

## Research papers

# Speciation, distribution and migration pathways of polycyclic aromatic hydrocarbons in a typical underground river system in Southwest China

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## ABSTRACT

Water, colloid, and suspended particulate matter (SPM) samples were collected during one given year at two sites from the Laolongdong (LLD) underground river in Southwest China and analyzed for 16 priority polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon (DOC), and particulate organic carbon (POC). The concentrations of the SPM-associated, colloid-associated, freely dissolved, and dissolved organic matter (DOM)-associated PAHs varied from 202 to 1731 ng/L, 142 to 956 ng/L, 228 to 1280 ng/L, and 7.3 to 173 ng/L, respectively. The mean percentages of 4- and 5–6 ring PAHs showed increasing trends along the order of the dissolved phase, colloidal phase and particulate phase. The behavior and fate of PAHs influence by DOC and POC were examined. Overall, organic carbon was the primary factor controlling the environmental behaviors and fates of the 16 PAH species in the LLD underground river. POC in underground river has more lipophilicity to PAHs in this study. The correlation analysis suggested that the migration pathways of PAHs from the surface soil to the underground river through the sinkholes and soil seepage water both had important contribution during the rainy season. However, PAHs mainly transferred through soil seepage water in the form of dissolved PAHs during the dry season.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in various environmental systems and have been considered a group of persistent organic priority pollutants by the United States Environmental Protection Agency (US EPA) because of their carcinogenic, mutagenic and toxic characters (Ball and Truskevycz, 2013; Bolden et al., 2017; Gao et al., 2018). The fate and transport of PAHs in the environment depends on their physico-chemical phase distribution. It is well known that PAHs are hydrophobic and considerably insoluble; these species prefer to associate with colloids, dissolved organic matter (DOM), or suspended particulate matter (SPM) in water, and they finally deposit in sediments. In fact, PAHs in water exist as dissolved PAHs, colloid-associated PAHs and SPM-associated PAHs (Xia et al., 2013), and the dissolved PAHs in aqueous environments include freely dissolved PAHs and DOM-associated PAHs (Shi et al., 2007; Moeckel et al., 2014). The speciation and distribution of PAHs in aquatic systems is primarily controlled

by the physico-chemical properties of individual species, such as vapor pressure, solubility, and sorption coefficient, as well as the characteristics of each phase (Shi et al., 2007). The sorption of PAHs to SPM, colloids, or DOM markedly impact the transport, fate, and ecological effects of PAHs. Many studies have indicated that the bioavailability and toxicity of PAHs are related to the speciation of PAHs (Dong, et al., 2013; Xia et al., 2013). The SPM can remove hydrophobic organic contaminants from solution and decrease the bioavailability and toxicity to aquatic organisms (Dong, et al., 2013). Due to the high organic carbon content and surface area (Majumder et al., 2014), colloids have played an important role in the distribution, fate, and behavior of these hydrophobic organic contaminants in aquatic environments (Yan et al., 2015; Sun and Zhou, 2015). Because of the high affinity of colloids toward PAHs, some studies have demonstrated that colloid-associated PAHs are not bioavailable (Gustafsson and Gschwend, 1997; Xia et al., 2013). DOM can interact with PAHs through hydrophobic binding, and form humic-solute complexes in an aqueous environment (Sabbah et al.,

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2004). Thus, PAHs tightly bound to DOM may have reduced bioavailability because their uptake by organisms is prevented (Cornelissen et al., 2009). Freely dissolved PAH concentrations represent an important aspect of bioavailability and risk assessment for PAHs in aquatic environments. Many studies have demonstrated that the bioavailability and toxicity of PAHs are directly proportional to freely dissolved PAH concentrations (Bao and Zeng, 2011; Xia et al., 2013). Thus, measuring the total concentration of PAHs present in natural waters means overestimating the ecological risk, as only the bioavailable fractions can cause toxic effects. Therefore, it is necessary to accurately measure the speciation and distribution of PAHs in natural waters to quantify contaminant transport and evaluate their chemical behavior in aquatic systems. Middelboe and Sondergaard (1995) suggested that organic matter in water could be classified as DOM ( $<0.22 \mu\text{m}$ ), colloidal organic matter ( $<0.7 \mu\text{m}$ , and  $>0.22 \mu\text{m}$ ), and particulate organic matter (POM) ( $>0.7 \mu\text{m}$ ). Therefore, according to the study of Middelboe and Sondergaard (1995), PAHs in water in this study can be classified as dissolved PAHs ( $<0.22 \mu\text{m}$ ), colloid-associated PAHs ( $<0.7 \mu\text{m}$ , and  $>0.22 \mu\text{m}$ ) and SPM-associated PAHs ( $>0.7 \mu\text{m}$ ).

Karst terrains cover over 30% of Chinese land mass (Yuan et al., 1994). These terrains are known for the thin soil cover that overlies soluble carbonate possessing enormous interconnected fissures, which means poor pre-purification, poor filtration, and rapid infiltration (Yuan, 2000). Thus, contaminants can directly infiltrate underground water through sinkholes, fissures, or other karst features (Schwarz et al., 2011; Lan et al., 2018). Hence, groundwater in karst terrains is particularly vulnerable to contamination. Schwarz et al. (2011) suggested that PAHs were effectively retained in soils even in highly vulnerable karst terrains. Nevertheless, during early spring, e.g., snowmelt, particle facilitated transport leads to elevated PAH concentration in groundwater that is above the safe drinking water limits. Therefore, SPM-associated PAHs can be mobilized from the surface water and soil to karst underground river through sinkholes (Lan et al., 2018).

Groundwater in karst terrains is an important resource, and approximately 25% of the world's population use it for a domestic water supply (Ford and Williams, 2007). There are approximately 2836 underground streams and rivers in the karst terrains in Southern China, and the total length is approximately 13919 km. The multiannual mean discharge of these underground rivers is approximately  $1482 \text{ m}^3/\text{s}$ , and they provide approximately  $1808 \times 10^8 \text{ m}^3/\text{a}$  of water (Yang, 1985). The contamination of PAHs in groundwater has drawn much attention around the world (Schwarz et al., 2011; Lan et al., 2018; Sun et al., 2019). However, a clearer understanding of the current trajectories and future threats of PAHs to groundwater quality can only be achievable through the introduction of the low-scale monitoring of representative karst underground river systems. Therefore, this study chooses the Laolongdong (LLD) karst underground river in Chongqing, Southwest China as our study area. The LLD karst underground river catchment is typical of many karst terrains. Moreover, the LLD underground river is an origin point for water sources used for agriculture, drinking water, and recreational activities. Our previous studies quantitatively provided the sources, levels, and transport of PAHs during rainfall in the LLD underground river system (Lan et al., 2016, 2018). In karst underground rivers, suspended organic and inorganic particles are ubiquitous and are important vectors for the transport and distribution of contaminants (Schwarz et al., 2011; Lan et al., 2018). The speciation and distribution of PAHs in groundwater is of great importance for risk assessment and contaminant remediation, but to date, little is known about the speciation and distribution of PAHs and the transport of different PAHs fractions in underground river. Therefore, it is essential to quantify the concentrations of different PAHs fractions, determine their distribution among water components (freely dissolved, DOM-associated, colloid-associated and SPM-associated), and to understand their behavior of PAHs in underground river systems. The objectives of the present study were as follows: (1) Variation and composition of different PAHs fractions (freely dissolved PAHs, DOM-associated PAHs, colloid-associated

PAHs and SPM-associated PAHs) in the LLD underground river; (2) Partitioning of the PAHs between SPM and water; (3) Transfer of different PAHs fractions in the LLD underground river system; (4) Establish a conceptual model for the transport of different PAHs fractions in the LLD underground river system.

## 2. Materials and methods

### 2.1. Sample sites and collection

The outlet of the LLD underground river is a tourist location including a cave that occurs at an elevation of 379 m and is about 1700 m in length. Water samples were collected from Sidengzi (SDZ) and Dixiahe (DXH) (Fig. 1). DXH is located at the entrance of the cave, and SDZ is located at the cave end. Individuals can row from DXH to SDZ through the underground river. The study area was reported in detail in our previous paper (Lan et al., 2018). Samples were collected monthly from May 2015 to April 2016. All wetted surfaces were of glass or stainless steel to avoid contamination. SPM samples were isolated by filtration through pre-combusted glass fiber filters (GF/F Whatman,  $0.7 \mu\text{m}$ ). Colloid samples were collected from fine-grained particles ( $>0.22 \mu\text{m}$  and  $<0.7 \mu\text{m}$ ) with a polytetrafluoroethylene (PTFE) filter membrane. Each filter was wrapped in aluminum foil and stored at approximately  $-26 \text{ }^\circ\text{C}$  until further analysis in the laboratory. The dissolved phase, operationally defined as the fraction that passes through the filters ( $0.22 \mu\text{m}$ ), was stored in pre-cleaned 1.25 L brown glass containers with airtight caps. The samples were stored at  $4 \text{ }^\circ\text{C}$ , and analyzed within three days.

### 2.2. Sample preparation and PAH analysis

Sample extraction and instrument analysis were reported in detail in our previous paper (Sun et al., 2019) and will be briefly described here. After freeze drying, the SPM and colloid samples were extracted by accelerated solvent extraction (ASE350, Thermo Scientific), cleaned via aluminum oxides and silica gel column chromatography, and analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A GC, 5975C MSD) in selected ion monitoring (SIM) modes with internal PAH standards. Filtered water samples were extracted by an automatic solid-phase extraction system (SPE-DEX 4790, Horizon Technology), and then analyzed by GC-MS in SIM modes with internal standards. The 16 priority PAHs that were monitored in this study were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), chrysene (Chry), benzo(a)anthracene (BaA), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DaA), and indeno(1,2,3-cd)pyrene (InP). The 16 PAH mixed stock standard was purchased from Dr. Ehrenstorfer GmbH Inc., Germany. The surrogate standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12), and internal standard (hexamethylbenzene) were purchased from the Supelco, USA.

### 2.3. Quality control and quality assurance

Method blanks (solvent) and spiked blanks (standards spiked into the solvent) were analyzed, and no interference was observed in these blanks. The instrument was calibrated every day with calibration standards, and the relative percent differences between the six-point calibration and the daily calibrations were less than 20% for all target analytes. The limit of detection of 16 individual PAHs and the mean recoveries of surrogate standards were showed in Tables S1 and S2, respectively. All results were recovery-corrected.

### 2.4. DOC and POC analysis

DOC and POC in the LLD underground river were measured by a total

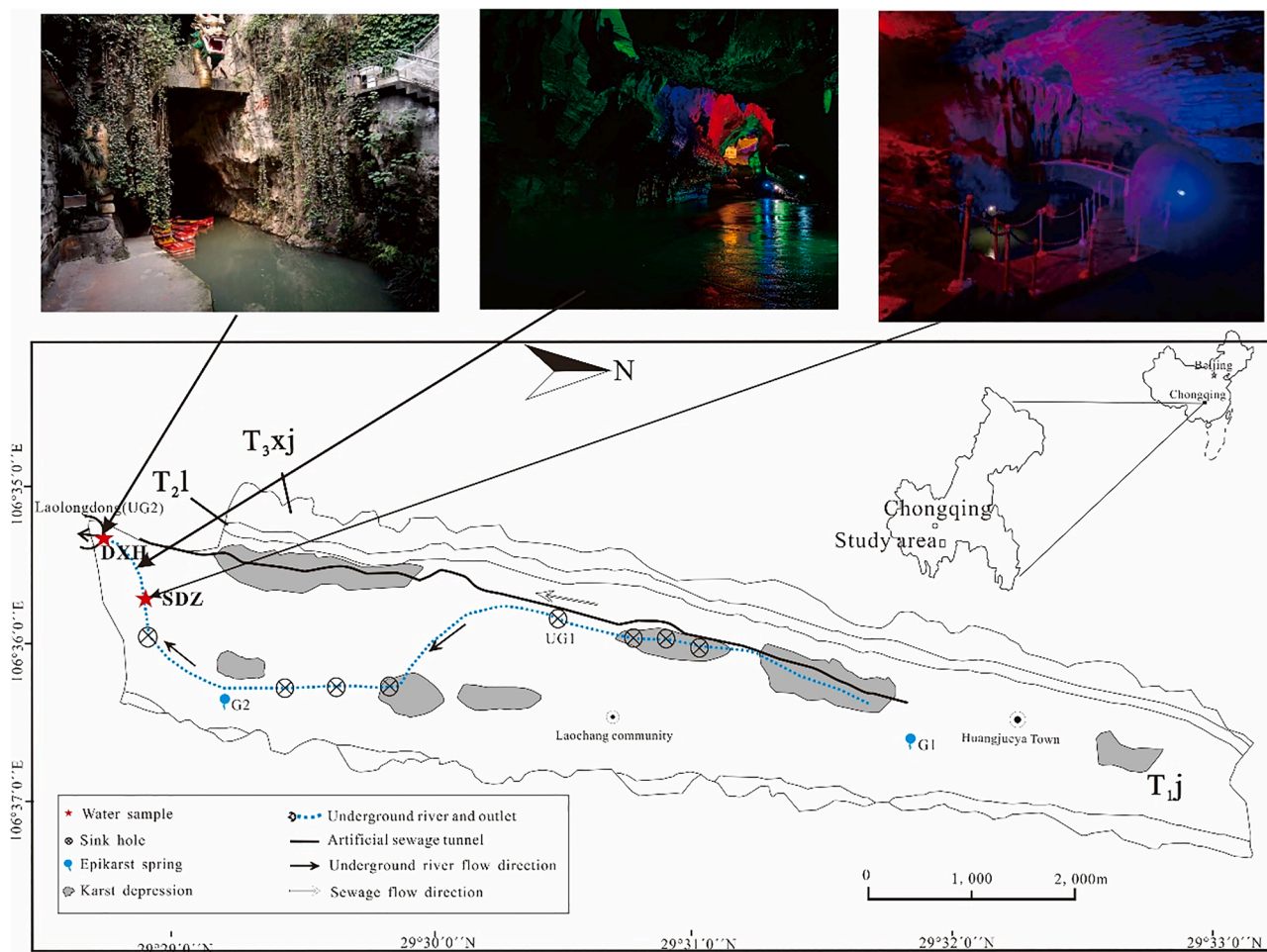


Fig. 1. The study area and sampling locations in LLD underground river.

organic carbon (TOC) analyzer (JENA 3100 TOC meter). The DOC and POC were determined in triplicate with a relative standard deviation less than 1%.

### 2.5. Estimation of freely dissolved PAHs and DOM-associated PAH content

Due to the high affinity of the PAHs to DOM, the freely dissolved PAH concentrations depend not only on the water flux but also on the partitioning between the DOM and aqueous phase (Xia et al., 2013; Moeckel et al., 2014). Therefore, it is difficult to measure the freely dissolved PAH concentration with traditional methods that require complicated phase separations. Some new techniques (e.g., fluorescence quenching, purging or sparging techniques, solid-phase microextraction (SPME), equilibrium dialysis, solubility enhancement, ultrafiltration, reverse-phase HPLC separation, size exclusion chromatography, and liquid-liquid extraction) have been used to determine the freely dissolved concentrations of chemicals in solutions containing DOC (Gustafson and Dickhut, 1997; Cornelissen et al., 2009; Bao et al., 2012; Xia et al., 2013). However, all of these methods for measuring freely dissolved PAHs in water have some type of limitation (Bao et al., 2012; Xia et al., 2013). According to the studies of Shi et al. (2007) and Moeckel et al. (2014), the freely dissolved PAH concentrations can be estimated if there is the proper knowledge of the  $K_{DOC}$  partition coefficients.

In this study, only the total dissolved PAH concentrations and DOC concentrations were measured, and the freely dissolved PAH concentrations can be calculated based on the measured DOC concentrations and the partition coefficient ( $K_{DOC}$ ), which was calculated as follows:

$$K_{DOC} = \frac{10^6 \times (C_{total} - C_{free})}{C_{DOC} \times C_{free}}$$

where  $C_{total}$  is the concentration of total dissolved PAHs (ng/L),  $C_{free}$  is the concentration of freely dissolved PAHs (ng/L), and  $C_{DOC}$  is the DOC concentration (mg/L).  $K_{DOC}$  values were taken from the literature (Li and Lee, 2000; Burkhard, 2000), and could be affected by various factors, such as sorbent characteristics or ionic strength (Shi et al., 2007). Thus, the calculated freely dissolved PAH content was only a rough approximation. The concentrations of DOM-associated PAHs were equal to the total dissolved PAH concentrations minus the free-dissolved PAH concentrations.

## 3. Results and discussion

### 3.1. Variation of different PAHs fractions in the LLD underground river

All PAHs were detected except Ant and DaA in the particulate phase at SDZ and DXH. All PAHs were detected except Ant, BaA, InP and DaA in the colloidal phase at DXH and SDZ. In contrast, Ant, BaA, Chry, BaP, DaA and BgP were not detected in the total dissolved PAHs at SDZ and DXH (Table S3). The dominant compounds in the total dissolved and colloid-associated PAH profiles at SDZ and DXH were Phe, followed by Nap and Flu. Phe, Flu, and Nap contributed to 34.5%–100% of the total dissolved PAHs, 50.4%–90.8% of the colloidal PAHs at DXH, and contributed to 13.8%–61.2% of the total dissolved PAHs, 38.6%–81.4% of the colloidal PAHs at SDZ. However, in the particulate phase, the

dominant compounds at SDZ and DXH were Phe, followed by Nap, BbF, Flu and Fla. Phe, Nap, BbF, Flu and Fla contributed 35.3%–93.8% in particulate PAHs at DXH, and 26%–93.3% at SDZ (Table S3).

The PAH distributions in particulate, dissolved and colloidal phases in the LLD underground river are shown in Fig. 2. A fairly high variation in values ranging between 211 and 1730 ng/L was observed for SPM-associated PAHs at DXH, and the mean value was 538 ng/L. The highest concentration was observed in February 2016. Colloid-associated PAHs at DXH varied from 157 to 956 ng/L with a mean value of 332

ng/L. The highest concentration was observed in May 2015. The total dissolved PAHs at DXH spanned a range from 234 to 1397 ng/L with a mean value of 513 ng/L. The highest concentration was observed in April 2016. SPM associated PAHs at SDZ varied from 202 to 827 ng/L with a mean value of 489 ng/L. Colloidal PAHs at SDZ varied from 142 to 930 ng/L with a mean value of 255 ng/L. The concentrations of the total dissolved PAHs at SDZ varied from 292 to 1269 ng/L with a mean value of 526 ng/L (Fig. 2 and Table S3). The highest concentrations of SPM-associated, colloid-associated and total dissolved PAHs at SDZ were

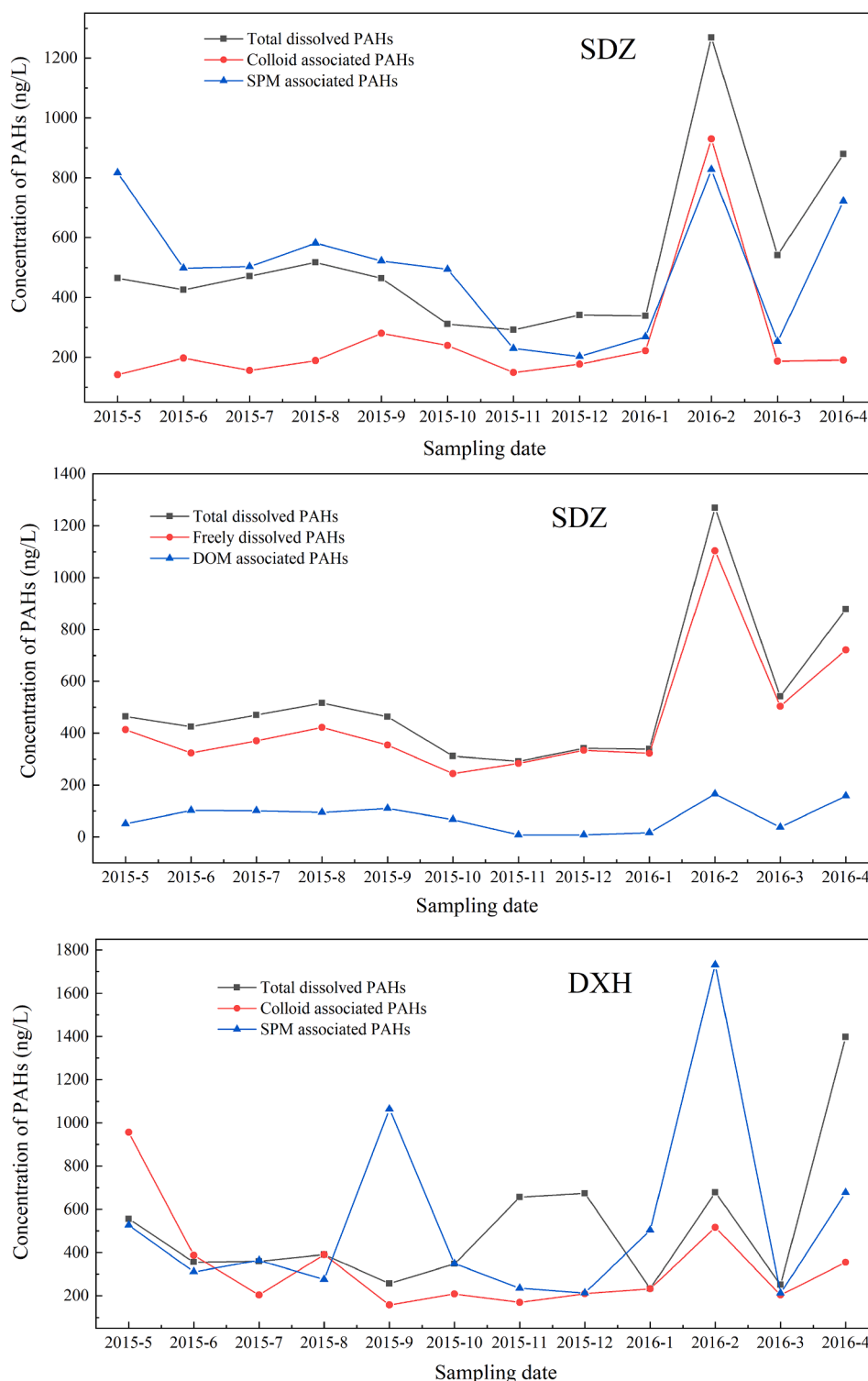


Fig. 2. Distribution of PAHs in the dissolved, colloidal, and particle phase in LLD underground river.

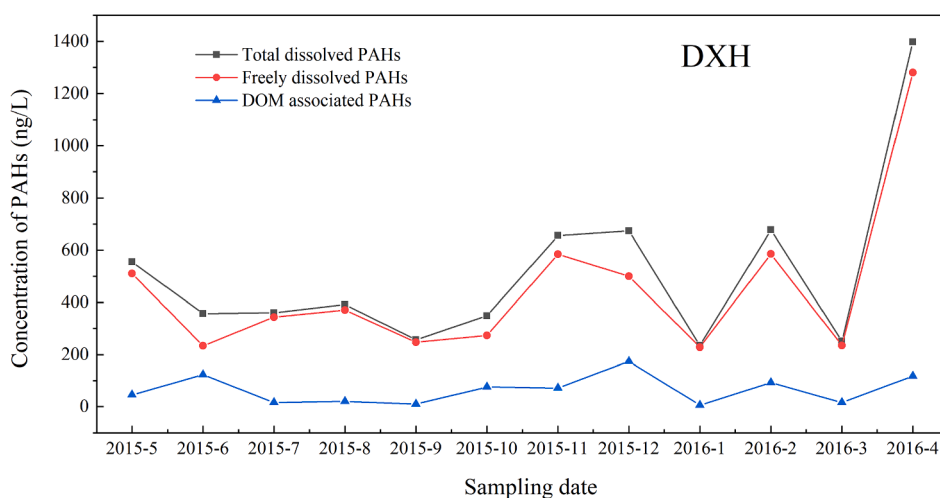


Fig. 2. (continued).

all observed in February 2016. The most pronounced events were connected to snowmelts in February 2016. The concentration of the SPM-associated PAHs at DXH was higher than that at SDZ. At SDZ, the mean concentration of the total dissolved PAHs was the highest, followed by SPM-associated and colloid-associated PAHs, while at DXH, the mean concentration of SPM-associated PAHs was the highest, followed by total dissolved PAHs and colloid-associated PAHs.

The concentrations of different PAHs fractions at SDZ and DXH exhibited different seasonal variations (Fig. 2). At SDZ, the concentrations of the total dissolved PAHs, colloid-associated PAHs and SPM-associated PAHs fluctuated greatly during the dry season from November 2015 to April 2016, and were relatively stable during the rainy season from May 2015 to October 2015. At SDZ, the mean concentration of the SPM-associated PAHs was the highest, followed by the total dissolved PAHs and colloid-associated PAHs during the rainy season. However, the mean concentration of the total dissolved PAHs was the highest, followed by the SPM-associated PAHs and colloid-associated PAHs (except February 2016) during the dry season. The above results indicated that PAHs in water at SDZ were dominated by the SPM-associated PAHs during the rainy season and dominated by the total dissolved PAHs during the dry season.

At DXH, the concentrations of the total dissolved PAHs were relatively stable during the rainy season, but fluctuated greatly during the dry season, similar to that at SDZ. The concentrations of the SPM-associated PAHs fluctuated greatly during a given year from May 2015 to April 2016. The concentrations of the colloid-associated PAHs remained relatively stable during a given year. At SDZ, the mean concentrations of the total dissolved PAHs and colloid-associated PAHs during the dry season (610 and 309 ng/L, respectively) were higher than those during the rainy season (442 and 201 ng/L, respectively). However, the mean concentration of the SPM-associated PAHs during the dry season (417 ng/L) was lower than the rainy season (562 ng/L). At DXH, the mean concentrations of the total dissolved PAHs and the SPM-associated PAHs during the dry season (648 and 595 ng/L, respectively) were higher than those during the rainy season (378 and 482 ng/L, respectively). However, the mean concentration of the colloid-associated PAHs during the dry season (281 ng/L) was lower than the rainy season (384 ng/L).

The distribution of the freely dissolved, DOM-associated, and total dissolved PAHs in the LLD underground river is shown in Fig. 2. Because the concentrations of freely dissolved PAHs and DOM-associated PAHs were calculated according to the total dissolved PAHs, the detection frequency of the freely dissolved PAHs and DOM-associated PAHs was the same as the total dissolved PAHs. At SDZ, the concentrations of the freely dissolved PAHs ranged from 244 to 1104 ng/L with a mean value

of 450 ng/L; the DOM-associated PAHs concentrations ranged from 7.34 to 165 ng/L with a mean value 76.5 ng/L. At DXH, the freely dissolved PAHs concentrations ranged from 228 to 1280 ng/L with a mean value of 449 ng/L; DOM-associated PAHs concentrations ranged from 5.91 to 173 ng/L with a mean value of 63.8 ng/L (Fig. 2 and Table S4). The concentrations of freely dissolved PAHs and DOM-associated PAHs at SDZ were close to those at DXH. Phe was the most dominant component in the freely dissolved phase at SDZ and DXH, accounting for approximately 30.3% and 32.5% of the freely dissolved PAH concentration on average, respectively, and Nap, Ace, and Flu were the next dominant PAHs in the freely dissolved PAHs at SDZ, accounting for about 20%, 14.3%, 13.1% of the freely dissolved PAH concentration on average, respectively. Nap, Flu, Fla were the next dominant PAHs in the freely dissolved PAHs at DXH, accounting for about 29%, 14.1%, 7.3% of the freely dissolved PAH concentration on average, respectively. However, BbF, BkF and InP dominated the DOM-associated PAHs at SDZ and DXH, accounting for about 56.1% and 56.3% of the DOM-associated PAH concentration on average, respectively.

As shown in Fig. 2, the concentrations of the DOM-associated PAHs at SDZ and DXH remained relatively stable during the given year from May 2015 to April 2016. At SDZ and DXH, the variation of freely dissolved PAH concentrations was similar to that of the total dissolved PAH concentrations. Freely dissolved PAH concentrations also remained relatively stable during the rainy season, and fluctuated greatly during the dry season. At SDZ, the concentrations of the total dissolved PAH were markedly higher than those of the freely dissolved PAHs during the rainy season. However, the freely dissolved PAH concentrations were close to the total dissolved PAH concentrations during the dry season. At DXH, the concentrations of the freely dissolved PAHs were close to those of the total dissolved PAHs during the given year. The concentrations of PAHs at SDZ and DXH exhibited an increasing tendency from January in agreement with the heaviest snowfall events, reaching the highest values in February. The snowfall in January 15, 2016 was the strongest over the past several decades in Chongqing, which could scavenge abundant PAHs from the atmosphere (Zhang et al., 2015). Therefore, snowmelt could mobilize PAHs to a maximum extent in February 2016 (Fig. 2).

### 3.2. Composition of the different PAHs fractions in the LLD underground river

The composition of dissolved, colloid-associated and SPM-associated PAHs by ring number in the outlet of the LLD underground river are shown in Fig. 3. The distribution pattern in the SPM-associated, colloid-associated and total dissolved PAHs at SDZ and DXH was kept with time

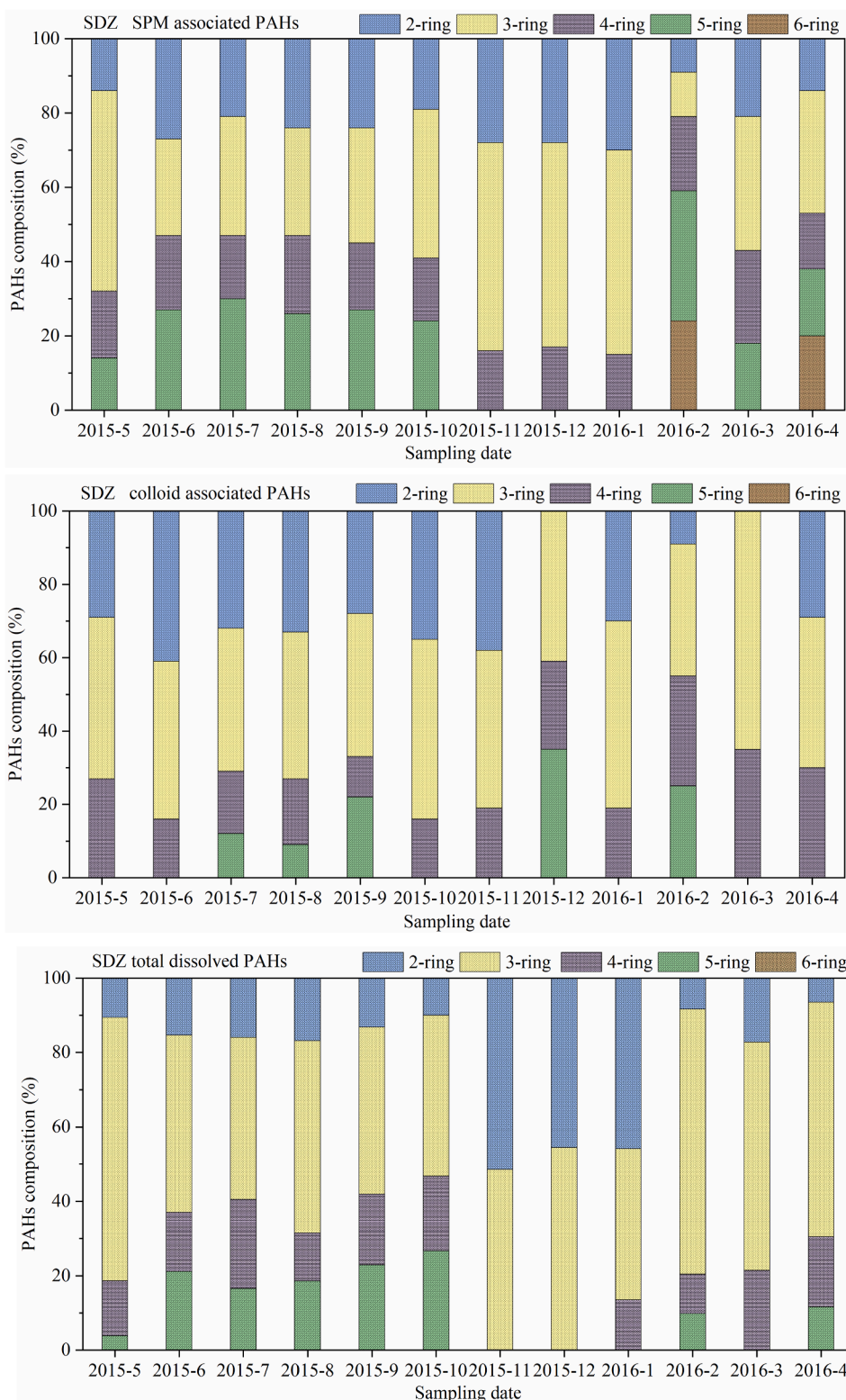


Fig. 3. Contribution of two- to six-ring PAHs to the sum of freely dissolved, DOM associated, colloid associated, and SPM associated PAHs in LLD underground river.

through the observed periods with a predominance of 3-ring PAHs, followed by 2-ring, 4-ring, 5-ring, and 6-ring PAHs. The contribution to PAHs fractions of 3-ring PAHs ranged from 38.3% to 53.4% with a mean value of 45.3% at SDZ, and ranged from 44.3% to 50.7% with a mean value of 47.4% at DXH. The contribution of 3-ring PAHs in the total dissolved phase (53.4% and 50.7% at SDZ and DXH, respectively) was

the highest, followed by the colloidal phase (44.2% and 47.2% at SDZ and DXH, respectively), and the particulate phase (38.2% and 44.3% at SDZ and DXH, respectively). Overall, the more water-soluble 2- and 3-ring PAHs dominate over the virtually water-insoluble and strongly hydrophobic 4 and 5–6 rings in the dissolved, colloidal, and particulate phases. However, the mean percentages of 4 and 5–6 rings PAHs showed

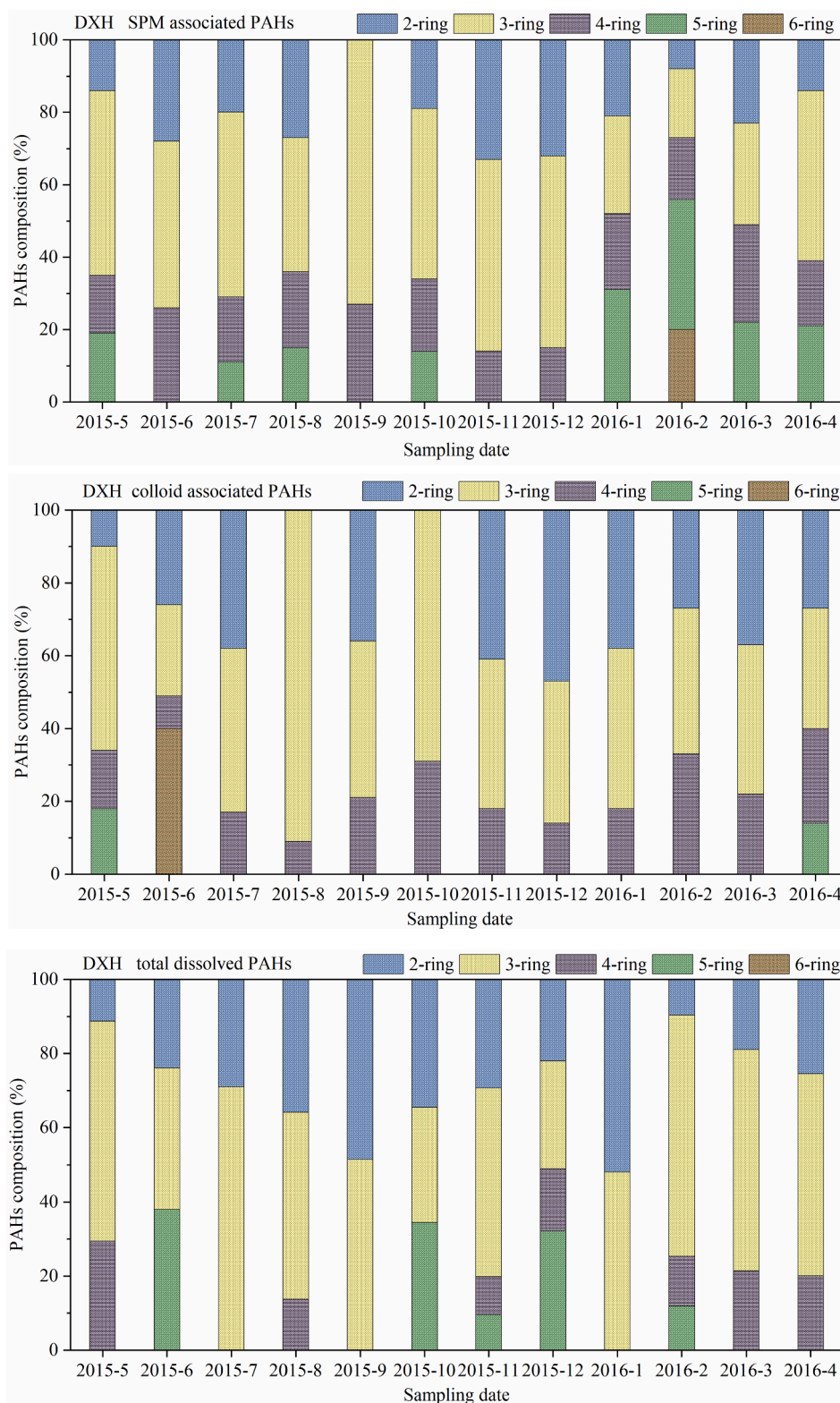


Fig. 3. (continued).

an increasing trend along the order of the dissolved phase, colloidal phase and particulate phase at SDZ (25.2%, 30.4% and 40.2%, respectively) and DXH (20.9%, 25.5% and 35.8%, respectively), while 2–3 ring PAHs showed an opposite trend (Fig. 3). These observations indicated that 2–3 ring PAHs were transported chiefly via the dissolved phase, followed by the colloidal phase and particulate phase. However, 4 and 5–6 rings PAHs were transported mainly through particulate phase,

followed by the colloidal phase and dissolved phase. The results indicate that highly hydrophobic substances strongly bind to the aquatic particulate phase, and these substances are likely to have leached from the soil into the groundwater in the first place.

The composition of freely dissolved PAHs and DOM-associated PAHs are shown in Fig. S1. The distribution pattern of the freely dissolved PAHs at SDZ and DXH was kept with time through the observed periods

with a predominance of the 3-ring PAHs, followed by the 2-ring PAHs, 4-ring PAHs and 5-ring PAHs. The distribution pattern in the DOM-associated PAHs at DXH was also kept with a predominance of 3-ring PAHs, but followed by the 5-ring, 4-ring, and 2-ring PAHs. However, the distribution pattern in the DOM-associated PAHs at SDZ was kept with a predominance of the 5-ring PAHs, followed by the 3-ring, 4-ring, and 2-ring PAHs. The contribution of the 2- and 3-ring PAHs to the freely dissolved PAHs ranged from 65.4% to 100% with a mean value of 82.6% at SDZ, and from 66.9% to 100% with a mean value of 86.1% at DXH. However, the contribution of the 4- and 5-ring PAHs to the DOM-associated PAHs ranged from 0 to 91.1% with a mean value of 62.1% at SDZ, and from 0 to 94.8% with a mean value of 54.2% at DXH. Based on the above results, the DOM associated phase contained relatively more abundant 4- and 5-ring PAHs than the freely dissolved phase. These results showed that the 4- and 5-ring PAHs seemed to have higher affinity to DOM than the 2- and 3-ring PAHs, and prefer to bind to the DOM owing to their lower aqueous solubility and hydrophobic nature; however, the 2- and 3-ring PAHs were more likely to dissolve in water due to their higher water solubility (Kang et al., 2016).

### 3.3. Contribution of the different PAHs fractions to PAHs in water

The contribution of the different PAHs fractions to the total PAHs in water at SDZ was relatively constant during the given year (Fig. 4). The freely dissolved, DOM-associated, colloid-associated and SPM-

associated PAHs exhibited similar seasonal trends at SDZ. However, there was a large variation in the contribution of the different PAHs fractions to the total PAHs in water at DXH during the given year. The PAHs in water were dominated by the SPM-associated PAHs during the given year, accounting for  $39 \pm 9.6\%$  and  $37 \pm 16.2\%$  at SDZ and DXH, respectively, followed by freely dissolved PAHs accounting for  $35.9 \pm 8.3\%$  and  $33.2 \pm 12.7\%$ , colloid associated PAHs accounting for  $19.6 \pm 6.5\%$  and  $24.8 \pm 10.9\%$ , and DOM associated PAHs accounting for  $5.5 \pm 3.1\%$  and  $5 \pm 4.8\%$ , respectively. Although the contribution of the DOM-associated PAHs was the lowest, it is clear from Fig. S1 that PAHs with five or more rings are relatively more abundant in the DOM-associated fraction, which imply a significant role of DOM in their transport. Overall, the freely dissolved PAHs had a higher contribution ( $42.6 \pm 3.5\%$  and  $38.7 \pm 7.8\%$  at SDZ and DXH, respectively) than the SPM-associated PAHs during the dry season ( $31.3 \pm 5.4\%$  and  $35.4 \pm 16.4\%$  at SDZ and DXH, respectively), while the SPM-associated PAHs had a higher contribution during the rainy season ( $46.7 \pm 5.6\%$  and  $38.5 \pm 17.4\%$  at SDZ and DXH, respectively). This is because the surface runoff during the rainy season is higher than that during the dry season, which can carry a considerable amount of soil particles into underground rivers through sinkholes, and resuspension is strengthened owing to the high velocity and discharge in the underground rivers during the rainy season. These observations indicated that PAHs in the LLD underground river were transported mostly via the freely dissolved PAHs during the dry season, and mainly in the SPM-associated PAHs

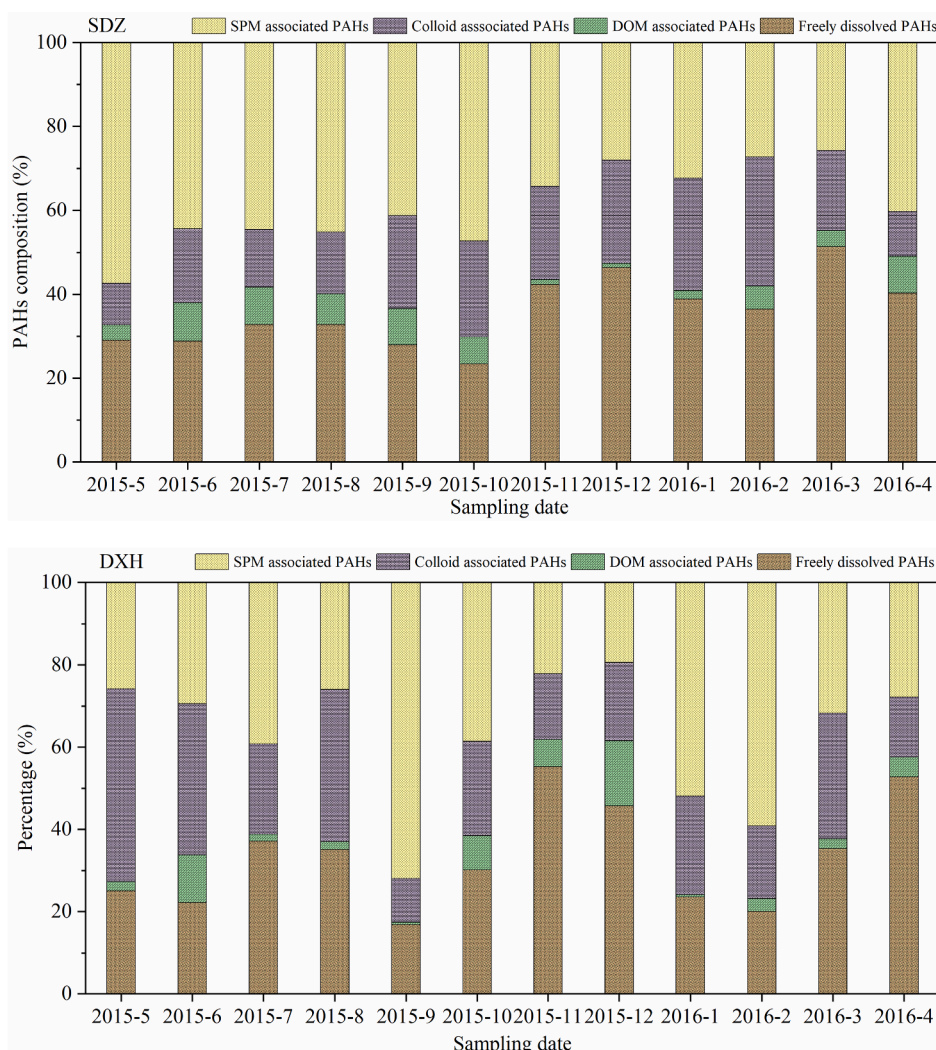


Fig. 4. Contribution of freely dissolved, DOM associated, colloid associated, and SPM associated PAHs to total PAHs concentrations in LLD underground river.



during the rainy season.

### 3.4. Factors affecting the content of different PAHs fractions

PAHs are hydrophobic and prefer to associate with DOM, colloids, or SPM. Therefore, DOC and POC are important factors affecting the behavior, fate, and toxicity of dissolved phase PAHs in underground water (Levy et al., 2017; Lan et al., 2018). In aquatic environments, the interactions between DOM or SPM and water are important mechanisms controlling the distribution and movement of PAHs (Zhou et al., 1999). The relationships between different PAHs fractions and DOC or POC are discussed according to Pearson's coefficient rank correlation in this study. A markedly positive correlation was observed between the total dissolved PAHs and DOC at SDZ (Fig. 5). The 2- and 3-ring PAHs accounted for 53–100% of the total dissolved PAHs, so a markedly positive correlation was found between the 2- and 3-ring dissolved phase PAHs and DOC at SDZ (Fig. S2). Due to the higher contribution of freely dissolved PAHs to total dissolved PAHs (>75%), a positive correlation can be inferred between the freely dissolved PAHs and DOC. Because the contribution of 2- and 3-ring PAHs to freely dissolved PAHs was >65%, a markedly positive correlation was also observed between (2 + 3) ring freely dissolved PAHs and DOC (Fig. S2). The above results indicate that the input of 2- and 3-ring PAHs in the underground water seems to be linked to the input of DOM. However, at DXH, the total dissolved PAHs and freely dissolved PAHs had no marked correlation with DOC concentration. The results indicate that the relationship between the dissolved PAH concentrations and DOC content is complex, and there

might be other factors, such as the POC content, hydrodynamic conditions and human activities (e.g. the disturbance of rowing), affecting the concentration of the dissolved phase PAHs at DXH (Shi et al., 2007).

A markedly positive correlation was observed between the DOM-associated PAHs and DOC at SDZ (Fig. S2). These results were similar to that of Shi et al. (2007) in Tianjin rivers, China. Although the contribution of 5- and 6- ring PAHs to the total dissolved PAHs (average 25.1%) was lower, positive correlation was also observed between 5- and 6-ring PAHs in dissolved phase and DOC. The contribution of 5- to 6-ring PAHs to the DOM-associated PAHs was more than 60% at SDZ and 79% at DXH (Fig. S2). Thus, it was not surprising that the statistical examination showed a positive correlation between 5- and 6- ring DOM-associated PAHs and DOC content. Moeckel et al. (2014) reported that the concentration of individual PAHs with greater than or equal to five rings was observed to be strongly correlated to the DOC content. This result was consistent with the results of this study at SDZ and DXH. The above results indicate that DOM was not only an important pool for dissolved high molecular weight (HMW) PAHs (4-ring, 5-ring and 6-ring), but also a facilitator for the accumulation of freely dissolved low molecular weight (LMW) PAHs (2-ring and 3-ring) at SDZ in the LLD underground river, although approximately 37.8% on average of LMW PAHs were directly associated with DOM. The markedly positive correlation between dissolved PAHs and DOC at SDZ indicates the input of dissolved PAHs can be linked to DOM inputs and it would seem intuitive that they are released simultaneously from the soil into the underground river.

The significantly positive correlation between the PAHs associated

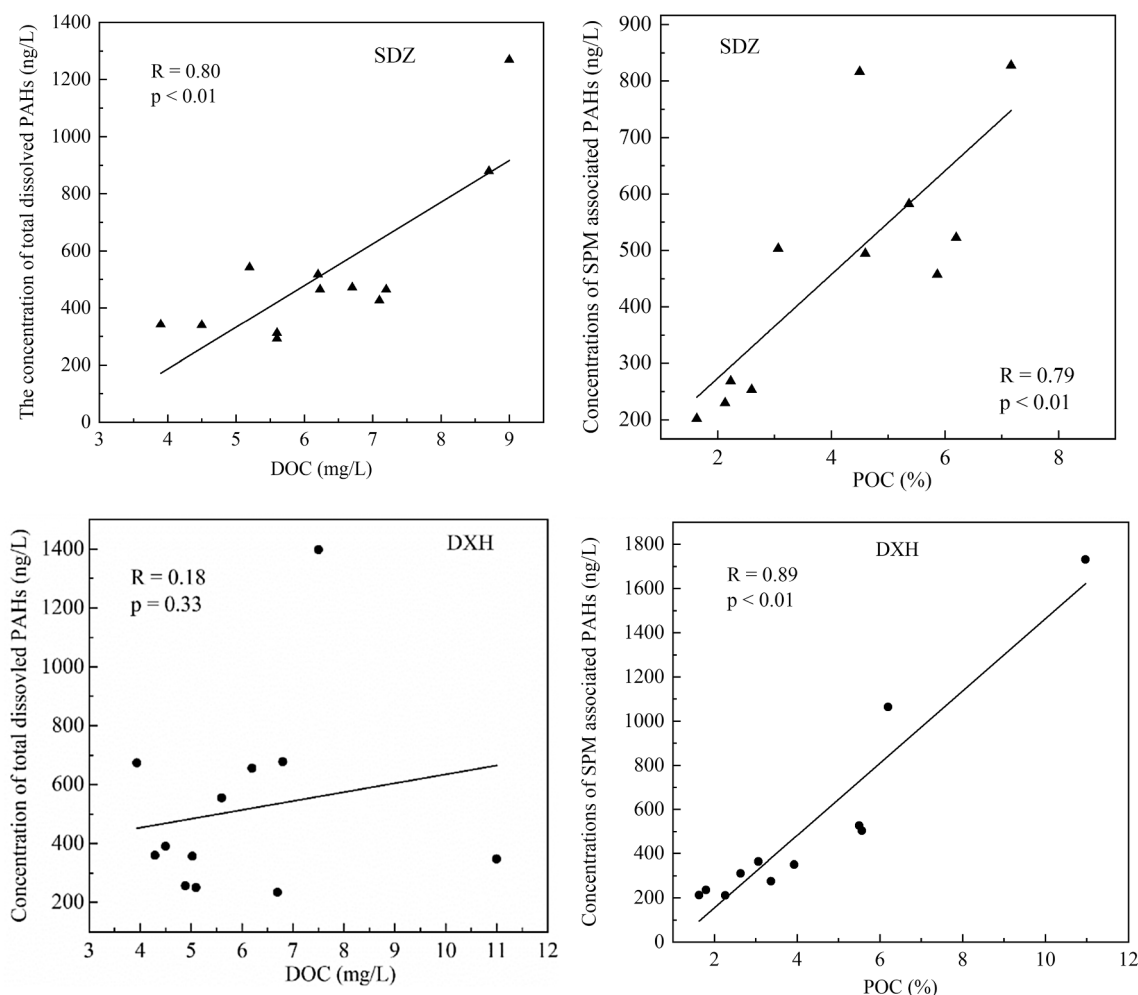


Fig. 5. Correlation between PAHs and DOC or POC in LLD underground river.

with SPM and POC at SDZ and DXH indicated that the concentrations of PAHs in the particulate phase were primarily controlled by POC (Fig. 5). However, the correlation coefficient at DXH is higher than that at SDZ, which indicates a better linear relationship formed under completely mixed steady conditions at DXH. With increasing SPM concentration, the probability of particle collisions and particle-DOM interactions would increase, leading to the reduction in sorption sites, which would allow the competitive sorption effect to become more significant (Zhou et al., 1999; Shi et al., 2007). Owing to the low vapor pressure and water solubility, HMW PAHs tended to be preferentially adsorbed by SPM. The statistical examination showed a significantly positive correlation between HMW PAHs in particulate phase and POC at SDZ and DXH (Fig. S2). In contrast to the freely dissolved PAHs, LMW PAHs in the particle phase were not markedly correlated with POC at SDZ. However, a positive correlation was found between LMW PAHs in the particle phase and POC at DXH. Therefore, the relationship between these LMW PAHs and POC is complicated.

Based on the above analysis, it was clear that DOC and POC were the major factors controlling the behavior and fate of dissolved PAHs and particulate PAHs at SDZ. POC was the only major factor controlling the behavior and fate of particulate PAHs at DXH. Due to the much easier measurement of DOC and POC, the levels of contamination by PAHs can be approximately estimated for further measurement and assessment. Furthermore, DOM or POM would markedly influence the bioavailability, aqueous solubility, environmental behavior and remediation of PAHs.

### 3.5. Partitioning of PAHs between SPM and water

Based on the above analysis, the interaction between SPM and water was one of the dominant processes controlling the speciation distribution and behavior of PAHs in the LLD underground river. PAHs indicated an increasing trend in the SPM-water phase partitioning from 2-ring up to 6-ring compounds in LLD underground river (Fig. S3). Nap, Acy, Ace, Flu, Phe, Fla, and Pyr dominated the dissolved PAH assemblages. On average, 71% and 58% of Nap, Acy, Ace, Flu, Phe, Fla, and Pyr were dissolved in the aqueous phase at SDZ and DXH, respectively. These seven PAHs were much more enriched in the particulate phase at DXH than at SDZ. However, 5-ring and 6-ring PAH showed the strongest enrichment in the particulate phase (mean values up to 82% and 89% at SDZ and DXH, respectively). Similar results were reported by Shi et al. (2007) for PAHs in Tianjin's rivers, where SPM-associated HMW PAHs reached up to 99%.

The values of the organic carbon normalized partition coefficient ( $K_{OC}$ ) can always be used to describe the relative affinity or attraction of PAHs to SPM and predict the degree of SPM-water partitioning (Fernandes et al., 1997; Shi et al., 2007). Therefore,  $K_{OC}$  could help quantitatively understand the processes that control the behavior and fate of PAHs in LLD underground rivers. The calculation details of  $K_{OC}$  are described in the literature (Fernandes et al., 1997; Shi et al., 2007). In this study, the increase in  $\log K_{OC}$  values of PAHs corresponded to the increase in the hydrophobicity, and were all close to or greater than the upper limit (Seth et al., 1999). However, the  $\log K_{OC}$  of Nap was much higher than the upper limit because Nap has a higher volatility than the other PAHs, and its concentration in water is lower, which resulting in the high  $\log K_{OC}$  value. This result suggests that PAHs were strongly adsorbed by SPM in the LLD underground river. Linear free-energy relationships were calculated to compare the partitioning of PAHs in the LLD underground river to the reference octanol/water system. Significant correlations were obtained between the logarithms of our  $K_{OC}$  and  $K_{OW}$  found in the literature (Kang et al., 2016) (Fig. 6). The slope of this regression equation gives a measure of the lipophilicity of sorbents relative to the reference octanol/water system (Fernandes et al., 1997). The slope at SDZ was close to 1, which indicated that the lipophilicity of SPM at SDZ was similar to octanol. However, the slope at DXH was higher than 1, which indicated SPM at DXH was more lipophilic than

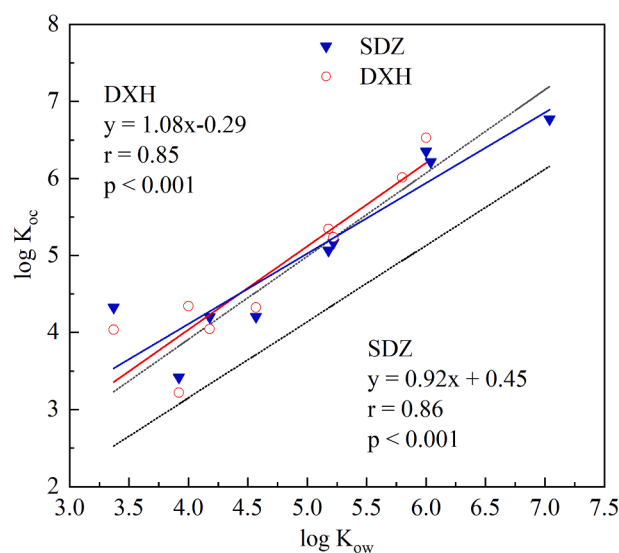


Fig. 6. Relationships between  $\log K_{OC}$  and  $\log K_{OW}$  for PAHs from the LLD underground river. The round dotted line represents the upper limit:  $\log K_{OC} = 1.08 \log K_{OW} - 0.41$  and lower limit:  $\log K_{OC} = 0.99 \log K_{OW} - 0.81$  (Seth et al., 1999).

octanol. The slope was higher than that reported by Fernandes et al. (1997) for the Seine river suspensions, Luo et al. (2008) for the Pearl river estuary and Ou et al. (2009) for the Yangtze estuary. These results suggest that POC in the LLD underground river has more lipophilicity to PAHs.

### 3.6. Migration pathways of PAHs in the underground river system

In karst terrains, PAHs are mainly transported by two migration pathways in the underground river system. One pathway involves slow-flowing soil seepage water in the karst fissures, infiltrating into the underground river, and the other involves conduit flows into the underground river (Schwarz et al., 2011; Lan et al., 2018). Considering that particles can act as carriers for organic pollutants, the mobilization of PAHs is likely to result from the movement of particles that are flushed through the system during a strong rainfall event. In particular, HMW PAHs present higher particle affinities and lower solubilities and they will mainly be transported by particulate phase. Dissolved PAHs can enter the underground river with the soil percolated water outflow (Sun et al., 2019).

In order to unveil the migration pathways of different PAHs fractions, the relationships between PAHs in the surface soil or soil seepage water and PAHs in the underground river were analyzed by Pearson's coefficient rank correlation. A significantly positive correlation existed between the total dissolved PAHs at SDZ and the soil seepage water PAHs at W1 (in upper reaches of the LLD underground river), W2 (in the middle reaches) and W3 (in the lower reaches) during the observation (Fig. S4). The above results indicated that a significant contribution of PAHs in soil seepage water to the total dissolved PAHs in underground river during the observation. As shown in Fig. S4, a strongly positive correlation exists between the SPM-associated PAHs at SDZ and surface soil PAHs, but a weakly positive correlation was observed between the SPM-associated PAHs at DXH and surface soil PAHs. In addition, a positive correlation was also observed between the colloid-associated PAHs at SDZ and DXH and PAHs in surface soil. The above results indicate that the PAHs associated with SPM and colloids at SDZ mainly come from surface soil. Furthermore, during the transport process from SDZ to DXH, some processes such as adsorption, desorption, volatilization and biodegradation will influence the SPM-associated PAH concentration and composition at DXH, especially human activities (e.g.,

rowing).

The above analysis suggests that the transport of PAHs in the LLD underground river system follows the conceptual model. First, particulate PAHs can be mobilized from the surface soil to the subsurface through the sinkholes, especially during strong precipitation events that can form surface runoff. Shevenell and McCarthy (2002) suggested that the mobilization of colloids depends on hydrological processes, such as heavy rain events; therefore, colloid-associated PAHs can be formed and transported to the underground river during the rainy season. In addition, Atteia et al. (1998) showed that the particles can be retarded by adhering to the conduit walls. Therefore, particles that adhered to the conduit walls during the dry season will be mobilized instantaneously, leading to a peak of the SPM-associated PAH concentrations that were measured at SDZ in the LLD underground river during the snowmelt in February 2016. In summary, particle and colloid-facilitated transport is one of the dominant mechanisms of PAH mobilization in this karst system. However, according to the above results, the contribution of the colloid was minor, when compared with the contribution of particle transport. Furthermore, PAHs can be mobilized in the form of dissolved PAHs (freely dissolved PAHs and DOM-associated PAHs). Dissolved PAHs can not only be mobilized from the surface soil to the underground river through the sinkholes but also mobilized through soil seepage

water, infiltrating into the underground river. During the rainy season, the migration pathways of PAHs from the surface soil to the underground river through the sinkholes and soil seepage water both had an important contribution (Fig. 7). During the dry season, however, dissolved PAHs are mainly mobilized through soil seepage water (Fig. 7).

#### 4. Conclusions

This study has provided important data on the variation in 16 priority PAHs in the dissolved phase, colloidal phase and particle phase of a typical karst underground river in Southwest China during a given year. Without the disturbance of human activity in the underground river, PAHs in water were dominated by the total dissolved PAHs, followed by the SPM-associated PAHs and colloid-associated PAHs during the dry season, and dominated by the SPM-associated PAHs, followed by the total dissolved PAHs and colloid-associated PAHs during the rainy season. The more water-soluble LMW PAHs dominate over the virtually water-insoluble and strongly hydrophobic HMW PAHs in the dissolved, colloidal, and particulate phases. However, the contribution of HMW PAHs showed an increasing trend along the order of the dissolved phase, colloidal phase and particulate phase. The environmental behavior and fate of PAHs were markedly influenced by organic content in each

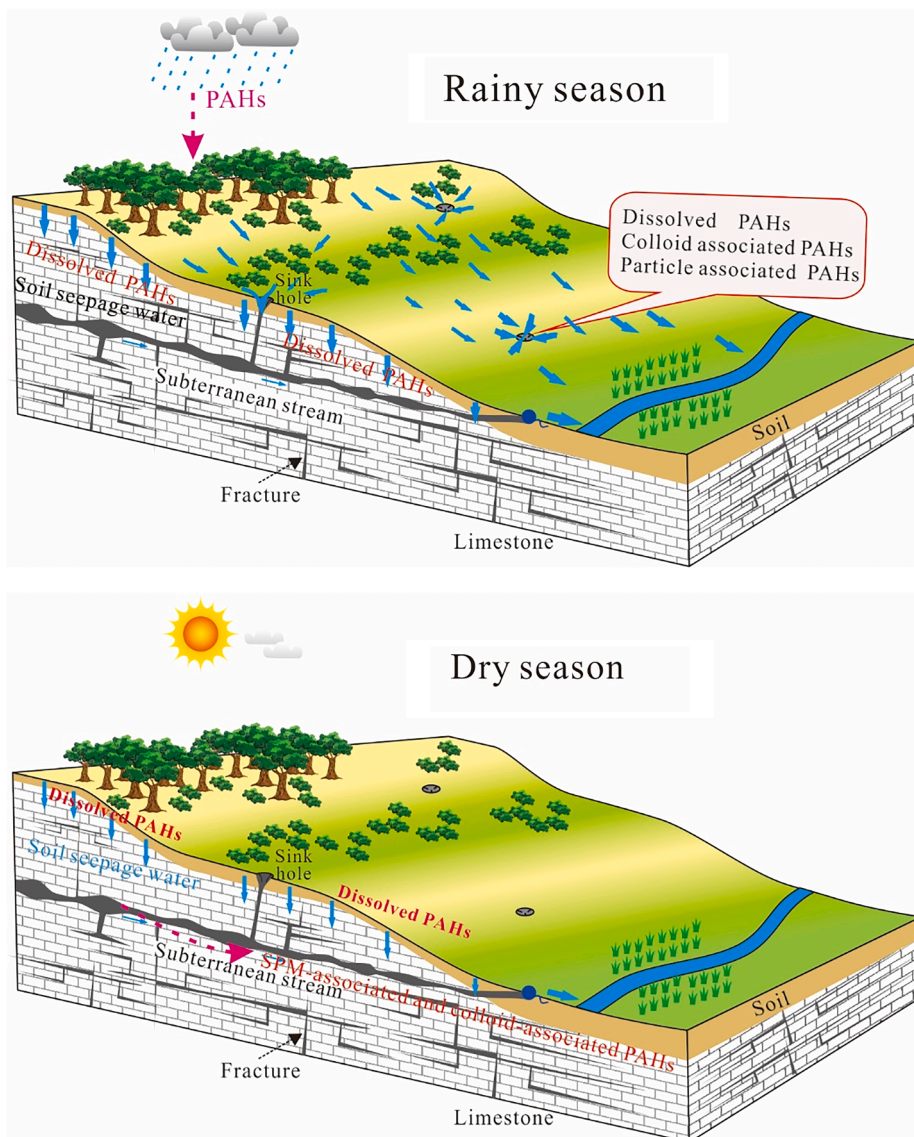


Fig. 7. Conceptual model for transport of PAHs in LLD underground river system.

phase, and POC has more lipophilicity to PAHs in the LLD underground river. The migration pathways of PAHs from the surface soil to the underground river through the sinkholes and soil seepage water both had important contribution during the rainy season. Dissolved PAHs are mainly mobilized through soil seepage water during the dry season.

#### CRedit authorship contribution statement

**Yuchuan Sun:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing. **Zhenglan Xie:** Investigation. **Kunyu Wu:** Writing - review & editing. **Jiacheng Lan:** Formal analysis. **Tian Li:** Investigation. **Daoxian Yuan:** Project administration, Resource.

#### 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.jhydrol.2020.125690>.

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