carcinogenic, while was low risk for adult. For As, it showed a high non-carcinogenic risk for both adults and children.

The carcinogenic risk and non-carcinogenic risk is different for people of different ages. It should be noted that the carcinogenic risk of HMs in adults was observed to be higher 1.65-2.28 times than that found in children. Conversely, the non-carcinogenic risk was higher in children than in adults (1.55-3.07 times). The reason for higher carcinogenic risk in adults may be due to the much higher exposure time, while the lower

Table 1. Carcinogenic risk posed by heavy metals.

		Adults		Children	
		Mean	Risk level	Mean	Risk level
Upper	Cr	3.25×10^{-4}	Moderate	1.75×10^{-4}	Moderate
	Co	5.84×10^{-9}	Low	2.75×10^{-9}	Low
	Ni	4.39×10^{-4}	Moderate	2.66×10^{-4}	Moderate
	As	1.53×10^{-4}	Moderate	6.71×10^{-5}	Moderate
Middle	Cr	4.06×10^{-4}	Moderate	2.19×10^{-4}	Moderate
	Co	5.54×10^{-9}	Low	2.61×10^{-9}	Low
	Ni	5.17×10^{-4}	Moderate	3.14×10^{-4}	Moderate
	As	1.69×10^{-4}	Moderate	7.43×10^{-5}	Moderate
Chanhe	Cr	3.70×10^{-4}	Moderate	1.99×10^{-4}	Moderate
	Co	5.54×10^{-9}	Low	2.61×10^{-9}	Low
	Ni	4.70×10^{-4}	Moderate	2.85×10^{-4}	Moderate
	As	1.58×10^{-4}	Moderate	6.92×10^{-5}	Moderate
Lower	Cr	3.28×10^{-4}	Moderate	1.77×10^{-4}	Moderate
	Co	5.54×10^{-9}	Low	2.61×10^{-9}	Low
	Ni	3.99×10^{-4}	Moderate	2.42×10^{-4}	Moderate
	As	1.87×10^{-4}	Moderate	8.23×10^{-5}	Moderate

Table 2. Non-carcinogenic risk posed by heavy metals.

		Adults		Children	
		Mean	Risk level	Mean	Risk level
Upper	V	5.00×10^{-1}	Low	7.77×10^{-1}	Low
	Cr	6.92×10^{-1}	Low	1.39	High
	Mn	3.76×10^{-1}	Low	9.07×10^{-1}	Low
	Co	9.70×10^{-3}	Low	2.98×10^{-2}	Low
	Ni	2.89×10^{-2}	Low	8.72×10^{-2}	Low
	Zn	8.06×10^{-3}	Low	2.40×10^{-2}	Low
	As	0.989	High	1.74	High
	Pb	2.76×10^{-1}	Low	8.04×10^{-1}	Low
Middle	V	4.52×10^{-1}	Low	7.01×10^{-1}	Low
	Cr	8.64×10^{-1}	Low	1.74	High
	Mn	3.48×10^{-1}	Low	8.40×10^{-1}	Low
	Co	9.21×10^{-3}	Low	2.83×10^{-2}	Low
	Ni	3.40×10^{-2}	Low	1.03×10^{-1}	Low
	Zn	4.71×10^{-3}	Low	1.40×10^{-2}	Low
	As	1.10	High	1.93	High
	Pb	2.13×10^{-1}	Low	6.19×10^{-1}	Low
Chanhe	V	5.01×10^{-1}	Low	7.77×10^{-1}	Low
	Cr	7.88×10^{-1}	Low	1.58	High
	Mn	3.79×10^{-1}	Low	9.15×10^{-1}	Low
	Co	9.21×10^{-3}	Low	2.83×10^{-2}	Low
	Ni	3.09×10^{-2}	Low	9.33×10^{-2}	Low
	Zn	4.40×10^{-3}	Low	1.31×10^{-2}	Low
	As	1.02	High	1.79	High
	Pb	1.62×10^{-1}	Low	4.72×10^{-1}	Low
Lower	V	4.87×10^{-1}	Low	7.55×10^{-1}	Low
	Cr	6.97×10^{-1}	Low	1.40	High
	Mn	3.36×10^{-1}	Low	8.13×10^{-1}	Low
	Co	9.21×10^{-3}	Low	2.83×10^{-2}	Low
	Ni	2.63×10^{-2}	Low	7.92×10^{-2}	Low
	Zn	5.98×10^{-3}	Low	1.78×10^{-2}	Low
	As	1.21	High	2.13	High
	Pb	1.79×10^{-1}	Low	5.21×10^{-1}	Low

non-carcinogenic risk is due to the smaller average body weight and average time in children [23].

The results of ILCRs model of PAHs implied that the carcinogenic risk among children is higher than that in adults, both at low to moderate risk levels (7×10^{-6}-3.5×10^{-5} for adults and 7.35×10^{-6}-3.68×10^{-5} for children) (Table 3). Seasonally, the carcinogenic risks of adults and children had the same trend. It is the highest in summer with CR range values of 7.89×10^{-6} to 9.21×10^{-5} and 8.27×10^{-6} to 9.66×10^{-5}, respectively. The lowest in autumn with CR range values of 6.33×10^{-6} to 1.46×10^{-5} and 6.65×10^{-6} to 1.53×10^{-5}, respectively. The mean value of CR in summer is 3.19 times higher than that in autumn. The higher carcinogenic risk in summer

Table 3. Seasonal variations of carcinogenic risk posed by PAHs.

		Autumn		Winter		Summer	
		Mean	Risk level	Mean	Risk level	Mean	Risk level
Adults	Upper	7.15×10^{-6}	Low	7.65×10^{-6}	Low	3.50×10^{-5}	Moderate
	Middle	7.55×10^{-6}	Low	8.17×10^{-6}	Low	2.35×10^{-5}	Moderate
	Chanhe	8.07×10^{-6}	Low	9.23×10^{-6}	Low	1.69×10^{-5}	Moderate
	Lower	1.11×10^{-5}	Low	7.00×10^{-6}	Low	1.14×10^{-5}	Moderate
Children	Upper	7.51×10^{-6}	Low	8.03×10^{-6}	Low	3.68×10^{-5}	Moderate
	Middle	7.93×10^{-6}	Low	8.57×10^{-6}	Low	2.46×10^{-5}	Moderate
	Chanhe	8.48×10^{-6}	Low	9.68×10^{-6}	Low	1.77×10^{-5}	Moderate
	Lower	1.17×10^{-5}	Low	7.35×10^{-6}	Low	1.20×10^{-5}	Moderate

may be due to the higher level of PAHs detected in summer. Regionally, the risk in the middle reaches of Ba River is higher, with Phe and Flu dominate, which may be produced by the large amount of coal burning.

Overall, the risk assessment showed that the carcinogenic risks of PAHs and HMs in this study area were low to moderated level. It is noted that Phe and Flu in the middle reaches in summer and As in the lower reaches in autumn have higher potential risk. And high non-carcinogenic risk for Cr and As were also observed.

Potential Relationships between Variables

Cluster analysis was performed on HMs, PAHs and BC to explore the potential relationship between them. The R software is applied to normalize and also to cluster variables, and then the cluster correlation analysis is displayed in the heat map (Fig. 7). The parameters within the same group indicate that they are significantly correlated, and it is more indicative of potential links with the source material between groups [68].

Seasonally (Fig. 7a), there are two primary variable groups, roughly affected by two major sources of pollution in the study area. HMs in this area primarily comes from the transport of regional pollutants, while PAHs are generally from local pollutant emissions over seasons. In autumn, the significant correlation between HMs and BC indicates that their sources of pollution are from the combustion of biomass and coal burning in the surrounding rural areas. In winter, 2-ring and 4-ring PAHs were significantly correlated, indicating that winter pollutants originated from coal combustion. In summer, the significant correlation of high-ring PAHs shows that they originated from motor vehicle emissions.

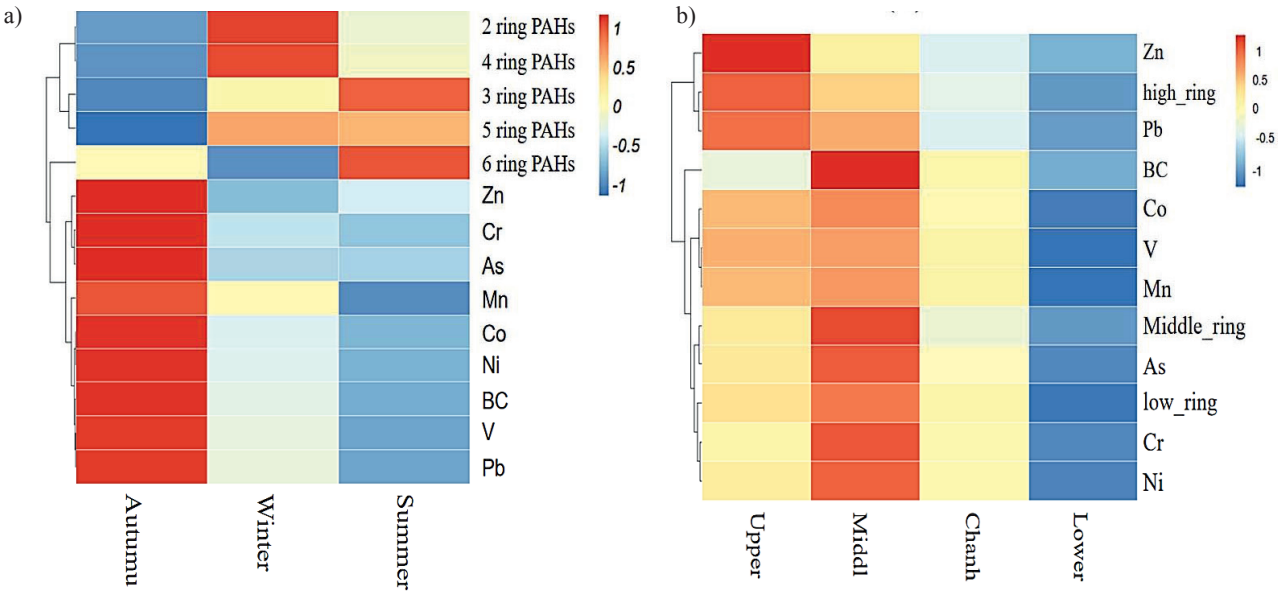

Fig. 7 Heat map showing variables (PAHs, HMs and BC) from Chan & Ba River drainage basin. a) Heat map showing variations in different seasons. b) Heat map showing relations between regional variables.

Regionally (Fig. 7b), it can be divided into three groups, high-ring PAHs, Zn and Pb in cluster 1, BC in cluster 2, and the rest (V, Co, Mn, As, Cr, Ni, low-ring and middle-ring PAHs) in cluster 3. The differences between those groups show total differences in two sources of pollutants. In the upper reaches of the Ba River, cluster 1 dominates, indicating that there were pollutants produced from motor vehicles emissions. In the middle reaches of the Ba River, cluster 2 and 3 dominate indicate that their sources are associated with coal combustion and biomass burning. The pollution of the Chan River and downstream is relatively low. This difference also reflects the concentration of industrial distribution in the middle reaches of the basin.

In fact, the pollution source in the study area has changed from energy pollution dominated by single coal combustion to mixed pollutants, converted from inorganic pollution to secondary organic pollutants. As for global warming, the process of pollutant occurrence is more complicated, and their range is not just limited to water and atmosphere transmission. Thus, nowadays the pollution of soil and groundwater, as well as the potential risks to human health, have already aroused our attention.

Conclusion

BC, PAHs and HMs in soils and river sediments were identified as primary pollutants in the Chan-Ba River drainage Basin. Seasonal variations of HMs were observed not significantly, which is attributed to the regional differences in pollutant emissions and sedimentary conditions in the surrounding area. Whereas, the concentrations of BC and PAHs vary seasonally, which is closely related to the intensity of local pollutant emissions and meteorological conditions. It is noted that low-ring PAHs are potential sources of soil and groundwater pollution. PCA analysis and potential correlation analysis indicate that the sources of pollutants in soils and river sediments are primarily from biomass and coal combustions and automobile emissions, indicating that the pollution source in the study area has changed from energy pollution dominated by single coal combustion to mixed pollutants, converted from inorganic pollution to secondary organic pollutants. The risk assessment shows that the carcinogenic risks of PAHs and of HMs were low to moderate, and it is noted that there are potential risks of Phe and Flu in soils and river sediments at the middle reaches in summer and As at the lower reaches in autumn. Therefore, pollution prevention, monitoring and classification management as well as controlling mechanisms in designated river basins are necessary to ensure the quality and safety of the ecological environment in the Chan & Ba River basin. In addition, the potential risk to the health of residents exposed to PAHs, BC and HMs in river sediments and soils should be encouraged to receive much more attention.

Acknowledgments

This research was supported by the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB40000000), and grants from National Natural Science Foundation of China (No. 41771218; 52100198), Fund of the State Key Laboratory of Loess and Quaternary Geology Chinese Academy of Sciences (No. SKLLQG 2033, 1827, 1618). We gratefully acknowledge the helpful and valuable comments by the editor and the anonymous reviewers. Finally, we sincerely thank all those for their efforts and contributions to the accomplishment of this research. Many thanks!

Author Contributions

All authors contributed to the study conception and design, material preparation, data collection and analysis were performed by Li Dongxue, Tan Tantan, Gu Maolin, Yuan Yubo, Lei Qiujing. The first draft of the manuscript was written by Tan Zhihai and Tan Tantan. All authors commented on previous versions of the manuscript and approved the final manuscript. The review of the manuscript were written by Han Yongming and Mao Longjiang.

Conflict of Interests

The authors declare no conflict of interests.

References

1. LIU Y.Y. Study on Urban River Ecological Landscape Design. Journal of Physics: Conference Series. 1549, 022090, **2020**.
2. LI Z.W. Heavy metal concentration speciation and ecological risk assessment of surface sediments in Songhua River. Dissertation, Lanzhou University of technology, **2019**.
3. YU P.G., TOON O.B., BARDEEN C.G., ZHU Y.Q., ROSENLOF K.H., PORTMANN R.W., THORNBERRY T.D., GAO R.S, DAVIS S.M., WOLF E.T., GOUW J.D., PETERSON D.A., FROMM M.D., ROBOCK A. Black carbon lofts wildfire smoke high into the stratosphere to form a persistent plume. Science (New York, N.Y.). **365** (6453), 587, **2020**.
4. ALI U., BAJWA A., CHAUDHRY M.J.I., MAHMOOD A., SYED J.H., LI J., ZHANG G., JONES K.C., MALIK R.N. Significance of black carbon in the sediment–water partitioning of organochlorine pesticides (OCPs) in the Indus River, Pakistan. Ecotoxicology & Environmental Safety. **126** (apr.), 177, **2016**.
5. QIAN, L., ZHANG, W., YAN, J., HAN, L., GAO, W., LIU, R., CHEN M. Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures. Bioresource Technology, **206**, 217, **2016**.
6. THIOMBANE M., PETRIK A., BONITO M.D., ALBANESE S., ZUZOLO D., CICCHELLA D., LIMA

A., QU C., QI S., VIVO B.D. Status, sources and contamination levels of organochlorine pesticide residues in urban and agricultural areas: a preliminary review in central-southern Italian soils. Environmental Science & Pollution Research, 1-22, **2018**.
7. BARAN A., KLIMKOWICZ-PAWLAS A., UKALSKA-JARUGA A., MIERZWA-HERSZTEK M., GONDEK K., SZARA-BĄK M., TARNAWSKI M., SPAŁEK I. Distribution of polycyclic aromatic hydrocarbons (PAHs) in the bottom sediments of a dam reservoir, their interaction with organic matter and risk to benthic fauna. Journal of Soils and Sediments, **21**, 2418, **2021**.
8. DONG Y.B., YAN Z.H., WU H.F., ZHANG G.Q., ZHANG H.C., YANG M.Z. Polycyclic Aromatic Hydrocarbons in Sediments from Typical Algae, Macrophyte Lake Bay and Adjoining River of Taihu Lake, China: Distribution, Sources, and Risk Assessment. Water, **13** (4), 470, **2021**.
9. ALI U., SWEETMAN A.J., RIAZ R., LI J., ZHANG G., JONES K.C., MALIK R.N. Sedimentary black carbon and organochlorines in Lesser Himalayan Region of Pakistan: Relationship along the altitude. Science of The Total Environment, 621, **2017**.
10. HOANG N. V., SHAKIROV R. B., THU T. H., SYRBU N.S., ESKOVA A.I. Characteristics of Sediment Heavy Metal Levels in Lead-zinc Ore Cho Don District Area, Bac Kan Province, Vietnam. Lithology and Mineral Resources, **56** (3), 278, **2021**.
11. GONG X.H., XIAO L.P., ZHAO Z.H., LI Q.Y., FENG F., ZHANG L., DENG Z.Y. Spatial variation of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from rivers in hilly regions of Southern China in the wet and dry seasons. Ecotoxicology & Environmental Safety, **156**, 322, **2018**.
12. AMEGAH A. K., JAAKKOLA J. Work as a street vendor, associated traffic-related air pollution exposures and risk of adverse pregnancy outcomes in Accra, Ghana. Int J Hyg Environ Health. **217** (2-3), 354, **2014**.
13. CUI H.B., ZHOU J., LI Z., GU C.H. Editorial: Soil and Sediment Pollution, Processes and Remediation. Front. Environ. Sci, **9**, 822355, **2021**.
14. ZHAO F.J., MA Y., ZHU Y.G., TANG Z., MCGRATH S.P. Soil Contamination in China: Current Status and Mitigation Strategies. Environmental Science & Technology, **49** (2), 750, **2015**.
15. SUN Z.H., HU Y.A., CHENG H.F. Public health risk of toxic metal (loid) pollution to the population living near an abandoned small-scale polymetallic mine. Science of The Total Environment, **718**, 137434, **2020**.
16. WU S., ZHOU S., BAO H., CHAN D., WANG C., LI B., XU B. Improving risk management by using the spatial interaction relationship of heavy metals and PAHs in urban soil. Journal of Hazardous Materials. **364** (FEB.15), 108, **2019**.
17. MONACO D, CHIANESE E, RICCIO A., DELGADO-SANCHEZ A., LACORTE S. Spatial distribution of heavy hydrocarbons, PAHs and metals in polluted areas. The case of "Galicia", Spain. Marine Pollution Bulletin. **121**(1-2), 230, **2017**.
18. ZHANG Q.N. Characterization and soil-air exchange of PAHs and OPFRs in air and soil of Dalian. Dissertation, Dalian University of Technology.**2019**.
19. LIU Q.Y., WU Y.H., ZHOU Y.Z., LI X.Y., YANG S.H., CHEN Y.X., QU Y.J., MA J. A novel method to analyze the spatial distribution and potential sources of pollutant combinations in the soil of Beijing urban parks[J]. Environmental Pollution, **284**, 117191, **2021**.
20. LIU Y.H., WANG X.S., GUO Y.H., MAO Y.M., LI H. Association of black carbon with heavy metals and magnetic properties in soils adjacent to a cement plant, Xuzhou (China). Journal of Applied Geophysics, **170** (4), 103802, **2019**.
21. VAEZZADEH V., YI X., RAIS F.R., BONG C.W., THOMES M.W., LEE C.W., ZAKARIA M.P., WANG A.J., ZHONG G.C., ZHANG G. Distribution of black carbon and PAHs in sediments of Peninsular Malaysia. Marine Pollution Bulletin, **172** (111), 112871, **2021**.
22. WANG J.H., YIN R.S., LI L., ZHAO W.G., LU S.C. Research on regulation of landscape flow of rubber dam group in Chanba River Basin based on finite traversal method. Water Resources and Hydropower Engineering, 1-14, **2022**.
23. YANG Y.Y., SHE Z.P., SONG J.X., ZHU D.W. Study on vegetation variation characteristics and influencing factors in different geomorphic zones in the Chanbahe River basin since 2000. Ecology and Environmental Sciences, **31** (2), 224, **2022**.
24. LI Y. Sedimentary records and sources of black carbon and polycyclic aromatic hydrocarbons in the sediments of Fuxian Lake. Nanjing Normal University. **2021**.
25. MIHANKHAH T., SAEEDI M., KARBASSI A.A comparative study of elemental pollution and health risk assessment in urban dust of different land-uses in Tehran's urban area. Chemosphere. **241**, 124984, **2020**.
26. ZOU Y.P., LIU J.L., LIU X.C., JIA J.L. Health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the soil around thermal power plants in southwest China. Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering. **56** (7), **2021**.
27. MEN C., WANG Y.F., LIU R.M., WANG Q.R., MIAO Y.X., JIAO L.J., SHOAIB M., SHEN Z.Y. Temporal variations of levels and sources of health risk associated with heavy metals in road dust in Beijing from May 2016 to April 2018. Chemosphere. **270**, 129434, **2021**.
28. PAN C., CHEN K, CHEN D. Effect of organics on heavy metal-contaminated river sediment treated with electro-osmosis and solidification/stabilization methods. Materials, **13** (6), **2020**.
29. OYEBAMIJI A., ODEBUNMI A., RUIZHONG H., RASOOL A. Assessment of trace metals contamination in stream sediments and soils in Abuja leather mining, southwestern Nigeria. Acta Geochimica. **37** (4), 592, **2017**.
30. BHUTTO S., XING X., SHI M., MAO Y., QI S. Occurrence and distribution of OCPs and PAHs in water, soil and sediment of Daye Lake. Journal of Geochemical Exploration. **226**, 106769, **2021**.
31. ZHANG Z., LU Y., LI H., TU Y., LIU B., YANG Z. Assessment of heavy metal contamination, distribution and source identification in the sediments from the Zijiang River, China. Science of the Total Environment. **645**, 235, **2018**.
32. MOTELAY-MASSEI A., OLLIVON D., GARBAN B., CHEVREUIL M. Atmospheric deposition of toxics onto the Seine Estuary, France: example of polycyclic aromatic hydrocarbons. Atmospheric Chemistry & Physics Discussions. **2** (5), 941, **2002**.
33. CAILLEAUD K., FORGET-LERAY J., SOUISSI S. Seasonal variations of hydrophobic organic contaminant concentrations in the water-column of the Seine Estuary and their transfer to a planktonic species Eurytemora affinis (Calanoied, copepod). Part 1: PCBs and PAHs. **70** (2), 0-280, **2007**.

34. HUANG R.J., GUO J., NI H.Y., CAO J.J. Carbon Isotope Composition and Source Analysis of Element Carbon Aerosol in Winter of Xi'an. Bulletin of Mineralogy, Petrology and Geochemistry, **38** (06), 1073-1080+1046, **2019**.
35. ZHAO C., LU X., YANG G., LI N., REN C. Nature radioactivity level in soil around Baqiao coal-fired power plant. Nuclear Electronics & Detection Technology. **32** (10), 1201, **2012**.
36. LIU L., WANG Y., YAO Y., HAN J., LI W., HAN Z. Concentration characteristics and the correlations of black carbon aerosols with meteorological factors and conventional pollutants in Xi'an. Environmental Monitoring in China. **32** (05), 45, **2016**.
37. YANG X., GUAN J., HE Y., WANG L., LIU H. Heavy metal pollution status and potential ecological risk in surface sediments of Wei River, Shaanxi. Environmental Science and Management. **43** (08), 176, **2018**.
38. GB 15618-2018, Soil environmental quality-Risk control standard for soil contamination of agricultural land. Beijing, China Environment Publishing Group, **2018**.
39. Xu Z.N. spatial and temporal distribution characteristics of DOM in water bodies of Xi'an city and the influence of drainage outlets on it. Liaoning University.**2021.**
40. ZHANG H. Characteristics of air pollution and source analysis of particulate matter in Xi'an. Xi'an University of Architecture and Technology. **2020**.
41. Xi'an Statistical Communique on National Economic and Social Development in 2019, **2020**. available at <http://xadrc.xa.gov.cn/xxgk/ghjh/ndjh/5ea69e8bf99d65761313118d.html>
42. LIN L., DONG L., MENG X., LI Q., HUANG Z., CRITTENDEN J. Distribution and sources of polycyclic aromatic hydrocarbons and phthalic acid esters in water and surface sediment from the three gorges reservoir. Journal of environmental sciences (China). **69**, 271, **2017**.
43. FAMIYEH L., CHEN K., XU J., SUN Y., GUO Q., WANG C., LV J., TANG Y., YU H., SNAPE C., HE J. A review on analysis methods, source identification, and cancer risk evaluation of atmospheric polycyclic aromatic hydrocarbons. Science of The Total Environment, **789** (1), 147741, **2021**.
44. THANG P.Q., KIM S.J., LEE S.J., YE J., SEO Y.K., BAEK S.O., CHOI S.D. Seasonal characteristics of particulate polycyclic aromatic hydrocarbons (PAHs) in a petrochemical and oil refinery industrial area on the west coast of South Korea. Atmospheric Environment, **198** (1), 398, **2018**.
45. ELZEIN A., STEWART G.J., SWIFT S.J., NELSON B.S., CRILLEY L.R., ALAM M.S., REYES-VILLEGAS E., GADI R., HARRISON R.M., HAMILTON J.F., LEWIS A.C. A comparison of PM2.5-bound polycyclic aromatic hydrocarbons in summer Beijing (China) and Delhi (India). Copernicus GmbH, **20** (22), 14303, **2020**.
46. JIA H., HUO J., FU Q., DUAN Y., LIN Y., HU X., CHENG J. Atmospheric characteristics and population exposure assessment of black carbon at a regional representative site in the Yangtze River delta region, China based on the five-year monitoring. Science of The Total Environment. **777**, 145990, **2021**.
47. TAN Z.H., WU C., HAN Y.M., ZHANG Y.Z., MAO L.J., LI D.X., LIU L., SU G.R., YAN T.T. Fire history and human activity revealed through poly cyclic aromatic hydrocarbon (PAH) records at archaeological sites in the middle reaches of the Yellow River drainage basin, China. Palaeogeography, Palaeoclimatology, Palaeoecology, **560**, **2020**.
48. ZHU Y., ZHANG Z., ZHAO X., JIE L. Accumulation and potential sources of heavy metals in the soils of the Hetao irrigation district, inner Mongolia, China. Pedosphere. **30** (2), 244, **2017**.
49. IARC (International Agency for Research on Cancer): Monographs on the Evaluation of Carcinogenic Risks to Humans, 100E, Indoor emissions from household combustion of coal, 515–532, Lyon, France, available at: https://publications.iarc.fr/122, **2012**.
50. RAMZI A., RAHMAN K.H., GIREESHKUMAR T.R., BALACHANDRAN K.K., JACOB V., CHANDRAMOHANAKUMAR N. Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Cochin estuary, India. Marine Pollution Bulletin, **114** (2), 1081, **2016**.
51. LIU D., LIN T., SYED J.H., CHENG Z., XU Y., LI K., ZHANG G., LI J. Concentration, source identification, and exposure risk assessment of PM2.5-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese cities. Scientific Reports, **7** (1), 10398, **2017**.
52. KUMAR B., VERMA V.K., KUMAR S. Source apportionment and risk of polycyclic aromatic hydrocarbons in Indian sediments: a review. Arabian Journal of Geosciences, **15** (6), 1, **2022**.
53. FANG B., ZHANG L., ZENG H., LIU J., YANG Z., WANG H.W., WANG Q., WANG M.M. $PM_{2.5}$-Bound Polycyclic Aromatic Hydrocarbons: Sources and Health Risk during Non-Heating and Heating Periods (Tangshan, China). International Journal of Environmental Research and Public Health, **17** (2), 483, **2020**.
54. AYYILDIZ E.G., ESEN F. Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) at Two Sites, in Bursa, Turkey: Determination of Concentrations, Gas–Particle Partitioning, Sources, and Health Risk. Archives of Environmental Contamination and Toxicology, **78** (4), **2020**.
55. TSAI Y.C., CHUNG C.Y., CHUNG C.C., GAU H.S., LAI W.L., LIAO S.W. The impact of typhoon Morakot on heavy metals of Dapeng Bay and pollution from Neighboring Rivers. Environmental Modeling & Assessment, **21** (4), 479, **2016**.
56. APATA A., OLOLODE I.A., OLADOJA N.A., ALABI B.A., OLOLODE O.O. Polycyclic aromatic hydrocarbons in selected rivers in southwestern Nigeria: Seasonal distribution, source apportionment and potential risk assessment. Regional Studies in Marine Science. **52**, 102318, **2022**.
57. FENG J.L., LI X.Y., GUO W., LIU S.H., REN X.M., SUN J.H. Potential source apportionment of polycyclic aromatic hydrocarbons in surface sediments from the middle and lower reaches of the Yellow River, China. Environmental Science and Pollution Research, **21** (19), 11447, **2014**.
58. HAN Y.M., BANDOWE B.A.M., SCHNEIDER T., PONGPIACHAN S., HO S.S.H., WEI H., WANG Q.Y., XING LI., WILCKE W. A 150-year record of black carbon (soot and char) and polycyclic aromatic compounds deposition in Lake Phayao, north Thailand. Environmental Pollution, 269, **2020**.
59. MAO D.Y., XIAO H.W., XIAO H.Y., ZENG Z.Q., HUANG L.L. Stable carbon isotopic composition and sources of black carbon during winter and summer in Southwest China. GEOCHIMICA **50** (01), 67, **2021**.
60. AFSHAR-MOHAJER N., WILSON C., WU C.Y., STORMER J.E. Source apportionment of atmospheric

polycyclic aromatic hydrocarbons (PAHs) in palm beach county, Florida. Journal of the Air & Waste Management Association. **66** (4), 377, **2016**.
61. LIN F., HAN B., DING Y., LI Q., ZHENG L. Distribution characteristics, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons in sediments from the Qinhuangdao coastal wetland, China. Marine Pollution Bulletin. **127**, 788, **2017**.
62. XU Y., HU J., YING Q., HAO H., WANG D., ZHANG H. Current and future emissions of primary pollutants from coal-fired power plants in Shaanxi, China. Science of the Total Environment. **595**, 505, **2017**.
63. CHEN H.Y., TENG Y.G., LU S.J., WANG Y.Y., WU J., WANG J.S. Source apportionment and health risk assessment of trace metals in surface soils of Beijing metropolitan, China. Chemosphere. **144**, 1002, **2016**.
64. BAI L., CHEN W., HE Z., SUN S., QIN J. Pollution characteristics, sources and health risk assessment of polycyclic aromatic hydrocarbons in PM2.5 in an office Buildings in northern areas. Sustainable Cities and Society, **53**, 101891, **2019**.
65. ZEIN A., DUNMORE R.E., WARD M.W., HAMILTON J.F., LEWIS A.C. Variability of polycyclic aromatic hydrocarbons and their oxidative derivatives in wintertime Beijing, China. Atmospheric Chemistry and Physics, 8741, **2019**.
66. WANG X., MIAO Y., ZHANG Y., LI Y., WU M., YU G. Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: occurrence, source apportionment and potential human health risk. Sci. Total Environ. **447**, 80, **2013**.
67. LI Y., ZHOU S.L., LIU K., WANG G.M., WANG J.X. Application of APCA-MLR receptor model for source apportionment of char and soot in sediments. Sci. Total Environ. **746**, 141165, **2020**.
68. YANG T., CHENG H., WANG H., DREWS M., LI S., HUANG W., ZHOU H., CHEN C.M., DIAO X. Comparative study of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) in corals, surrounding sediments and surface water at the Dazhou Island, China. Chemosphere. **218**, 157, **2019**.