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RESEARCH ARTICLE

The distribution and sources of polycyclic aromatic hydrocarbons in shallow groundwater from an alluvial-diluvial fan of the Hutuo River in North China

Jincui WANG (✉)[1,2], Yongsheng ZHAO[1], Jichao SUN[2], Ying ZHANG[2], Chunyan LIU[2]

1 College of Environment and Resources, Jilin University, Changchun 130026, China
2 Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China

Abstract This paper has investigated the concentration and distribution of polycyclic aromatic hydrocarbons in shallow groundwater from an alluvial-diluvial fan of the Hutuo River in North China. Results show that the concentration levels of 16 priority polycyclic aromatic hydrocarbons range from 0 to 92.06 ng/L, do not conform to drinking water quality standards in China (GB 5749-2006). However, the concentration figures of priority polycyclic aromatic hydrocarbons are much lower than that of other studies conducted elsewhere in China. In addition, highly-concentrated polycyclic aromatic hydrocarbons (50–92 ng/L) are fragmentarily distributed. The composition of polycyclic aromatic hydrocarbons from this study indicates that low molecular polycyclic aromatic hydrocarbons are predominant in groundwater samples, medium molecular compounds occur at low concentrations, and high molecular hydrocarbons are not detected. The polycyclic aromatic hydrocarbon composition in groundwater samples is basically the same as that of gaseous samples in the atmosphere in this study. Therefore, the atmospheric input is assumed to be an important source of polycyclic aromatic hydrocarbons, no less than wastewater discharge, adhesion on suspended solids, and surface water leakage. Ratios of specific polycyclic aromatic hydrocarbons demonstrate that they mainly originate from wood or coal combustion as well as natural gas and partially from petroleum according to the result of principal component analysis. On the whole, conclusions are drawn that the contamination sources of these polycyclic aromatic hydrocarbons are likely petrogenic and pyrolytic inputs. Future investigations by sampling topsoil, vadose soil, and the atmosphere can further verify aforementioned conclusions.

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E-mail: wangjcui@126.com

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs, Table 1) are ubiquitous contaminants in the atmosphere, water, soil, sediments, and organisms (Lee et al., 2005; Yang et al., 2013). Owing to their toxicity, mutagenicity, and carcinogenicity, 16 PAHs are listed as priority pollutants according to U.S. Environmental Protection Agency (Table 1). These hydrocarbon compounds are generated by natural and anthropogenic processes including incomplete combustion, oil spills, urban runoff, and industrial and domestic wastewater as well as atmospheric fallout of vehicle exhaust and industrial emissions (Zakaria et al., 2002) which then penetrate into the environment in various ways.

PAHs can accumulate and withstand long-range transport. Improper treatment of PAH emissions and leakage of polluted surface water, sewage irrigation in agricultural fields, disposal of solid wastes, and leaching of contaminated soil have all resulted in PAH pollution in groundwater.

As far back as 2001, some low-ring PAHs were detected in groundwater from 18 American states (Focazio et al., 2008); subsequently more surveys on PAH pollution in groundwater were carried out in other countries (Masih et al., 2008; Saba et al., 2012). Now, the investigations in the main plains of East China show that up to 44 kinds of poisonous and harmful organic pollutants are frequently detected in shallow groundwater, among which BaP is one of the main sources of excessive PAHs (Wen et al., 2012).

Once an essential water source for Shijiazhuang in North China, the Hutuo River flowed all year round before 1959.

Table 1 Abbreviations and properties of polycyclic aromatic hydrocarbons

Compounds	Abbreviations	The number of rings	Solubility/($mg \cdot L^{-1}$)	Log Kow [a)]
Polycyclic aromatic hydrocarbons	PAHs			
Naphthalene	Nap	2	31.7	3.37
Acenaphthylene	Acy	2	1.93	4.00
Acenaphthene	Ace	2	3.42	3.92
Fluorene	Flu	2	1.9	4.18
Phenanthrene	Phe	3	1.29	4.57
Anthracene	Ant	3	0.076	4.54
Fluoranthene	Fla	3	0.26	5.22
Pyrene	Pyr	4	0.14	5.18
Benzo(a) anthracene	BaA	4	0.01	5.91
Chrysene	Chr	4	0.002	5.86
Benzo(b) fluoranthene	BbF	4	0.001	5.80
Benzo(k) fluoranthene	BkF	4	0.0007	6.00
Benzo(a) pyrene	BaP	5	0.0038	6.04
Indeno(1,2,3-cd) pyrene	InP	5	0.062	6.50
Dibenzo(a,h) anthracene	DiA	5	0.0005	6.75
Benzo(g,h,i) perylene	BgP	6	0.00026	6.50

a) Mackay et al. (1992).

However, an artificial outflow limit from two large reservoirs, the Gangnan Reservoir and Huangbizhuang Reservoir, together with an arid climate have resulted in interim water flow during reservoir drainage or even in wet years.

Now the Hutuo River has already been cutoff due to wastewater pollution and ubiquitous garbage in the river channel (Li, 2012; Li et al., 2014; Liang et al., 2014). Thick fog and atmospheric haze is also a serious problem in this area (Lin, 2014).

In the alluvial-diluvial fan of the Hutuo River, groundwater is the major water supplier to industries, agriculture, and everyday life. However, as recharged by surface water, shallow groundwater has already been polluted. Although research on groundwater pollution concerning conventional inorganic components, halohydrocarbons, and chlorinated benzenes were conducted mainly in the Hutuo River Plain (Li et al., 2011, 2014), few have analyzed the distribution and accumulation of PAHs in shallow groundwater from the alluvial-diluvial fan of the Hutuo River. Therefore, this paper has dug into the above issues to provide references for groundwater quality and contamination assessment, which are conducive to preventing PAH pollution and protecting groundwater resources in this area.

2 Study area

The alluvial-diluvial fan of the Hutuo River is located on a piedmont sloping plain of 500 km^2 between the eastern side of Taihang Mountain and the North China Plain, whose ground elevation ranges from 50 to 100 m. The fan lies between 37°50′N to 38°20′N and 114°15′E to 115°00′E (Fig. 1). The annual average precipitation is about 520 mm, which is partially contained in the form of surface water (in the Zhouhan River, Shijin Irrigation Canal, and Wangyang Ditch). This area, one of the most important food and cotton areas in Hebei Province, has a high yield of wheat, corn, and cotton.

The Quaternary alluvial-diluvial deposits within the study area are mainly composed of sandy gravel, fine silt, sandy loam, and clay. Groundwater is mainly in the pores of loose Quaternary rock strata (Jia et al., 1981), which can be divided into four aquifer groups. Aquifer I and II are the main exploitation layers. In particular, Aquifer II is mainly composed of gravel, medium-coarse sand, sandy loam, and clay in upper Pleistocene and lower Holocene deposits. Decreasing groundwater recharge sources such as atmospheric precipitation, lateral flow, seepage from rivers and canals, as well as well irrigation regression together with increasing groundwater exploitation have resulted in the continuous fall of groundwater level and constant expansion of depression cones, thus generating a noticeable watershed in the eastern part of study area.

On the top of the alluvial-proluvial fan, the continuous aquiclude barely exists between aquifers. The shallow aquifers featuring high horizontal and vertical permeability are mostly composed of cobbles and gravels. Aquifer group III has a slightly lower water level compared to the

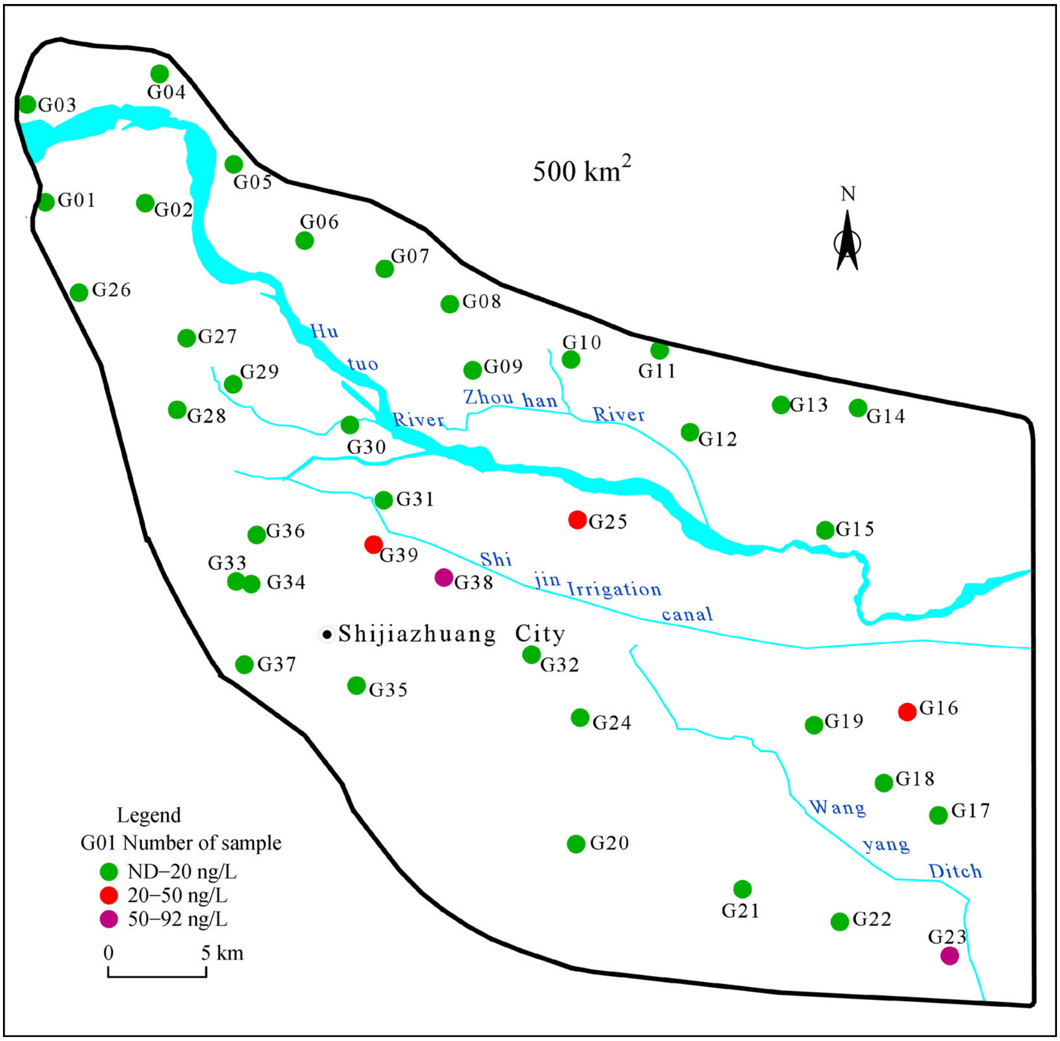

Fig. 1 The study area, sampling locations, and PAH distribution in the alluvial-diluvial fan of the Hutuo River, North China.

shallow aquifer group due to large-scale groundwater exploitation. As a result, vertical recharge of deep groundwater can be assumed to be a source of shallow groundwater (Zhang et al., 2000).

3 Sampling and analytical methods

3.1 Sample collection

A total of 39 samples of shallow groundwater were collected in October 2015. All the sampling wells were commonly utilized for domestic and/or industrial purposes. The depths of the wells ranged from 25 to 120 m while groundwater was sampled from 10 to 80 m. Samples were collected after purging at least 3 borehole volumes and physicochemical parameters were measured on-site by a WTW Multi 340i/SET multi-parameter instrument (Germany).

Collected by a stainless-steel sampler at the depth of 50 cm below water table, samples were then instantly sealed in brown glass bottles without air and kept in a refrigerated box.

3.2 Preparations and testing

All water samples sent to ALS Technichem (HK) Pty Ltd.'s laboratory were extracted by separatory funnel and tumbler techniques according to US EPA Method 3510C. Water samples mixed with NaCl, surrogates, and the extract (acetone: dichloromethane = 1:1) were extracted twice. Acid was added to adjust the pH level to be less than 2. Then the extract was mixed with Na_2SO_4 purified at 400°C. Going through filtration, water bath in Caliper at 40°C, and then concentration after blow-off treatment by N_2, the mixture was treated by internal standard and remained to be tested. Gas chromatography/mass spectrometry (GC/MS) according to US EPA Method 8270 was used to define PAH concentration.

3.3 Quality control and statistical analysis

All data were subject to strict quality control procedures. Six surrogate standards were added to all samples to monitor sample extraction, cleanup, and analysis. The average recovery rate of surrogate standards varied from 75% to 92%. One blank and one sample control spike were set to run with every 10 samples. No PAHs were detected in the blank and the recovery rate of the sample control spike was from 80% to 93%.

Apart from PAH distribution drawn by Mapgis6.7, statistical analyses of PAH concentrations in the groundwater samples were done by PASW statistics 19.0 (SPSS Inc., USA) and Origin 8. In addition, principal component analysis (PCA) was used to confirm PAH sources in study area.

4 Results and discussion

Parameters measured on site show that the average water temperature (T) of shallow groundwater is 15.5°C and its pH is between 7.08–7.90 which means that shallow groundwater is alkaline. Dissolved oxygen (DO) is below 4.0 mg/L in 74% of the samples. The mean electrode potential (Eh) is 116.0 mv and electric conductivity (EC) is 750–1111 μs/cm (Table 2).

4.1 PAH residual

The total and individual concentrations of 16 PAHs were listed in Table 3 and Table 4. Most components of PAHs were detected in the groundwater with a mean concentration of 9.58 ng/L. The levels of naphthalene (Nap, Table 1) (2.59 ng/L) and phenanthrene (Phe, Table 1) (2.52 ng/L) were highest, which account for 27.0% and 26.3% of total PAHs respectively. Individual detected rates of fluorine (Flu, Table 1), anthracene (Ant, Table 1), Phe, acenaphthylene (Acy, Table 1), and Nap were all more than 50%, especially Nap at 89.7%. 2–3 ring PAHs (Nap, Acy, Ace, Flu, Phe, Ant, Fla, Table 1) are predominant among individual PAHs, and 5–6 ring PAHs (BaP, InP, DiA, BgP, Table 1) are not detected. This composition of PAHs in groundwater samples is similar to the water samples from the Guozhuang karst system in the northern part of China (Shao et al., 2014).

The overall concentration of PAHs in shallow groundwater from the study area is below 92.06 ng/L, much lower than that in some regions of China, such as the Xihe River Area in Shenyang City (159.1–483.7 ng/L) (Luo et al., 2011), irrigation areas along the Hunhe River in Liaoning Province (3668–23,505 ng/L) (Zhang et al., 2007), the Guozhuang karst system in Shanxi Province (2137–9037 ng/L) (Shao et al., 2014), the upper region of Sihu Lake Basin in the Jianghan Plain (55.86–224.63 ng/L) (Gong et al., 2015), the suburb of Taihu Plain (4–32,449 ng/L) (Cui et al., 2008), and Yunnan Province (58.0–275.5 ng/L) (Lü et al., 2009). In summary, PAH contamination of shallow groundwater in Hutuo River's alluvial-diluvial fan still remains at a low level.

4.2 Space distribution of PAHs

The distribution of PAHs in shallow groundwater in the study area is shown in Fig. 1. Concentrations of total PAHs in all the samples are in line with the standards for drinking water quality in China (GB 5749-2006), and BaP is not detected. The concentration of benzo(a)anthracene (BaA, Table 1) in sample G37 exceeds the standards of 2015 EPA Human Health Ambient Quality Criteria (concerning the consumption of water + organism) (Table 4). BaA concentration is below 20 ng/L in 87% samples, and ranges between 20–50 ng/L in sampling sites G16, G25, and G39. For the areas of G23 and G38, the PAH concentration is between 50–92 ng/L.

4.3 Distribution patterns of PAHs

In order to distinguish the proportions of low-molecular (LM), medium-molecular (MM) and high-molecular (HM) PAHs in different environment mediums, sixteen PAH compounds are divided into three groups: 2–3 ring PAHs (Nap, Acy, Ace, Flu, Phe, Ant, Fla), 4 ring PAHs (Pyr, BaA, Chr, BbF, BkF), and 5–6 ring PAHs (BaP, InP, DiA, BgP) (Table 1). LM PAHs account for a higher percentage compared to MM PAHs, indicating that LM PAHs are predominant in groundwater samples. Furthermore, the percentage of different PAHs from the highest to the lowest is 2 ring, 3 ring, and 4 ring, which shows that 2 ring PAHs dominate in groundwater samples. All PAHs analyzed in our study demonstrate relatively high octanol–water partition coefficients (i.e., log Kow$\geqslant$4, Table 1), with the exception of the lightest PAHs such as Nap (log Kow 3.4). Therefore, PAHs are likely to be found in both sediments and soil in the form of mobile constituents, rather than existing in the aqueous phase with a very low solubility (Table 1) (Quesada et al., 2014).

Generally, PAHs mainly exist in vapor and particulate

Table 2 Field measured parameters

	pH	T/°C	DO/(mg·L^{-1})	Eh/mv	EC/(μs·cm^{-1})
Range	7.08–7.90	14.5–17.2	0.03–13.76	48.7–208	749.9–1110.9
Mean	7.51	15.5	3.46	116.0	775.5

Table 3 The concentration (ng/L) of individual compounds in each site

Sample number	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	InP	DiA	BgP	ΣPAHs
G01	nd[b)]	nd	nd	nd	nd	nd	nd	nd	0.19	0.25	nd	nd	nd	nd	nd	nd	0.44
G02	2.15	0.86	1.05	2.50	4.94	0.46	2.80	1.74	nd	nd	nd	nd	nd	nd	nd	nd	16.52
G03	0.02	0.05	0.06	0.01	0.10	0.15	0.01	0.01	nd	nd	nd	nd	nd	nd	nd	nd	0.42
G04	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01
G05	0.02	0.07	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.09
G06	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01
G07	0.65	0.14	0.07	0.16	0.89	0.05	0.10	0.15	0.06	0.32	nd	nd	nd	nd	nd	nd	2.57
G08	1.86	1.35	0.46	0.80	6.38	0.43	1.36	1.03	0.16	0.20	0.19	0.11	nd	nd	nd	nd	14.33
G09	0.01	0.02	nd	nd	0.01	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.06
G10	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01
G11	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02
G12	1.27	0.11	0.04	0.09	0.40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.93
G13	2.27	0.98	0.27	1.02	2.66	0.09	0.36	0.26	nd	0.04	nd	nd	nd	nd	nd	nd	7.94
G14	2.03	3.09	1.28	3.03	7.51	0.55	0.93	0.60	0.06	0.10	nd	nd	nd	nd	nd	nd	19.20
G15	0.09	nd	nd	nd	0.02	0.01	0.02	0.01	nd	nd	nd	nd	nd	nd	nd	nd	0.15
G16	23.04	3.70	2.06	4.33	6.30	0.29	0.81	0.54	0.37	0.16	nd	nd	nd	nd	nd	nd	41.62
G17	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02
G18	0.02	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.04
G19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
G20	0.36	0.08	nd	0.02	0.09	0.02	0.02	0.03	nd	nd	nd	nd	nd	nd	nd	nd	0.60
G21	1.14	0.64	0.17	0.63	3.86	0.07	0.80	0.44	nd	nd	nd	nd	nd	nd	nd	nd	7.76
G22	0.01	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03
G23	5.95	2.46	0.82	35.28	4.92	0.09	0.92	0.50	0.44	0.12	nd	nd	nd	nd	nd	nd	51.55
G24	0.01	0.03	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.05
G25	0.99	1.98	1.07	4.04	13.73	0.41	1.33	0.77	0.60	0.16	nd	nd	nd	nd	nd	nd	25.11
G26	0.40	0.04	0.08	0.04	0.06	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.62
G27	0.01	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03
G28	0.93	1.06	0.73	1.78	3.46	0.15	1.36	0.92	1.17	0.18	nd	nd	nd	nd	nd	nd	11.75
G29	5.69	1.52	1.04	2.38	4.06	0.24	0.56	0.36	0.22	0.05	nd	nd	nd	nd	nd	nd	16.14
G30	0.12	0.02	nd	nd	0.04	0.02	0.02	0.02	nd	nd	nd	nd	nd	nd	nd	nd	0.23
G31	0.13	0.02	nd	0.02	0.02	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.20
G32	0.63	0.43	nd	0.04	0.09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.19
G33	1.07	0.43	0.28	1.29	4.65	0.17	0.76	0.52	0.43	0.14	nd	nd	nd	nd	nd	nd	9.75
G34	nd	0.13	nd	nd	0.01	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.17
G35	0.02	0.07	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.08
G36	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
G37	1.01	0.95	0.58	5.02	0.02	0.06	3.04	1.82	2.17	0.60	nd	nd	nd	nd	nd	nd	15.28
G38	30.98	8.33	5.54	14.43	26.85	1.16	2.36	1.34	0.74	0.33	nd	nd	nd	nd	nd	nd	92.15
G39	17.90	3.21	1.31	3.74	7.25	0.37	0.91	0.61	0.43	0.15	nd	nd	nd	nd	nd	nd	35.92

b) nd = not detected.

phases in the atmosphere. 2–3 ring PAHs are predominant in the vapor phase while 4 ring PAHs equally exist in both vapor and particulate phase. The 5–6 ring PAHs are mainly in the particulate phase (Zhang, 2016). In North China, the average concentration of 15 kinds of PAHs in vapor and particulate phases was 550 ng/m^3, and the PAHs only in the

Table 4 Residual levels of PAHs in shallow groundwater and standards for water quality

PAHs	Residual levels/(ng·L^{-1})			Standards/(μg·L^{-1})	
	Range	Mean	SD	China	US EPA
Nap	nd–30.98	2.59	6.58		
Acy	nd–8.33	0.82	1.59		
Ace	nd–5.54	0.43	0.98	-	70
Flu	nd–35.28	2.07	6.04	-	50
Phe	nd–26.85	2.52	5.06		
Ant	nd–1.16	0.12	0.23	-	300
Fla	nd–3.04	0.47	0.80	-	20
Pyr	nd–1.82	0.30	0.49	-	20
BaA	nd–2.17	0.18	0.41	-	1.2×10^{-3}
Chr	nd–0.60	0.07	0.13	-	0.12
BbF	nd–0.19	0.00	0.03	-	1.2×10^{-3}
BkF	nd–0.11	0.00	0.02	-	1.2×10^{-2}
BaP	nd	nd	nd	0.01	1.2×10^{-4}
InP	nd	nd	nd	-	1.2×10^{-3}
DiA	nd	nd	nd	-	1.2×10^{-4}
BgP	nd	nd	nd		
ΣPAHs[c)]	nd–92.06	9.58	18.42	2	-

c) ΣPAHs calculated by total concentration of the 16 PAHs.

vapor phase accounted for 37%. The predominantly gaseous PAHs are LM compounds (mostly Acy, Flu, and Phe), while 5–6 ring PAHs are not found in vapor phase. The HM compounds are dominant in the particulate phase (Liu et al., 2007). PAHs both in the atmosphere and on the surface are carried to the vadose zones and then infiltrate into groundwater by atmospheric precipitation. PAHs in both the vapor and particulate phases will generate absorption, transformation, and probably molecular fractionation, which is a complicated geological and geochemical process. Due to the lipophilic property and low solubility, PAHs in water bodies always adsorb onto the particulate materials, while LM PAHs mainly exist in natural water (Vilanova et al., 2001). The PAH composition in groundwater is basically consistent with that of gaseous samples in the atmosphere in this study. Therefore, the atmospheric input of PAHs cannot be excluded, no less than wastewater discharge, adhesion on suspended solids, and surface water leakage, which need to be verified in further studies.

4.4 Sources of PAHs

Researchers from different countries have conducted thorough researches on PAH sources in the atmosphere, rivers, and soils/sediments (Yunker et al., 2002; Doong and Lin, 2004; Jarsjö et al., 2005; Park et al., 2011; Zhang et al., 2013), but the technologies used to identify the sources of PAHs in groundwater still remain in the early stage. Due to the similar physical and chemical properties, isomers in maternal PAHs show similar distribution and dilution features. Therefore, isomer ratios can remain roughly the same from emission source to receptor environment. The isomer ratio is widely adopted by researchers to identify PAH sources in the environment (Yunker et al., 2002). When PAHs on the ground surface migrate downward, the behavioral difference of isomers may be accompanied by absorption, transformation, and probably molecular fractionation. This complicated geological and geochemical process owns the features of elusiveness, time-lagging, and complexity. In this case, the pollution source in groundwater cannot be accurately defined if utilizing the ratio method directly. This study did not contain complete composition electropherograms of pollution sources in the study area. In addition, the Quaternary alluvial-diluvial deposits within the study area are mainly composed of sandy gravel, fine silt, sandy loam, and clay, which limit the effects by different components of PAHs. So a preliminary conclusion can be drawn that this method can be used to determine the source of pollution indirectly, and other methods can be used as references to check the results. Further verification should be made by sampling topsoil and vadose soil.

Therefore, the ratios of Ant/(Ant + Phe), Fluoranthene/(Fluoranthene + Pyrene), and BaA/(BaA + Chrysene) are widely used. Fluoranthene, pyrene and chrysene are abbreviated as Fla, Pyr, and Chr, respectively (Table 1). The Ant is generally lower than that of Phe contained in petroleum products. However, the process of combustion will generate more Ant (Zhang et al., 2012). So Ant/(Ant + Phe) ratios which are higher than 0.1 can indicate pyrolytic origin, whereas values lower than 0.1 indicate petrogenic origin. Fla/(Fla + Pyr) ratios less than 0.5 are defined as of petrogenic origin, whereas the ratios higher than 0.5 are correlated to wood or coal combustion (Doong and Lin, 2004; Guo et al., 2007). BaA/(BaA + Chr) ratios higher than 0.35 indicate their pyrolytic origin, whereas values lower than 0.35 are of petrogenic origin (Yunker et al., 2002).

In order to investigate the PAH sources in the study area, Ant/(Ant + Phe) versus Fla/(Fla + Pyr) and BaA/(BaA + Chr) versus Fla/(Fla + Pyr) are applied in the study (Fig. 2). Figure 2(a) illustrates that PAHs in shallow groundwater mainly originate from petroleum combustion in terms of Ant/(Ant + Phe) instead of wood and coal combustion according to Fla/(Fla + Pyr). However, Figure 2(b) illustrates that PAHs are mainly generated from wood and coal combustion. As a matter of fact, coal is one of the most important sources of energy in the study area. In 2012, the total consumption of coal was 6.1×10^7 t, accounting for 85.06% of total primary energy consumption (Zhang et al., 2015). Crude oil is another important energy source in Shijiazhuang City (Liang and Qi, 2009). Consequently, PAHs in shallow groundwater mainly come from wood and coal combustion and partially from petroleum.

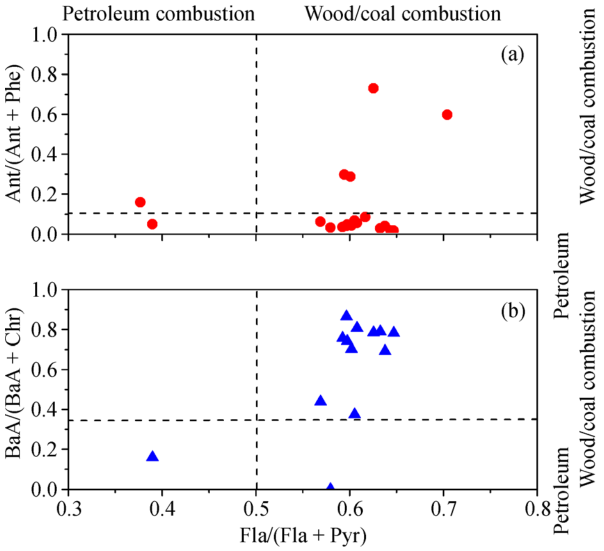

Fig. 2 Plot of the isomeric ratio (a) Ant/(Ant + Phe) vs. Fla/(Fla + Pyr) and (b) BaA/(BaA + Chr) vs. Fla/(Fla + Pyr).

Although the composition and ratios of selected PAH compounds can be taken as indirect indicators of PAH sources, the relationship among different factors and their contribution percentage to contamination are not clear. PCA is widely recognized as a useful receptor model for quantifying sources and profiles in the absence of knowledge of hypothetical sources. To interpret factors extracted by PCA in an easier way, the axis of each factor can be rotated. Between the two kinds of rotation methods (orthogonal and oblique), VARIMAX, a commonly used orthogonal rotation method, is adopted in this study. Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd) pyrene, dibenzo(a,h) anthracene, and benzo(g,h,i) perylene are abbreviated BbF, BkF, BaP, InP, DiA, and BgP, respectively (Table 1). All these substances are excluded in the input dataset due to almost no detection. Factors with eigenvalues higher than 1.0 are picked out (Fig. 3). The data of factor loading extracted by PCA are shown in Table 5 and Fig. 4. Individual PAHs with factor loading higher than 0.8 are selected to identify the sources based on the value of each factor loading.

Table 5 VARIMAX-rotated factor loadings of PCA

PAHs	Factor loadings	
	F1	F2
Nap	**0.89** $^{d)}$	0.14
Acy	**0.95**	0.28
Ace	**0.94**	0.29
Flu	0.49	0.28
Phe	**0.92**	0.27
Ant	**0.89**	0.30
Fla	0.43	**0.83**
Pyr	0.41	**0.84**
BaA	0.10	**0.93**
Chr	0.22	**0.86**
% Variance	48.59	34.06

d) Factor loadings over 0.8 were highlighted in bold.

Two factors, which account for 82.65% of the cumulative variance, are picked out (Fig. 3). Among them, factor 1 (48.59% of the total variance) mainly contains acenaphthene (Ace, Table 1), Ant, Phe, and Acy with moderate loadings of NaP. Park et al. (2011) reported that LM PAHs such as Ace, Acy, and Nap were usually generated from petrochemicals associated with the iron and steel industry, while Phe and Ant were closely related to coal or wood combustion (Simcik et al., 1999). In addition, Acy has been commonly used as an indicator of wood combustion (Zuo et al., 2007). Incomplete combustion of biomass is also presumed to be a Nap sources (Grover et al., 2013). Therefore, factor 1 could be identified as petroleum and coal/wood combustion. Factor 2 (34.06% of the total) suggests high loadings of BaA, Chr, Pyr, and Fla. BaA and Chr are mainly generated from natural gas combustion (Kavouras et al., 2001; Motelay-Massei et al., 2007), while Pyr and Fla are always accompany coal combustion (Simcik et al., 1999). Thus, factor 2 can be assumed to be highly correlated to natural

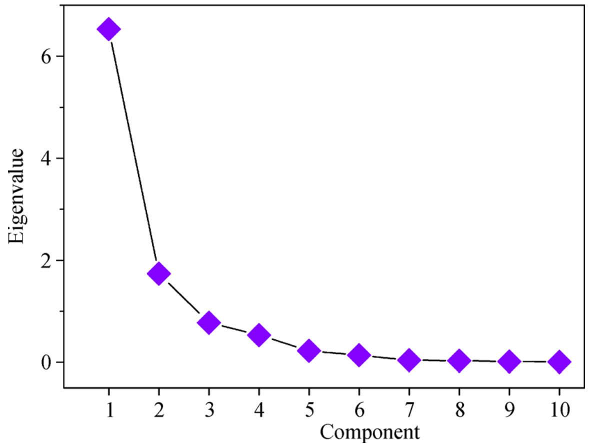

Fig. 3 Screen plot of eigenvalues of 10 components calculated from PAH concentrations.

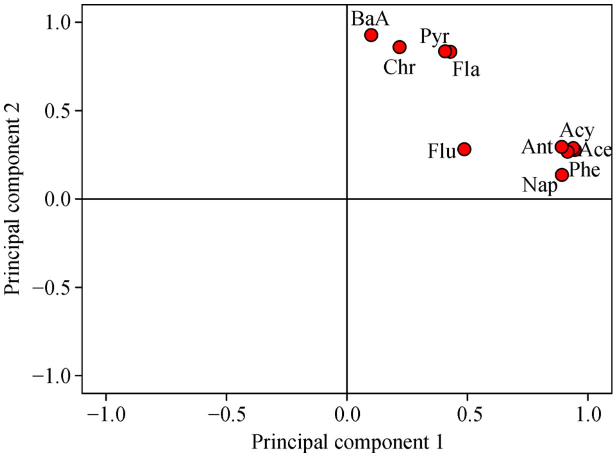

Fig. 4 Factor loadings for PAHs of shallow groundwater in the study area.

gas and coal combustion. On the whole, the contribution of coal combustion and petrogenic source identified by PCA can surpass the results gained by ratio method. Corresponding indicators and contribution rates can clarify different discharge sources of PAHs.

5 Conclusions

The Hutuo River, which was once an essential water source of Shijiazhuang in North China, suffers greatly today from wastewater pollution and ubiquitous garbage in its river channel. In the alluvial-diluvial fan of the Hutuo River, groundwater is the main water source for industries, agriculture, and everyday life. However, the shallow groundwater, which is recharged surface water, has been affected by the pollution of the Hutuo River. Therefore, this study focuses on PAH pollution and apportions sources of PAHs in the shallow groundwater. The results are as follows.

The concentration levels of 16 priority PAHs range from 0 to 92.06 ng/L, which are not all in line with drinking water quality in China (GB 5749-2006) and are much lower than that of reported in other studies of China. In addition, highly-concentrated PAHs (50–92 ng/L) are fragmentarily distributed. The PAH composition indicates that LM PAHs are predominant in groundwater samples, MM PAHs are also detected at low rates, and HM PAHs have not been found. The composition of polycyclic aromatic hydrocarbon in groundwater is basically consistent with that of gaseous PAHs in the atmosphere in this study. Therefore, the atmospheric input is expected to be an important source of PAHs, no less than wastewater discharge, adhesion on suspended solids, and surface water leakage. The evaluation results of PAH sources according to calculated ratios of specific PAH compounds show that PAHs are mainly generated from wood and coal combustion. The results of principal component analysis show a secondary petroleum combustion source. Furthermore, the principal component analysis suggests that natural gas is also a main source. On the whole, the PAH contamination comes from both petrogenic and pyrolytic inputs. Further verification should be made by sampling topsoil, vadose soil, and the atmosphere.

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