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Sources and pollution path identification of PAHs in karst aquifers: an example from Liulin karst water system, northern China

Xiao Wu [a], Xubo Gao [a,b,*], Ting Tan [a], Chengcheng Li [a], Ruyao Yan [c], Zeyong Chi [a], Yu Feng [a], Peili Gong [a], Jiancong Fang [a], Xingzhou Zhang [a], Kaisaerjiang Aihemaiti [a], Dong Xu [d]

[a] State Key Laboratory of Biogeology and Environmental Geology and School of Environmental Studies, China University of Geosciences, Wuhan 430074, PR China
[b] Karst Dynamics Laboratory, MNR and GZAR, (Institute of Karst Geology, CAGS), Guilin, Guangxi 541004, PR China
[c] Water Resources Bureau of Lvliang City, Shanxi Province, Lishi 033000, PR China
[d] Hubei Provincial Academy of Eco-environmental Sciences, Wuhan 430070, PR China

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ABSTRACT

Karst water, with constituting major sources for water supply worldwide, is vulnerable and prone to be polluted. In this study, it is reported that karst water polycylic aromatic hydrocarbons (PAHs) pollution is caused by the infiltration of surface runoff in the bared carbonate areas, which is of universal significance for the protection of groundwater resources in karst region. Hydro-geochemistry, stable isotopes (δD, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) and characteristic ratio method were conducted together to illustrate the concentration, distribution, sources and pollution path of polycyclic aromatic hydrocarbons in groundwater in the Liulin karst water system of northern China. The results showed that total concentration of polycyclic aromatic hydrocarbons ranged from 39.25 to 16,830 ng/L in groundwater, with Naphthalene being the dominant component, and the median value increased gradually along the flow path. The highest polycyclic aromatic hydrocarbons concentrations in karst water were mainly observed in the coal mining and the discharge areas. Based on the characteristic ratios, the polycyclic aromatic hydrocarbons in the study area mainly come from local incomplete combustion of woods, fossil fuels, coal and liquid fuels. The slight shift of δD and $\delta^{18}O$ and moderate $^{87}Sr/^{86}Sr$ ratios suggest that the polycyclic aromatic hydrocarbons in karst water is mainly polluted by surface runoff during rain events in the bared karst region. The leakage of river water may partly contribute to the polycyclic aromatic hydrocarbons in some karst water, which normally located close to the karst water - river water mixing line. This study provides a new technical method for tracing the sources and identifying the pollution paths of organic pollution in a karst water system.

1. Introduction

As a class of ubiquitous environmental pollutants, high concentrations of PAHs can cause serious environmental and health problems, such as damage of kidney and liver, inflammation of the skin, and so on (Sato and Aoki, 2002; Sarigiannis et al., 2015; Khpalwak et al., 2019). The occurrence, mobility, bioaccumulation, environmental toxicity and sourcing of PAHs are of concern and have been extensively studied in various environmental and biological media (Harrison et al., 1996; Mitra and Bianchi, 2003; Mai et al., 2003; Liang et al., 2008; Lu et al., 2008; Ravindra et al., 2008; Callén et al., 2014; Manoli et al., 2016; Kuśmierz et al., 2016; Lee et al., 2018).

The environmental PAHs mostly yielded from anthropogenic activities, such as home cooking, plant burning, gasoline combustion and industrial processes. Only a small part of PAHs come from natural activities, like volcanic eruptions, wild fires and so on (Benner et al., 1989; Neilson, 1998; Kalaitzoglou et al., 2004; Yang et al., 2013; Gao et al., 2011; Alves et al., 2016; Gysel et al., 2018; Li et al., 2019). The PAHs can easily reach karst aquifers via penetrating through vadose zone (Smail et al., 2012; Garcia-Flores et al., 2013; Sun et al., 2019). As a kind of persistent organic pollutants, the monitoring of PAHs in the subsurface environment is of great important for the protection of human and ecological safety (Cerniglia, 1992; Doong and Lin, 2004; Li et al., 2017). A full understanding of the occurrence, source apportionment and pollution path of PAHs will be helpful for the proper management of groundwater resources (Nielsen et al., 1996; Webster

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[*] Corresponding author at: No. 388, Lumo Road, 430074 Wuhan, China.
E-mail address: xubo.gao.cug@gmail.com (X. Gao).

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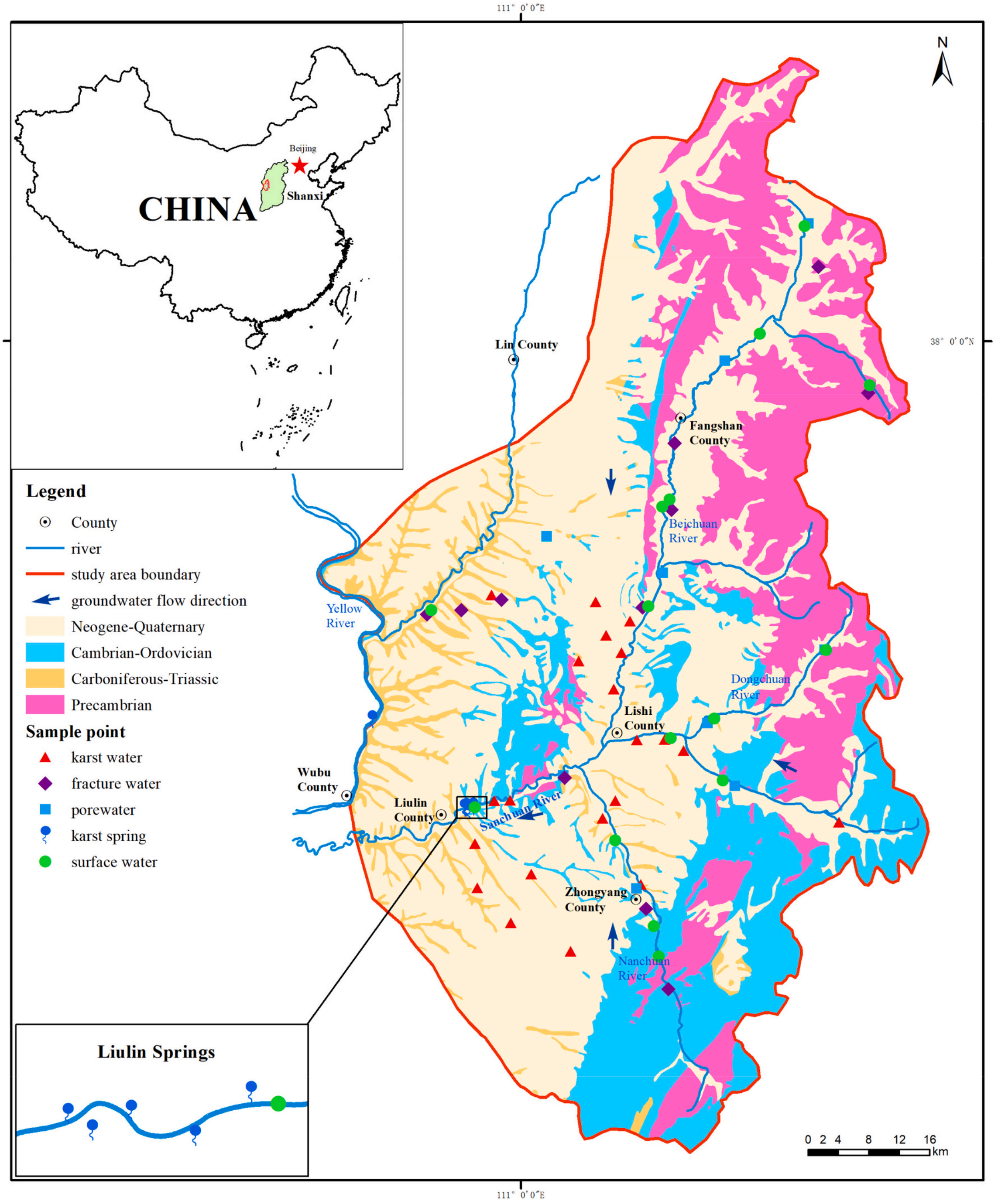

Fig. 1. Simplified hydrological map of the Liulin karst water system with water sample sites in this study.

et al., 2018; Jiang et al., 2020).

Karst groundwater is the primary water resource for approximately 25% of the world's population (Olarinoye et al., 2020). In China, karst area accounts for 33% of the country's land surface and yields nearly a quarter of the country's groundwater resources (Yuan, 1994). Karst aquifers are under high risk of pollution input from human activities due to the existence of sinkholes, caves and fractures (Heinz et al., 2009; Li et al., 2020; Gao et al., 2010; Schwarz et al., 2011; Wang et al., 2015). In the past six decades, processing and utilization of coal and oil have been intensively developed around the world (Guo et al., 2005; Zhang et al., 2016; Hindersmann and Achten, 2018). Whether human activities like coal mining or exhaust gas emission could cause PAHs pollution in karst water system, and how does the PAHs enter karst aquifers are still remained unclear in north China karst area. As an important mining and a typical karst area in northern China, Liulin karst spring basin is taken as an example to identify the distribution, sources and pollution paths of PAHs, by employing hydrogeochemistry, stable isotopes (δD, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) and characteristic ratio method together. To our knowledge, this is the first effort to using hydrochemistry-stable isotopes (δD, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) to evaluate the PAHs' behaviors in karst water, providing a new technical method for tracing the sources of organic pollution in a karst spring system.

2. Study area

The Liulin karst water system is located in western Shanxi Province,

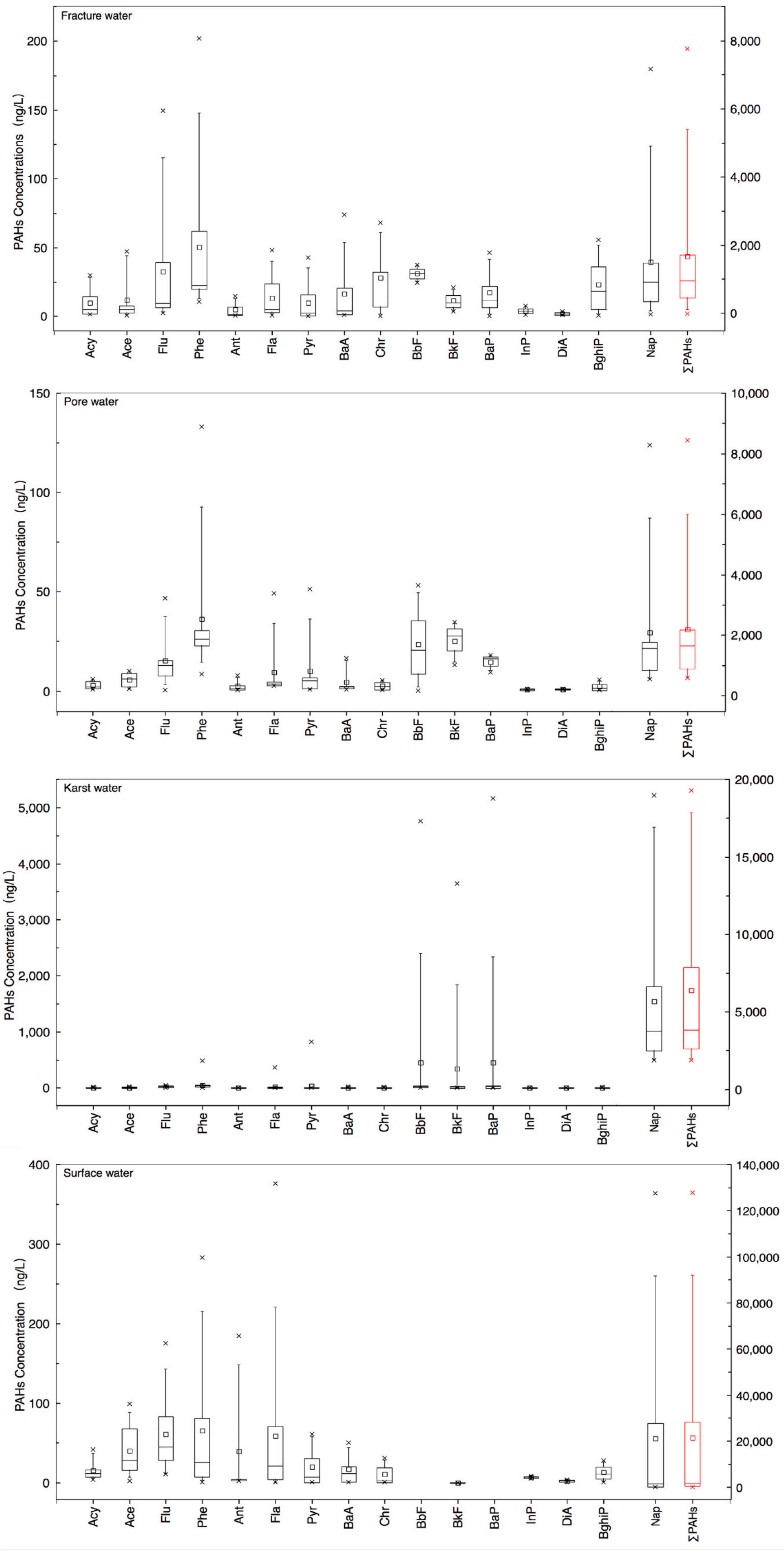

Fig. 2. Box-whisker plot of concentrations of 16 PAHs components in water samples (The concentrations of Nap and ∑PAHs according to the right y-axis).

northern China (Fig. S1). It covers an area of 6281 km^2 and takes up 25% of the Ordovician carbonate rocks of the karst aquifer outcrop. The surface elevation ranges from 800 m asl (above sea level) in the west to 2800 m asl in the east. With a typical arid and semi-arid warm temperate continental monsoonal climate, the annual average precipitation in the Liulin karst water system is 486 mm (Wang, 2007). Approximately 66% of the precipitation is concentrated between July to September (Wei, 2013), and the annual average evaporation is 1186 mm. The perennial mean air temperature is 9.2 °C, maximum 39.9 °C and minimum −27.4 °C. Sanchuan River and its three tributaries (Beichuan River, Dongchuan River, and Nanchuan River) are the major rivers flowing through the whole catchment in north, south, east and flow to west.

The study area is located between the Lvliang anticline and the Ordos platform, with the formations ascending trend from east to west. The main outcropping stratums are Archean metamorphic rocks, Cambrian-Ordovician carbonate rocks, Carboniferous-Permian coal-bearing sandstones and shales, and Tertiary-Quaternary deposit sediments. Groundwater from middle Ordovician karst aquifer is one of the most important sources of water supply (Du, 2009). This aquifer is comprised of limestone, dolomite, and gypsum interbedded marl, with a total thickness above 500 m.

The karst groundwater system is mainly recharged in the bared carbonate in the south, east and north mountain areas. Leakage of river water serves as additional recharge sources. The buried carbonate areas, covered by thick sandstone and mudstone layers, serves as the flow-through area, with the waters flowing from the north, east and south parts of study area towards the Liulin springs. Places where the springs emerge in the Sanchuan River valley constitute the dominant discharge regions of the groundwater system. The springs are distributed along the Sanchuan River bank where the elevation ranges from 790 to 801 m asl (Fig. S2, Pei and Liang, 2005). The annual average discharge of the spring groups ranges between 0.36 m^3/s to 4.69 m^3/s from 1990 to 2019.

3. Material and methods

A total of 47 groundwater samples were collected from wells and springs from December 2015 to October 2020, including 9 pore water samples, 11 fracture water samples, and 27 karst water samples. Fifteen surface water samples were collected from the major rivers across the study area (Fig. 1).

The mutable parameters, including temperature, dissolved oxygen (DO) and pH, were measured in situ immediately during sampling, by pre-standardized potable meters (HACH HQ40d). Bicarbonate and carbonate ions (HCO_3^-, CO_3^{2-}) were determined on the sampling day using the Gran titration method (Gran, 1952). Major cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}) were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo Electron Corporation IRIS Intrepid II XSP). Major anions (Cl^-, SO_4^{2-} and NO_3^-) were determined by ion chromatography (IC, Metrohm 761 Compact). The ionic balance error of the analyses was within the standard limit of ±5%.

Samples for stable isotopes ($\delta^{18}O$, δD and $^{87}Sr/^{86}Sr$) analysis were filtered through 0.22 μm membranes and collected in 500 mL PET bottles respectively which had been carefully rinsed before sampling. Stable isotopes ($\delta^{18}O$ and δD) of water samples were determined via liquid water isotope analyzer (IWA-35-EP). The strontium isotope ($^{87}Sr/^{86}Sr$) was measured using plasma sourced multi-collector mass spectrometry (MC-ICP-MS, Nu plasma II), expressed in the standard notation delta per mil (‰).

Samples for PAHs were collected in 2.5 L brown ground-glass stoppered flasks, which had been rinsed in sulfuric acid potassium dichromate lotion and heated at 180 °C for 4 h before using. The collection of water samples for PAHs detection was performed according to the method suggested by Shao et al. (2014a). It is briefed as: 1) To filtrate water with a 0.45 μm glass microfiber filters; 2) A solid-phase extraction was used for PAHs extraction; 3) The extractants were subsequently transferred to a chromatographic column for cleanup and elution of PAHs; 4) The final volume of 0.5 mL eluate was obtained after rotary evaporation and nitrogen flush. The stock standard of PAHs was purchased from AccuStandara (USA). Methanol, dichloromethane and n-hexane (analytical grade) were purchased from CNWBOND (Germany). The PAHs concentrations were determined at the State Key Laboratory of Biological and Environmental Geology, China University of Geosciences (Wuhan). The condition of the instrument is summarized in Appendix S1. All data were subject to strict quality control procedures.

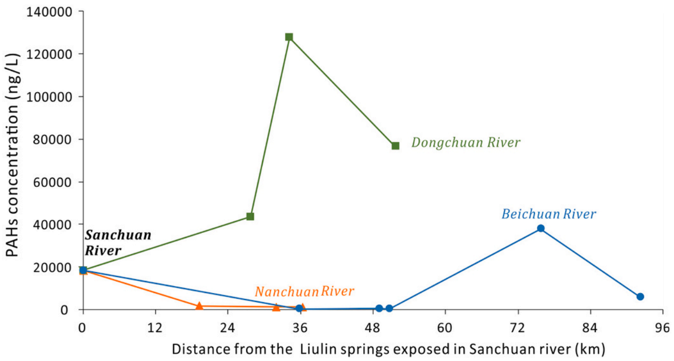

Fig. 3. Spatial distribution of PAHs in main rivers in the study area.

4. Results and discussion

4.1. Concentration and composition of PAHs

The statistical summary of the PAHs concentrations in water samples from the Liulin karst water system is given in Table S1.

The total concentration of PAHs ($\sum$PAHs) ranged from 39.25 ng/L to 16,830 ng/L in groundwater with a mean value of 3463 ng/L. The PAHs contents of groundwater samples in recharge area were from 527.8 ng/L to 2171 ng/L with a median value of 1112 ng/L. In runoff area, PAHs contents varied from 39.35 ng/L to 16,830 ng/L (median value of 1580 ng/L). The maximum, median and minimum concentrations of PAHs in groundwater in discharge area were 15,273 ng/L, 7047 ng/L and 2104 ng/L, respectively. It can be seen that the median content of PAHs in groundwater shows an increasing trend along the flow path. The contents of PAHs in surface water varied greatly, from 59.8 ng/L to 127,696 ng/L, with the mean value of 21,164 ng/L.

The contents of 16 PAHs components in the fracture water (FW), pore water (PW), karst water (KW) and surface water (SW) were statistically analyzed (Fig. 2). It is observed that Naphthalene (Nap) was the dominant PAHs in the water body in the study area, with higher contents in most of karst water (average value of 3981 ng /L). Other PAHs in karst water were between 0.7 ng/L-34.9 ng/L. Among them, the contents of Fluorene (Flu), Phenanthrene (Phe) and Benzo[*b*]fluoranthene (BbF) were moderate high (19.2 ng/L-34.9 ng/L) while Anthracene (Ant), Chrysene (Chr), Indeno[1,2,3-*cd*]pyrene (InP), Dibenzo[*a*,*h*]anthracene (DiA), Benzo[*ghi*]perylene (BghiP) contents were low (< 3 ng/L). Pore waters were characterized by moderately higher contents of Flu, Phe, BbF and Benzo[*k*]fluoranthene (BkF) (15.3 ng/L-36.4 ng/L), and lower values of Acenaphthylene (Acy), Ant, InP, DiA, BghiP (< 3 ng/L). The average content of Nap in fissure groundwater was 1727 ng/L, and other PAHs ranged between 2.2 ng/L and 50.2 ng/L, with the lowest contents of PAHs found in Ant, InP and DiA (< 5 ng/L). The highest contents of Nap were observed in surface water, with the average value of 20,944 ng/L and the contents of Acenaphthene (Ace), Flu, Phe, Ant, and Fluoranthene (Fla) were higher than 40 ng/L.

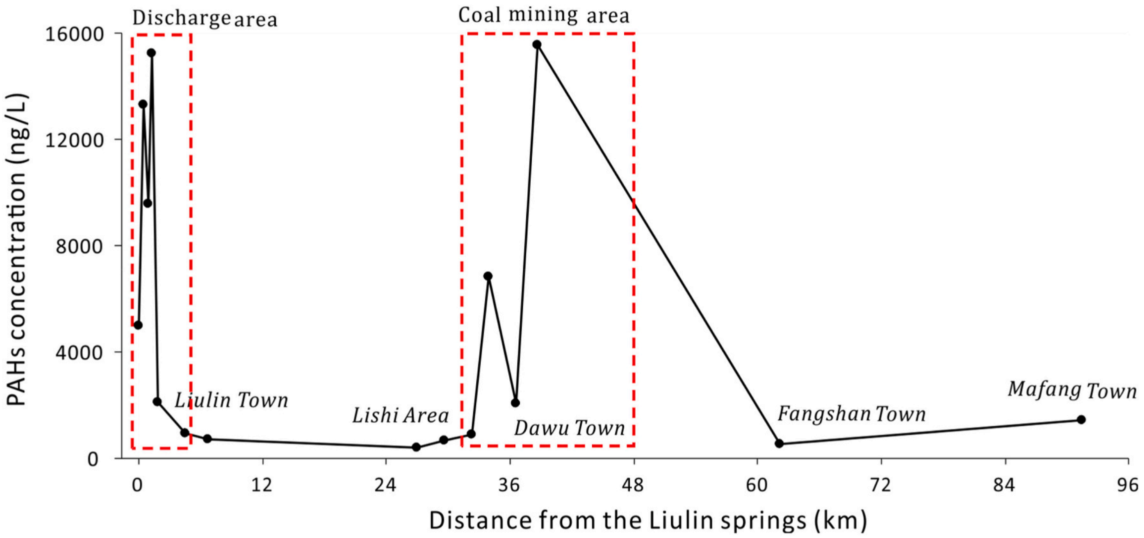

Fig. 4. Spatial distribution of PAHs in groundwater along the flow path.

4.2. Spatial distribution of PAHs

4.2.1. Distribution in surface water

The PAHs concentrations were relatively high in Sanchuan River and its three main tributariers (Beichuan River, Dongchuan River and Nanchuan River; Table S1, Fig. 3). Higher contents of PAHs were observed in the upstream of Beichuan River and Dongchuan River, where population are concentrated. With the fast urbanization, emission of the vehicles and petrol stations could yield PAHs pollution to air, soil and the river (Larsen and Baker, 2003; Wang et al., 2017; Wei et al., 2015). Therefore, urbanization related to anthropogenic activities is the main factor for PAHs pollution in these areas. The content of PAHs in Nanchuan River was the lowest, and showed a gradual increase trend from upstream to downstream, further indicating the potential impact of big towns (urbanization) on river water PAHs pollution.

4.2.2. Distribution in groundwater

The variations of PAHs concentration along the groundwater flow path (from Mafang town to the Liulin Spring groups) were drawn to illustrate the spatial distribution of PAHs in karst water (Fig. 4). In the northern recharge area, the water-bearing stratum is basically metamorphic rock. Two fracture water samples in Mafang and Fangshan Town were used for representation. Along the flow path, karst groundwater PAHs rose sharply when flowing through the coal mining area (Dawu town) and the town area with heavy population (Liuling town). This indicated that the PAHs in karst water were likely to come from the local contamination, such as coal combustion or traffic gas emission.

The outcrop strata are mainly Ordovician and Quaternary, covered by clastic rocks and coal seams around Dawu Town, where a large number of coal-mining industries bloom. It is well known that coal mining and the incomplete combustion of coke and coal will produce PAHs-rich contaminants (Lee et al., 2005; Liu et al., 2009; Huang et al., 2014; Buha-Markovi et al., 2020). Hence, it is reasonable to infer that the abnormally high content of PAHs in karst water is related to the local coalmines in the area. When the karst water is blocked by the impermeable rocks at the discharge area and eventually turns into a group of karst springs in Sanchuan River, the groundwater depth is getting shallower. Due to the increase of population and improvement of social development in the big towns in the discharge area, groundwater is easy to be polluted by vehicle emissions, fuel combustion, and increasing petroleum stations, etc. Therefore, urbanization is another major factor responsible for the pollution of PAHs in karst water in the area.

4.3. Source analysis of PAHs

The sources of PAHs are mainly from the combustion of fossil fuels, grass, woods, and the discharge of crude oil related material (Guo et al., 2007; Hu et al., 2013; Ozaki et al., 2020). To distinguish the possible sources among them, the characteristic ratio method has been proved to be an effective way (Olivella et al., 2006; Tan et al., 2011). As isomer

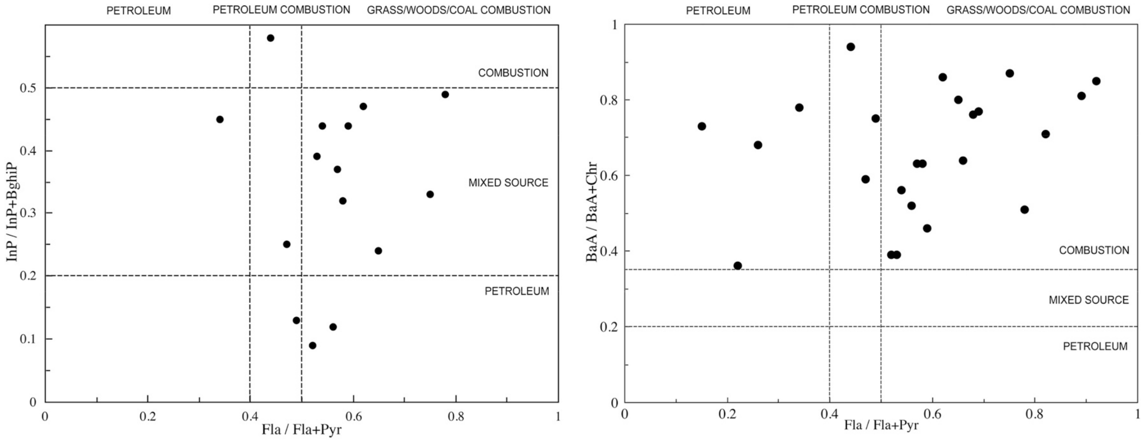

Fig. 5. Plot of the isomeric ratios for source identification.

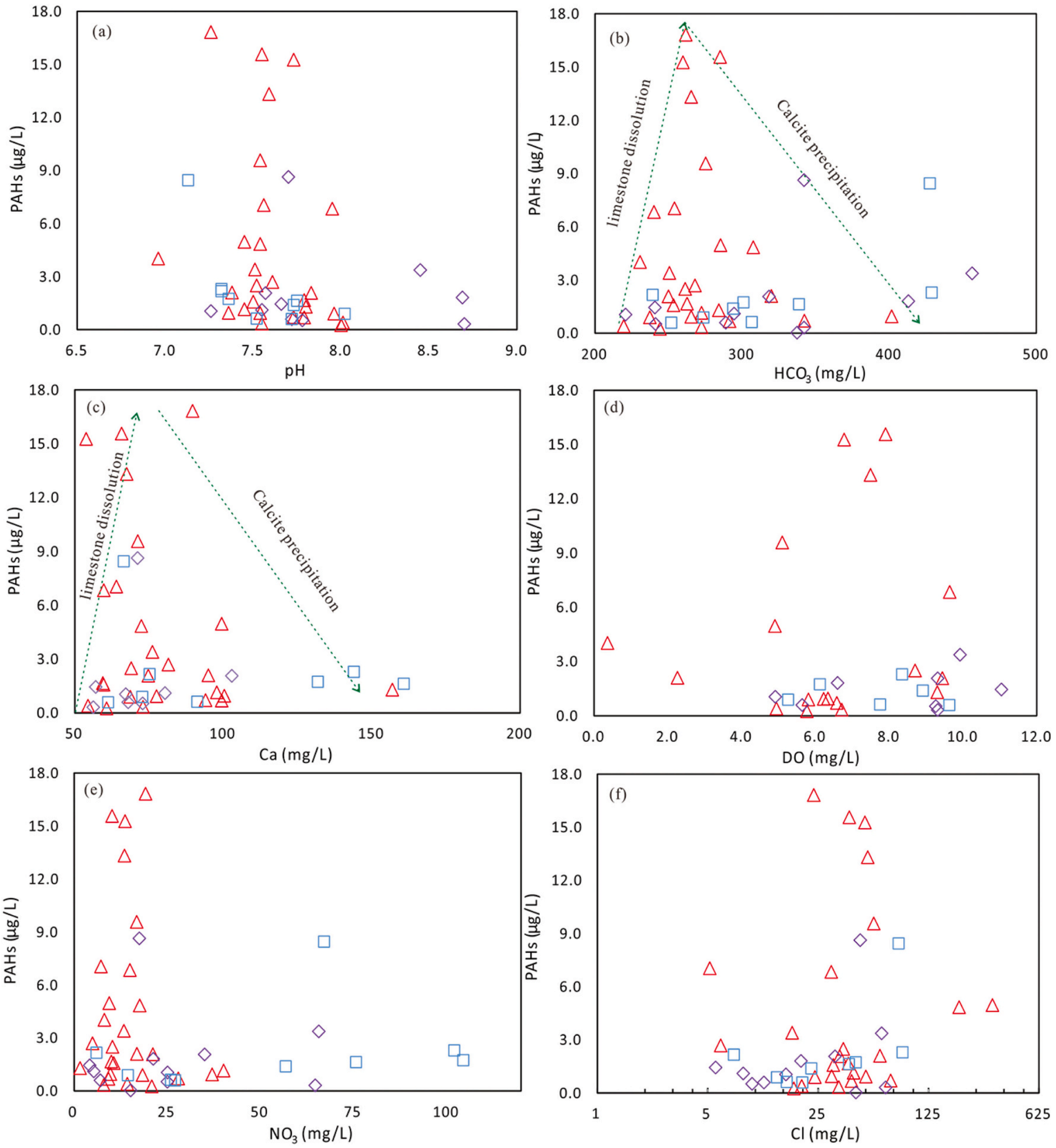

Fig. 6. Scatter plots of PAHs with hydrochemical parameters (△karst water ◇fracture water □pore water).

compounds often have similar thermodynamic distribution coefficients and dynamic mass transfer coefficients, the content ratios of individual PAHs components, like Fla/Pyr (Pyrene) and Benzo[*a*]anthracene (BaA)/Chr, are widely used (Kannan et al., 2005; Jiao et al., 2012). The identification standards of the relationship between the ratios and the sources are given in Fig. 5 (Yunker et al., 2002).

To identify the sources of PAHs in the Liulin karst water system, InP/(InP + BghiP) and BaA/(BaA + Chr) versus Fla/(Fla + Pyr) scatter map were plotted in Fig. 5. The Fla/(Fla + Pyr) ratio of karst water is mostly greater than 0.5 in the study area, indicating that the PAHs is sourcing from the incomplete combustion of fossil fuels. Meanwhile the InP/(InP + BghiP) ratio of karst water is between 0.2 and 0.5, which suggest that karst water may receive PAHs from mixed sources: combustion and petroleum. The ratio of BaA/Chr is generally used as an indicator to judge the atmospheric transportation distance of PAHs: a small BaA/Chr ratio indicates that PAHs are migrated over long distances to contaminated sites (Wang et al., 2012; Wiriya et al., 2013). Conversely, a larger BaA/Chr ratio indicates a greater proportion of PAHs from local sources, as response to the less volatile advantage of BaA. It can be seen from the plot BaA/(BaA + Chr) versus Fla/(Fla + Pyr) that the content of non-volatile BaA in karst groundwater is higher than that of Chr (BaA/(BaA + Chr) > 0.5), illustrating that the PAHs mainly come from the local pollution sources.

4.4. Pollution path identification

4.4.1. Hydrogeochemistry

Scatter diagrams of $\sum$PAHs concentration with pH, DO, HCO$_3^-$, Ca^{2+}, NO$_3^-$, and Cl$^-$ are shown in Fig. 6. Studies have shown that, under neutral conditions, limestone has the largest adsorption capacity for Phe (Shao et al., 2014b), which means a lower PAHs concentration is expectable in karst water with pH of 6.5–7.5. However, karst water with higher $\sum$PAHs concentration has the pH values around 7.5 (Fig. 6a), indicating that pH may not be the most pivotal factors for the distribution of PAHs in karst water.

The relationship between PAHs concentration versus HCO$_3^-$ and Ca^{2+}

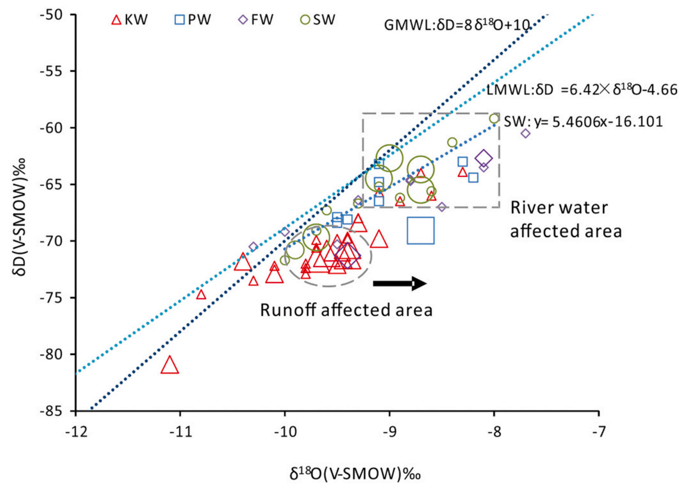

Fig. 7. The δ^{18}O and δD plot with PAHs concentration of water samples in the study area (PAHs concentrations were illustrated by the size of the symbols).

contents (Fig. 6b and c) give us clues that the dissolution/precipitation of carbonate may play an important role in the mobilization of PAHs in karst water. It is noticed that bicarbonate and calcium contents are positively related with the PAHs concentration at lower HCO_3^- and Ca^{2+} values. As we all know that the increased HCO_3^- and Ca^{2+} concentration stands for the strengthening of karstification and dissolution of calcite/dolomite. Batch adsorption experiment conducted by Shao et al. (2014b) show that the dissolution of limestone leads to the elevation of Phe concentration in aqueous solution. It is possible that the dissolution of carbonates causes the reduction of the sorption sites, releasing more PAHs into karst water. The decrease of PAHs concentration with the further increase of HCO_3^- and Ca^{2+} contents may be due to the secondary precipitation of calcite and enhanced adsorption ability.

It is also found that higher PAHs concentration mostly present in karst water samples with higher values of dissolved oxygen (DO) (Fig. 6d). This further confirmed that the PAHs in groundwater mainly come from the input of outdoor environment. Groundwater with higher PAHs concentration normally has a moderate Cl^- concentration (Fig. 6f). Generally, low chloride concentration exist in carbonate aquifers, the elevated Cl^- concentration supports the hypothesis that the PAHs in groundwater is caused by the input of external pollutants.

According to the field investigation, the overall concentration of nitrate in karst water is lower than that of fissure water and Quaternary groundwater. Karst waters, with a higher PAHs concentration, show low to moderate nitrate contents. The lack of nitrate in carbonate aquifers suggests that it is derived from outside. However, karst waters with higher PAHs concentration are not found in the samples with higher nitrate concentration (Fig. 6e). This indicates that agricultural activities (considered as the major pollution sources of nitrate in the area) are not the main factor for the PAHs contamination in karst water. Several Quaternary groundwater are characterized by higher NO_3^- and PAHs concentration, suggesting the possible PAHs pollution of shallow Quaternary groundwater by agricultural activities, such as irrigation or straw combustion, etc.

4.4.2. Environmental stable isotopes

1) δD and δ^{18}O

Stable isotopes (oxygen and hydrogen) have been widely applied as a natural tracer for providing valuable information on sources, pathways and water exchange in groundwater systems (Clark and Fritz, 1997; Gao et al., 2010; Binder et al., 2019). The relationship between δ^{18}O and δD in the Liulin karst system was illustrated in Fig. 7, along with the global meteoric water line (GMWL: $\delta D = 8\delta^{18}O + 10$, Craig, 1961) and the local meteoric water line (LMWL: $\delta D = 6.42\delta^{18}O - 4.66$, Deng et al., 2012). The PAHs concentrations of karst water, pore water, fracture water and surface water were illustrated by the size of the symbols.

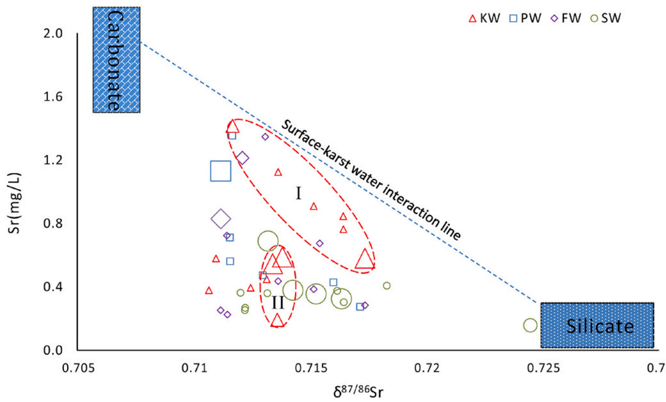

Fig. 8. The ^{87}Sr/^{86}Sr and Sr concentration plot with PAHs concentration of water samples in the study area (PAHs concentrations were illustrated by the size of the symbols).

The δ^{18}O and δD of surface and groundwater in the Liulin karst water system mostly fall on or close to the local atmospheric precipitation line, indicating that the groundwater and surface water in the study area are mainly supplied by precipitation. Part of the surface and groundwater are affected by evaporation, shifting to the right of the precipitation line. The surface water with high PAHs content lie near to the evaporation line, reflecting the local pollution sources. It is also suggested that the leakage of surface water to karst water occurs in the area, as basing on the δ^{18}O and δD scatter map. Several karst water samples fall into the group of surface water samples, suggesting that the leakage of surface water to karst water occurs in the area. However river water leakage does not significantly lead to the elevation of PAHs concentration in karst water, based on the low PAHs contents in these samples. Lower PAHs contents were also observed in karst water samples located near the rainfall line, indicating the direct input of PAHs by rain infiltration into karst aquifers is limited. It is interesting to note that karst waters with higher PAHs contents are mainly positioned below the surface water evaporation line and keep a distance from the precipitation line. The most possible explanation for this deviation is that these karst waters are recharged by the runoff water formed during the rain events. Under the effect of surface runoff, large areas of bared karst stratum in Liulin provide convenience for bulk atmospheric PAHs entering into karst system through fissures and/or fractures. On the other hand, under the interaction of bared karst rocks with air and water, significant oxygen isotopic exchange will take place between runoff water and the strata, resulting in the enrichment of ^{18}O in the recharged water. Hence the δ^{18}O and δD values for these high PAHs karst groundwater slightly shift from meteoric water line, without an intense evaporation process.

2) ^{87}Sr/^{86}Sr

The ^{87}Sr/^{86}Sr value in groundwater mainly depends on the composition of Sr isotopes of the aquifers, due to that the fractionation of Strontium (Sr) isotope is not significant in low-temperature geochemical process of groundwater (Wang et al., 2006; Frost et al., 2015). Thus, Sr isotope is widely used in understanding the water-rock interaction processes and tracing karst water recharge sources. In this study, variations of Sr and PAHs concentrations with ^{87}Sr/^{86}Sr were discussed to further determine the pollution path of PAHs in Liulin karst water system.

Surface waters mostly have higher ^{87}Sr/^{86}Sr values of 0.712–0.725 and lower to moderate high Sr contents (0.156 mg/L-0.688 mg/L) in the study area (Fig. 8). Most of the karst waters have a lower to moderate

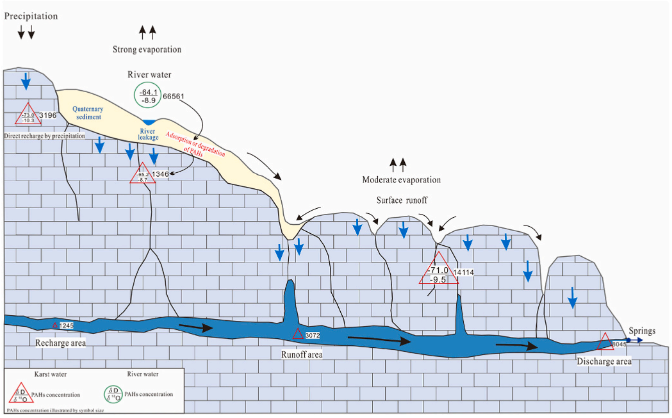

Fig. 9. Conceptual model diagram showing the pollution paths of PAHs in karst water.

high $^{87}Sr/^{86}Sr$ values, with relatively higher Sr contents than surface waters. Previous studies have shown that the average $^{87}Sr/^{86}Sr$ value of land-based silicate is 0.720 (Goldstein and Jacobsen, 1988), while the value of $^{87}Sr/^{86}Sr$ of limestone and dolomite is about 0.707 and 0.711 respectively (Laffoon et al., 2012; Gaillardet et al., 2014). According to the $^{87}Sr/^{86}Sr$ and Sr concentration scatter map (Fig. 8), the karst waters in the study area can be divided into two subgroups. In group I, karst waters are located near the karst water-surface water mixing line, illustrated the potential effect of river water leakage. In this group, most of the karst waters show low PAHs contents, suggesting that river water leakage is not the main pathway for karst water PAHs pollution. Karst waters in group II, normally stay away from the karst water-surface water mixing line with moderate high $^{87}Sr/^{86}Sr$ ratios (ca. 0.7135) and high PAHs concentration. This is consistent with the hypothesis above that under the influence of surface runoff, a large amount of atmospheric sourced PAHs (by dry and wet deposition) may enter the aquifers through the karst fissures.

In brief, based on the hydrogeochemistry and stable isotopes investigation, it is demonstrated that surface runoff infiltration is the main pathway of PAHs pollution in karst water in the study area (Fig. 9). River water leakage may partly contribute to the PAHs contamination in some karst and pore waters.

5. Conclusions

This research investigated the concentration, distribution, sources and pollution paths of PAHs in karst water in Liulin karst water system, northern China. It is generally assumed that the deterioration of karst groundwater quality in northern China is mainly caused by the river leakage recharging. Through our research, we found that although the organic contamination in groundwater, specifically for PAHs pollution, will certainly be affected by surface water leakage, but it's not the main pollution path. In this study, hydrochemistry, environmental isotopes (δD, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) and characteristic ratios were employed together to identify the pollution paths of PAHs in karst water. The main conclusions are:

1) The total concentration of PAHs ranged from 39.25 ng/L to 16,830 ng/L in groundwater with Nap as the predominant component, and the value increased gradually along the flow path on the whole. The highest PAHs concentrations in karst water were mainly observed in the coal mining areas and the discharge areas.
2) The PAHs mainly coming from the locally incomplete combustion of wood, fossil fuels and coal based on the Fla/(Fla + Pyr), InP/(InP + BghiP) and BaA/Chr ratios. The hydrochemistry, δD and $\delta^{18}O$ isotopes and $^{87}Sr/^{86}Sr$ value suggested that the PAHs in karst water mainly come from the infiltration of runoff water in the bared karst areas, small partials from the river water leakage.

To our knowledge, our work is the first effort to using hydrochemistry-stable isotopes (δD, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) to analyze the PAHs' behavior in karst water. It provides a new technical method to trace the sources and identify the pollution paths of organic contamination in a karst water system. In addition, it is necessary to further strengthen the monitoring and investigation in karst area, for better understanding the characteristics of organic pollution and the pollution migration mechanism.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2021.103810.

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