



# Polycyclic aromatic hydrocarbon contamination in a highly vulnerable underground river system in Chongqing, Southwest China



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## ABSTRACT

The concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) were investigated in the water, sediment and topsoil of the Laolongdong underground river system (LURS) of Chongqing, Southwest China. The total concentrations of PAHs ranged from 81.5 to 8089 ng/L in water, from 58.2 to 1070 ng/g in sediment, and from 277 to 3301 ng/g in topsoil. These levels of PAHs are relatively low compared to other karst areas. Low molecular weight (LMW) PAHs were dominant in water, sediment, topsoil samples, and high molecular weight (HMW) PAHs were more common in topsoil and sediment. The high levels of LMW PAHs in groundwater and sediment suggested relatively recent local sources of PAHs that were transported into the aquifer via wastewater discharge and surface water leakage. The similar composition of PAHs in topsoil and sediment samples suggested that the sediment originated from topsoil and that PAHs in sediment and topsoil had similar origins. The source of PAHs contamination was diagnosed by using PAH isomer ratios and a principal component analysis (PCA) method. The results indicated that PAHs mainly originated from vehicles, coal combustion and petrogenic sources. Significant correlations of PAHs with total organic carbon (TOC) in topsoil and sediment indicated that TOC was an important factor affecting PAHs content.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that are widespread in many environments (Maioli et al. 2011; Yang et al. 2013). Health concerns regarding PAHs relate to their carcinogenicity, mutagenicity and toxicity (Liu et al. 2005; Sharma et al. 2007). PAHs originate mainly from incomplete combustion of fossil fuels such as coal and oil, wood, and other organic materials (Johnsen and Karlson 2007; Yunker et al. 2002). PAHs are hydrophobic, with low aqueous solubility, and tend to associate with particulate matter (Tolosa et al. 2004). Previous studies in China have focused on the distribution and sources of PAHs in surface rivers and coastal waters, in suspended solid matter, and in sediments (Guo et al. 2009; Shi et al. 2005; Shi et al. 2007; Yang et al. 2013). A few studies have focused on PAHs contamination in karst environments. Karst tiankengs (sinkholes), are also known as “large collapse dolines”, which can act as a trap for PAHs, especially for heavy molecular weight PAHs (Oramah et al. 2008; Wang et al. 2009). In north China, the Guozhuang karst water

system, is a representative karst study area, where concentrations, distributions, and origins of PAHs in topsoil, suspended solids, and groundwater have been studied. However, there is little information about PAHs occurrence in soils and waters of a karst underground river system such as that in Chongqing, Southwest China.

Karst groundwater systems are particularly vulnerable and prone to contamination because of their unique hydrogeological characteristics. Karst systems often have a double-layer structure and little or no soil cover. Movement of rain, surface, and ground water results in poor pre-purification and filtration and rapid infiltration. Surface waters often directly discharge into karst aquifers and groundwater, resulting in water contamination (Yuan et al. 1993). In addition, water flow in a karst system is often conduit-dominated with short residence times leading to low self-purification capacity (Sasowsky and Wicks 2000). The Laolongdong underground river system (LURS) in this study is a typical example of anthropogenic activities impacting the quality of karst groundwater. It also provides an example of land-use in a rural area where villages, factories, mines, and motorways are sources of PAHs. The study objectives were to: determine the concentration and distribution of PAHs in surface water, underground water, sediment and topsoil from LURS; quantify the main sources of PAHs in the system; and understand the effect of karst hydrogeology on PAHs contamination of the LURS.

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## 2. Materials and methods

### 2.1. Study area description

The LURS is located in a limestone karst valley at the center of the Chongqing municipality, Southwest China (Fig. 1). The system has a total area of 12.6 km<sup>2</sup>, with about 11 km<sup>2</sup> covered by Mesozoic-Triassic carbonate rocks. The climate is subtropical monsoonal with mean annual temperature of 18.7 °C and a mean annual precipitation of 1100 mm. Karst depressions, sinkholes, and karst fissures are widely distributed around the entire karst valley with some epikarst spring outcroppings. The Laolongdong underground river originates in the valley and has a length of 6 km and a constant discharge of 50 to 80 L/s.

The valley setting is generally rural. Farm land, urban residences, and many small factories and mines in the valley produce a variety of effluents. There is no treatment plant for waste water except for one simple sewage treatment pond. Without wastewater management, sewage leaks out and overflows during the wet season into farm land and sinkholes, and then infiltrates or moves directly into the underground river. Wastewater from industrial and residential sources can also directly discharge into sinkholes.

### 2.2. Sampling description and sample collection

To study the contamination and behavior of PAHs in LURS, 21 topsoil sample points, 2 groundwater sample sites (G1, G2), and 3 surface water sample sites (S1, S2, S3) were selected. Sampling locations are shown in Fig.1. All topsoil samples were collected from agricultural land in the karst depression. G2 is the outlet of the underground river and an entrance to the Laolongdong cave which is a tourism cave with a 1 km trail access. G1 is a karst window, that was formerly a tourist cave. S1 and S3 are karst sinkholes into which waste water is discharged. Waste water only receives simple treatment before being discharged into S3.

A total of 21 topsoil samples (0–20 cm) were taken from agricultural areas in December 2012 using stainless steel shovels and spoons. Each sample was a composite of three to five subsamples. All topsoil samples were air-dried at room temperature, sieved through a 60-mesh sieve (0.25 mm), and then preserved in desiccators at –20 °C prior to analysis.

A total of 12 groundwater samples were collected from September 2012 to November 2013 at G2. Only 2 groundwater samples were collected at G1 because of nearby exploration and construction. A total of 17 surface water samples were collected between October 2012 and November 2013 at S1, S2 and S3. All water samples were collected in individual 1 L clean brown glass bottles. After collection, the water samples were immediately transported to the laboratory and stored in desiccators at 4 °C prior to analysis.

A total of 13 sediment samples from the underground river were collected at G1(3 samples) and G2 (10 samples) between December 2012 and November 2013. All samples were vacuum freeze-dried at –60 °C, sieved through a 60-mesh sieve (0.25 mm), refrozen and kept at –20 °C prior to analysis.

### 2.3. Sample extraction

For determination of PAHs, about 10 g of soil or sediment sample was weighed and kept in a cleaned filter paper (extracted for 72 h). Then 10 g of anhydrous sodium sulfate was added. After homogenization and spiking with five PAH surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), activated Cu was added for desulphurization, and then extracted with 125 mL dichloromethane (DCM) for 24 h at 45 °C. Final extracts were concentrated to 5 mL and solvent-exchanged to hexane and then purified using an aluminum/silica column chromatography. The eluted solvent was vacuum-evaporated to 2 mL, transferred to a GC vial, and then concentrated to a final volume of 0.2 mL under a gentle nitrogen stream. An internal standard hexamethylbenzene (4 µL) was added to the samples prior to the instrumental analysis.

Water sample extractions were based on a modified procedure of US EPA method 525.2. Samples were filtered with Whatman GF/F (0.45 µm effective pore) for 1 L into an amber bottle. Then surrogate standards (2 µL) were added to the water samples which were passed through a solid phase extractor (SPE-DEX controller 4700/4790, Horizon Technology). The extracts were concentrated to 5 mL, and then passed through a column packed with anhydrous sodium sulfate to remove water. The solutions were concentrated to 5 mL, passed through a silica gel column, evaporated to 0.8 mL, transferred to a GC vial and then concentrated to 0.2 mL under a stream of purified N<sub>2</sub>. Hexamethylbenzene was added to the samples for GC-MS analysis.

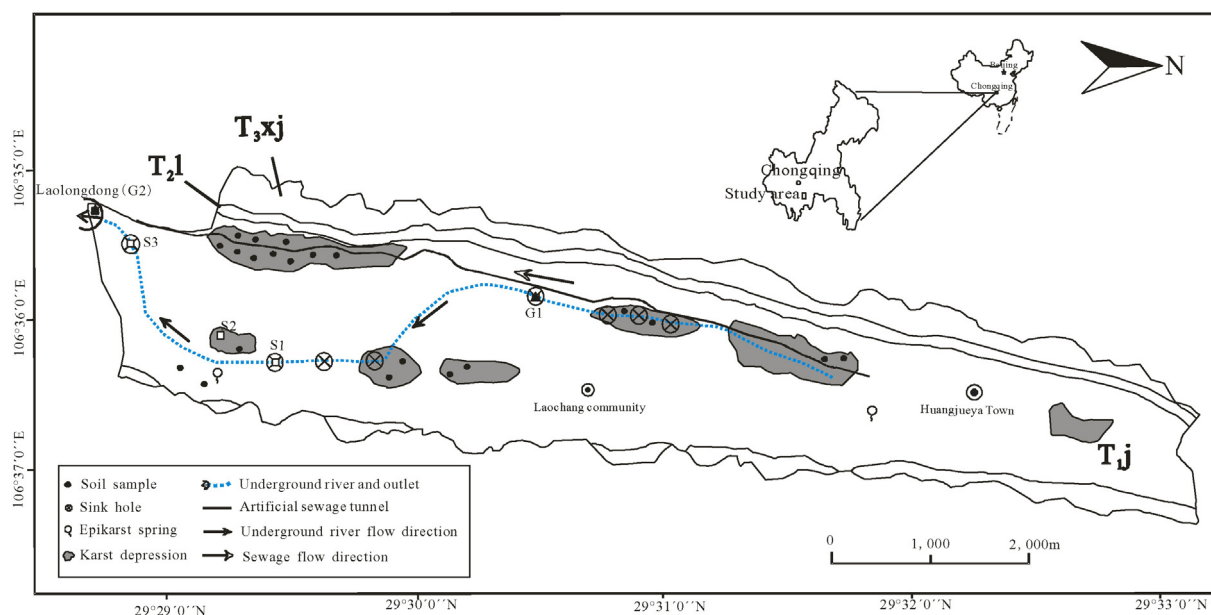


Fig. 1. Study area and sampling locations in the Laolongdong underground river system, Chongqing Province, southwestern China. G1, G2 – groundwater, S1, S3 – waste water discharged into sinkholes, S2 – surface water in a kaste depression.

## 2.4. PAH analysis

PAHs were analyzed using an Agilent 7890 A/5975C GC–MS equipped with a HP-5MS capillary column (30 m × 0.32 mm × 0.25 μm). The GC operating conditions were as follows: injector temperature 280 °C, temperature program 50 °C (for 1 min), ramped to 200 °C at 20 °C·min<sup>-1</sup>, and then ramped to 290 °C at 10 °C·min<sup>-1</sup> for 15 min. Helium was used as the carrier gas at a constant flow rate of 1 mL·min<sup>-1</sup>. The mass selective detector operated in the electron impact (EI) mode (70 eV), ion source temperature 300 °C, and the selected ion-monitoring (SIM) mode.

## 2.5. Quality control

After analysis of every 10 samples, procedural blanks, standard-spiked blanks, and parallel samples were analyzed simultaneously for quality assurance and control. Quantification was performed using an internal calibration method based on a five-point calibration curve for each individual component. Recoveries of all the PAHs ranged from 56% to 115%, the method detection limits averaged 0.5 ng·g<sup>-1</sup> to 3.1 ng·g<sup>-1</sup> for 10 g soil or sediment samples and varied from 0.2 to 1.5 ng·L<sup>-1</sup> for the 1 L water samples. No detectable PAHs were found in the procedural blanks.

## 2.6. TOC and pH analysis

Total organic carbon content of soil samples was determined by the potassium dichromate oxidation method. Soil pH was determined with a hand-held water quality meter (WTW, HQ340d, USA) in a 1:2.5 suspension in H<sub>2</sub>O.

## 2.7. PCA analysis

Principle component analysis (PCA) is a multivariate analytical tool used to reduce many unrelated original index variables and to extract a small number of factors which explain most of the variance of the original index. PCA has been widely used for receptor modeling of environments to identify sources of PAHs in China (Ma et al. 2010; Ma et al. 2011). PCA was performed on 16 variables consisting of PAH concentrations of topsoil with the varimax rotation method. Two factors were obtained and the profiles of the factor loadings were used to infer the

possible sources of PAHs. The analyses were performed using the SPSS statistical software package (SPSS 17.0).

## 3. Results and discussion

### 3.1. Concentrations of PAHs

#### 3.1.1. PAHs in soil

The concentrations of PAHs in topsoil ranged from 277 to 3301 ng·g<sup>-1</sup>, with a mean of 750.4 ± 636.6 ng·g<sup>-1</sup> (Table 1). Concentrations of ∑ PAH<sub>scarce</sub> accounted for 36.2% of ∑ PAHs and varied from 72.1 to 1801 ng·g<sup>-1</sup>, with a mean of 750.4 ± 636.6 ng·g<sup>-1</sup> 310.0 ± 373.8 ng·g<sup>-1</sup>. China has no standard soil quality guidelines for permissible PAH concentrations. Contamination standards for PAHs in soil have been established elsewhere (Maliszewska-Kordybach et al. 2007). PAHs pollution levels in soil can be divided into four groups: not contaminated, <200 ng·g<sup>-1</sup>; weakly contaminated, 200–600 ng·g<sup>-1</sup>; contaminated, 600–1000 ng·g<sup>-1</sup>; heavily contaminated, >1000 ng·g<sup>-1</sup>. PAHs concentrations of 21 soil samples collected in the study area all exceeded 200 ng·g<sup>-1</sup>, meaning that all of the sites fell into the “contaminated” group. A total of 57% of the samples would be classified as weakly contaminated, 29% and 14% of the samples would be classified as contaminated and heavily contaminated, respectively. The mean concentrations of PAHs were about 23-fold lower than those from the Guozhuang karst water system (mean value of 17,174 ng·g<sup>-1</sup>) (Shao et al. 2014) and 4× lower than that in agriculture soil of the “Schwäbische Alb” catchment in Germany (Schwarz et al. 2011).

#### 3.1.2. PAHs in water

Concentrations of the 16 U.S. EPA priority PAHs in water at different LURS sites are listed in Table 1. PAHs were divided into low (LMW), medium (MMW), and high (HMW) molecular weight categories. Most PAH compounds were detected in water samples. However, the majority of HMW PAHs were not detected. This could be related to higher solubility of the LMW PAHs and conversely lower water solubility of HMW compounds. The concentrations of ∑ PAHs ranged from 81.5 to 8089 ng·L<sup>-1</sup> with a mean of 1320 ± 2090 ng·L<sup>-1</sup> in the underground river (S1 and S3) and from 77.3 to 2443 ng·L<sup>-1</sup> with a mean of 732.7 ± 720.8 ng·L<sup>-1</sup> in surface water, respectively. The greatest concentration was at G2 (8089 ng·L<sup>-1</sup>) in September 2012 and the lowest was at S3 (77.3 ng·L<sup>-1</sup>). The concentrations at G2 were higher than the

**Table 1**  
PAHs concentrations in water, sediment and topsoil in Laolongdong catchment, mean ± S.D.

	Underground water (ng/L)		Surface water (ng/L)			Sediment (ng/g, dw)		Soil (ng/g, dw)
	G1 (n = 12)	G2 (n = 2)	S2 (n = 10)	S1 (n = 3)	S3 (n = 4)	G2 (n = 12)	G1 (n = 2)	Topsoil (n = 21)
Nap	151 ± 99.9	120 ± 35.8	256 ± 277	331 ± 390	89.8 ± 42.8	94.7 ± 106	517 ± 625	146 ± 92.6
Acy	230 ± 228	42.9 ± 7.7	160 ± 168	76.2 ± 81.5	69.4 ± 76.8	10.4 ± 10.2	129 ± 136	17.8 ± 11.4
Ace	68.4 ± 84.1	69.1 ± 12.2	47.6 ± 54.4	47.2 ± 38.5	34.8 ± 44.9	9.2 ± 5.3	52.0 ± 9.19	18.6 ± 9.07
Flu	257 ± 322	106 ± 23.2	161 ± 177	47.8 ± 41.4	158 ± 172	33.6 ± 18.5	131 ± 23	66.3 ± 37.3
Phe	440 ± 990	115 ± 29.8	174 ± 197	25.2 ± 23.2	26.4 ± 21	49.0 ± 36.4	171 ± 43.2	73.4 ± 58.1
Ant	28.7 ± 64.1	22.4 ± 3.78	10.7 ± 12.1	105 ± 175	2.47 ± 2.85	2.34 ± 2.38	17.3 ± 7.09	4.96 ± 6.69
Fla	165 ± 372	27.0 ± 6.3	57.1 ± 68.0	1.57 ± 2.72	5.77 ± 6.4	14.7 ± 15	104 ± 28.4	30.3 ± 30.8
Pyr	97 ± 216	18.7 ± 4.2	32.8 ± 39.3	0.62 ± 1.08	2.27 ± 3.51	14.6 ± 15.6	69.4 ± 23.8	23.1 ± 25.7
BaA	N.D	19.2 ± 1.5	N.D	N.D	N.D	9.17 ± 11.3	38.3 ± 5.44	16.5 ± 17.8
Chry	0.64 ± 0.82	16.3 ± 2.8	0.35 ± 0.57	N.D	0.09 ± 0.17	38.7 ± 47.9	81.6 ± 35.6	69.3 ± 68.0
BbF	N.D	26.6 ± 1.4	N.D	N.D	N.D	28.7 ± 33.3	144 ± 21.5	60.3 ± 57.4
BkF	N.D	7.9 ± 0.98	0.36 ± 1.13	N.D	N.D	14.6 ± 12.2	86.8 ± 39.6	54.5 ± 79.8
BaP	N.D	14.5 ± 0.1	N.D	N.D	N.D	13.9 ± 18.5	66.1 ± 36.9	20.1 ± 24.2
InP	N.D	N.D	N.D	N.D	N.D	8.33 ± 12.7	390 ± 192	40.8 ± 31.6
DaA	0.27 ± 0.63	N.D	N.D	1.1 ± 1.9	N.D	4.99 ± 8.05	21.8 ± 25.1	48.4 ± 117
BgP	N.D	N.D	N.D	N.D	N.D	21.0 ± 30.4	154 ± 176	62.3 ± 43.3
∑ PAHs	1.44 × 10 <sup>3</sup> ± 2.25 × 10 <sup>3</sup>	605 ± 128	899 ± 875	635 ± 356	389 ± 361	368 ± 343	2.17 × 10 <sup>3</sup> ± 1.24 × 10 <sup>3</sup>	753 ± 636

Note: N.D not detected.

∑ PAHs-total concentration of the 16 PAHs.

other sites (Table 1). This may be because the underground river was affected by sewage from Huangjueya Town before April 2013. The lowest concentration at S3 might result from simple primary treatment of the wastewater. Relatively higher concentrations were detected at S1, due to contamination by wastewater from human settlements and factories. S2 is a low karst depression that is very susceptible to pollution. Concentrations of PAHs in LURS waters were much lower than those in the Guozhuang karst area of northern China, an area highly polluted by coal mining and industrial waste (Shao et al. 2014). However, PAHs concentrations in LURS waters were greater than those from the “Blautopf” karst spring in Germany (Schwarz et al. 2011).

### 3.1.3. PAHs in sediment

All 16 EPA priority PAHs were present in all sediment samples (Table 2). The mean concentrations of PAHs in the sediment were  $2173 \pm 1244 \text{ ng}\cdot\text{g}^{-1}$  at G1 and  $367.9 \pm 342.6 \text{ ng}\cdot\text{g}^{-1}$  at G2. Total concentrations of 7 potentially carcinogenic PAHs ( $\sum \text{PAH}_{\text{scarce}}$ ) (BaA, Chry, BbF, BkF, BaP, InP, DaA) ranged from 10.1 to 1071  $\text{ng}\cdot\text{g}^{-1}$  and were also much greater at G1 than at G2.

According to the pollutant levels suggested by Baumard et al. (1998), the relative contamination levels can be classified into four categories as follows: (a) low, 0–100  $\text{ng}\cdot\text{g}^{-1}$ ; (b) moderate, 100–1100  $\text{ng}\cdot\text{g}^{-1}$ ; (c) high, 1000–5000  $\text{ng}\cdot\text{g}^{-1}$ ; and (d) very high, >5000  $\text{ng}\cdot\text{g}^{-1}$ . Sediments at G1 and G2 can be characterized as having low to moderate PAHs pollution and high PAHs pollution, respectively. Compared to cave sediments from the “Schwäbische Alb” catchment in a rural German setting with little industry (Schwarz et al. 2011), PAHs concentrations in sediments of this study were greater.

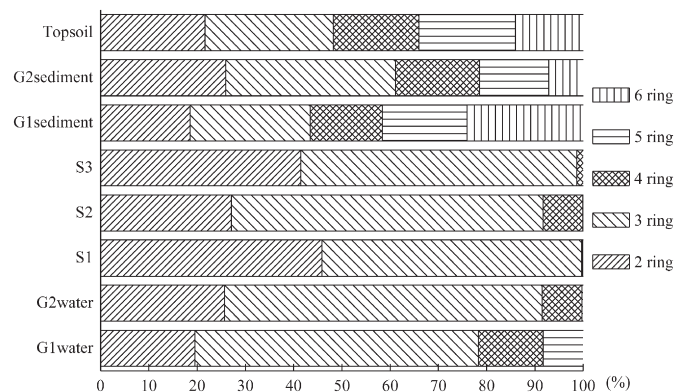
### 3.2. PAHs composition

PAHs composition in the study area varied with sample time and site (Fig. 2). PAHs in water were dominated by 2–3 ring PAHs, which accounted for 78.3% in G1, 91.5% in G2, 99.7% in S1, 91.7% in S2 and 98.7% in S3 of total PAHs, respectively. However, MMW PAHs and HMW PAHs only accounted for 8% of total PAHs from all water sample sites. MMW PAHs had low detection frequencies, and HMW PAHs such as six-ring PAHs were not detected. These observations were similar to the results in Guozhuang karst groundwater (Shao et al. 2014) and Tianjin rivers in north China (Shi et al. 2005), which are attributed to the relatively higher vapor pressure and water solubility of LMW PAHs than HMW PAHs. LMW PAHs predominated in groundwater (G2) suggesting a relatively recent local source of PAHs most likely from wastewater discharge and surface water leakage (S2). The

**Table 2**  
Varimax rotated principal component matrix of 16 PAHs from topsoil in the study area.

PAH	Ring	Principal component	
		1	2
Nap	2	0.338	<b>0.849</b>
Acy	3	0.388	<b>0.762</b>
Ace	3	0.286	<b>0.900</b>
Flu	3	0.365	<b>0.825</b>
Phe	3	<b>0.753</b>	0.585
Ant	3	<b>0.696</b>	0.403
Fla	4	<b>0.766</b>	0.528
Pyr	4	<b>0.790</b>	0.503
BaA	4	<b>0.846</b>	0.505
Chry	4	<b>0.870</b>	0.448
BbF	5	<b>0.835</b>	0.393
BkF	5	<b>0.755</b>	0.556
BaP	5	<b>0.877</b>	0.457
InP	6	<b>0.900</b>	0.203
DaA	5	<b>0.724</b>	0.515
BgP	6	<b>0.876</b>	0.206
Variance/%		77.6	7.8
Estimated source		combustion	petroleum

Boldfaced type indicates PCA loading values higher than 0.70.



**Fig. 2.** PAHs composition in different sample site and environment media from Laolongdong catchment. S1, S3 – waste water discharged into sinkholes, S2 – surface water in a kaste depression. Proportion values represent averages.

percentage of M-HMW PAHs to total PAHs in soil and sediment were relatively higher than that in water samples, which was similar to the Liangtan River (Liu et al. 2013) and Guozhuang karst water system (Shao et al. 2014). HMW PAHs with low vapor pressure and low water solubility (Sun et al. 2009) tended to be preferentially adsorbed by particulates and sediments (Zhu et al. 2008). However, LMW PAHs predominated in sediment (G2) and topsoil samples (Fig. 2). Approximately 61% of the total concentrations were represented by PAHs with two to four rings in G2 and 66% that in topsoil. This was similar to Tianjin river data (Shi et al. 2005). The proportion of LMW PAHs was 43.4% and 41.6% of HMW PAHs in the sediment in G1.

Different sources of PAHs have different PAHs patterns. The HMW PAHs (4- to 6-ring) are mainly from high-temperature combustion processes, while the LMW PAHs (2- to 3-ring) mainly originate from low- or moderate-temperature combustion processes (Harrison et al. 1996; Mai et al. 2003; Soclo et al. 2000). LMW PAHs originate not only from combustion sources but also from diagenesis, i.e. they occur “naturally” in oil. Based on the analysis of PAHs composition above, PAHs in topsoil probably originated from petroleum and high-temperature combustion processes. Presence of high levels of LMW PAHs in soils, thus, may indicate an oil spill or a petrogenic origin. The detailed sources of PAHs in this area will be discussed in section 3.4.

### 3.3. Relationship of PAHs between G2 and the other sites

As discussed in section 3.1.1, the PAH concentrations at G2 were greater than those at the other sites (Table 1) because the underground river was affected by sewage from Huangjueya Town before April 2013. However, the mean concentration of PAHs in water at G2 was only  $422 \pm 246 \text{ ng}\cdot\text{L}^{-1}$  from May 2013 to November 2013 which was lower than that at G1 ( $605.3 \pm 127.8 \text{ ng}\cdot\text{L}^{-1}$ ), S1 ( $635.4 \pm 355.6 \text{ ng}\cdot\text{L}^{-1}$ ) and S2 ( $899.4 \pm 874.9 \text{ ng}\cdot\text{L}^{-1}$ ), but higher than that at S3 ( $388.8 \pm 361.4 \text{ ng}\cdot\text{L}^{-1}$ ). The concentrations of PAHs in water at G2 were lower than those at G1 and S1. The possible reason was that G1 and S1 are located upstream relative to G2. PAHs were transported to G2 via the karst conduit, and may have been adsorbed by the carbonate and the sediment in the conduit. Additional evidence involves the difference of PAHs composition between G1 and G2 (Fig. 2). The 2–3 ring PAHs in water were dominant at G1 and G2, and the percentage of 2–3 ring PAHs to total PAHs was only 78.3% at G1, but 91.5% at G2. In contrast, the proportion of 4–5 ring PAHs (six-ring PAHs were not detected in G1 or G2) in water at G1 (27.7%) was higher than that at G2 (8.5%) and five ring PAHs only accounted for 0.24% at G2, but 8.3% at G1. These data also suggested that PAH adsorbed by carbonate and sediment in the conduit due to low solubility and particle affinity of high molecular weight PAHs. It is possible that the higher molecular weight PAH scan accumulate and persist for a longtime in the underground



river sediment. PAHs at S2 were transported to G2 via surface water leakage processes and PAHs might be filtered and adsorbed by soil. Schwarz et al. (2011) found that even in the highly vulnerable karst catchment, PAHs were effectively retained in the soils.

A similar result was found in the sediment between G1 and G2. Fig. 3 showed that PAHs in the sediment at G2 had the similar composition profiles to G1 and topsoil. The correlation was >0.9, indicating that the sediments at G2 mainly come from the transport of the upstream water and surface soil. The mean concentration of PAHs at G2 was  $2173 \pm 1244 \text{ ng}\cdot\text{g}^{-1}$ , declining to  $367.9 \pm 342.6 \text{ ng}\cdot\text{g}^{-1}$  at G1. The 2–3 ring PAHs accounted for 61.1% at G2 and declined to 43.4% at G1. This suggests that 2–3 ring PAHs have a higher aqueous transport capability with farther migration distance compared to lower aqueous transport capability and shorter migration distance for 4–6 rings PAHs.

### 3.4. Sources of the PAHs

It is necessary to accurately identify the sources of PAHs for PAHs pollution control and remediation. As a karst system has a double layered structure. PAHs in the underground river come from the surface environment. However, due to many confounding factors, such as differences in volatility, water solubility, affinity to organic carbon, etc. (Yunker et al. 2002), PAHs would be redistributed when transported into the underground river from surface environment. That's why PAHs in water were dominated by LMW PAHs, MMW PAHs had low detection frequencies, and HMW PAHs were not detected. Changes in diagnostic ratios from surface to underground in a karst system are unavoidable. Consequently, isomeric ratios of PAHs could not accurately identify the sources of PAHs pollution underground. In addition soil is the primary recipient of contamination in the system. Therefore, only need to identify the sources of PAHs in soil can represent the source of PAHs in the system.

#### 3.4.1. Isomeric ratios of PAHs

PAH isomer pair ratios such as  $\text{Ant}/(\text{Ant} + \text{Phe})$ ,  $\text{Fla}/(\text{Fla} + \text{Pyr})$ ,  $\text{BaA}/(\text{BaA} + \text{Chry})$ , and  $\text{InP}/(\text{InP} + \text{BgP})$  have been widely used to distinguish environmental sources of PAHs (Guo et al. 2009; Orecchio 2010; Shao et al. 2014; Yang et al. 2013; Yunker et al. 2002). Different diagnostic ratios of PAHs can be used to identify origin sources, as summarized by Yunker et al. (2002). An  $\text{Ant}/(\text{Ant} + \text{Phe})$  ratio of 0.1 is usually defined as the petroleum/combustion transition point.  $\text{Fla}/(\text{Fla} + \text{Pyr}) < 0.4$  implies petroleum,  $> 0.5$  suggests combustion of coal and biomass, and  $0.4–0.5$  implies petroleum combustion. A ratio of  $\text{BaA}/(\text{BaA} + \text{Chry}) < 0.2$  implies petroleum,  $0.2–0.35$  indicates either petroleum or combustion, and  $> 0.35$  implies combustion.  $\text{InP}/$

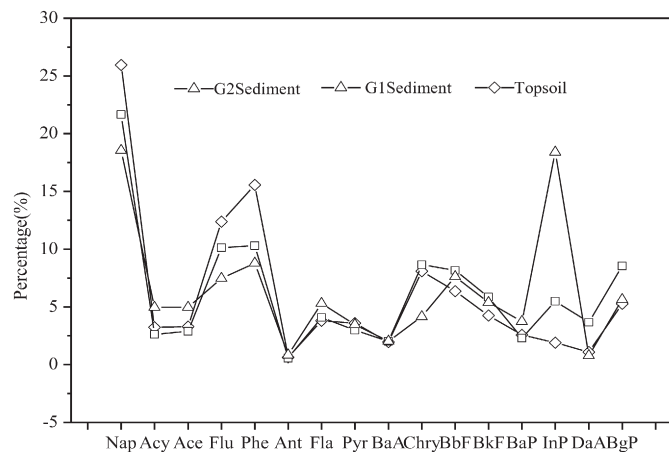


Fig. 3. PAHs composition profiles in sediment and topsoil in the catchment. Plotted values represent averages.

$(\text{InP} + \text{BgP}) < 0.2$  indicates petroleum,  $0.2–0.5$  indicates petroleum combustion, and  $> 0.5$  indicates combustion of coal or biomass.

Fig. 4 shows the topsoil sample data. The ratios of  $\text{Ant}/(\text{Phe} + \text{Ant})$  ranged from 0.02 to 0.19, and only one sample was greater than 0.10, indicating that petroleum was the main source of the PAHs.  $\text{Fla}/(\text{Fla} + \text{Pyr})$  and  $\text{InP}/(\text{InP} + \text{BgP})$  suggested that PAHs in topsoil originated from combustion sources. However,  $\text{Ant}/(\text{Phe} + \text{Ant})$  and  $\text{BaA}/(\text{BaA} + \text{Chry})$  showed that PAHs were derived primarily from petroleum sources, with a lower occurrence of PAHs from mixes and combustion sources. We concluded that a mixed pattern of PAH sources was found in the study area soils.

#### 3.4.2. PCA analysis

The rotated factors of 16 normalized PAHs from the topsoil are presented in Table 2. Two principal components explained approximately 78.6% and 7.8% of the total variance, respectively. Factor 1 was dominated by Ant, Phe, Fla, Pyr, BbF, BkF, BgP, Chry, BaA, and InP. BgP is a PAH compound characteristic of vehicle emissions (Nielsen et al. 1996; Simcik et al. 1999). Vehicle emissions also produced considerable Chry (Harrison et al. 1996). BaA is commonly produced from gasoline and diesel combustion (Lee et al. 2004), and InP is an indicator of diesel combustion (Li and Kamens 1993). Ant, Phe, Fla, Pyr, BbF and BkF are typical indicator compounds of coal combustion (Bzdusek et al. 2004; Harrison et al. 1996; Larsen and Baker 2003; Simcik et al. 1999). Therefore, factor 1 represented the vehicle emission and coal combustion sources. Factor 2 was highly weighted by Nap, Ace, Flu, and Acy which were petrogenic PAHs characterized by the predominance of 2 and 3-rings (Yunker et al. 2002). Therefore, factor 2 represented a petrogenic source.

In recent decades, a rapid increase in motor vehicles in this study area due to tours, cement production, and mining activities, provided the sources of traffic-related PAHs. There are also gas stations and automobile repair stations in the area. Related activities such as vehicle

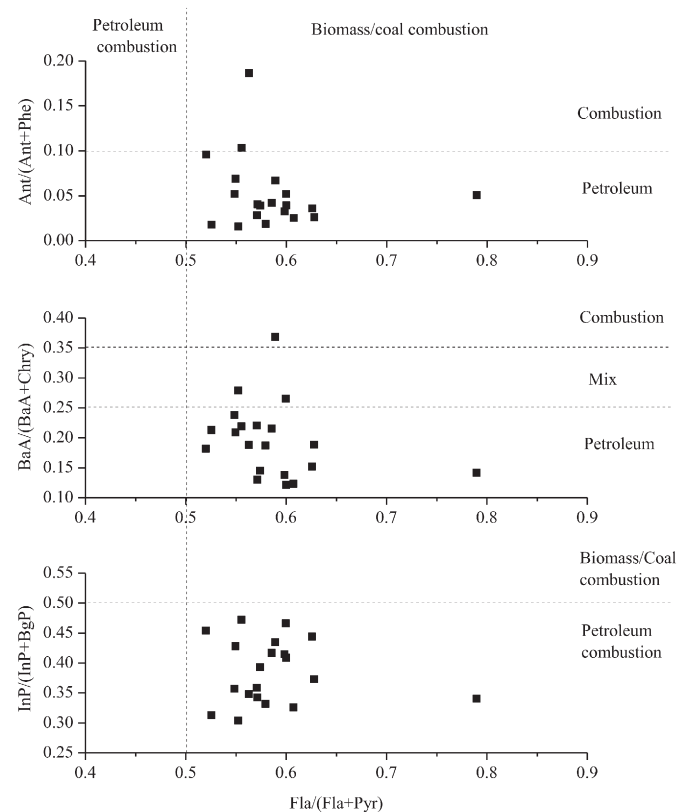


Fig. 4. Plots for the ratios of  $\text{Ant}/(\text{Ant} + \text{Phe})$  vs.  $\text{Fla}/(\text{Fla} + \text{Pyr})$ ,  $\text{BaA}/(\text{BaA} + \text{Chr})$  vs.  $\text{Fla}/(\text{Fla} + \text{Pyr})$ ,  $\text{InP}/(\text{InP} + \text{BgP})$  vs.  $\text{Fla}/(\text{Fla} + \text{Pyr})$ .

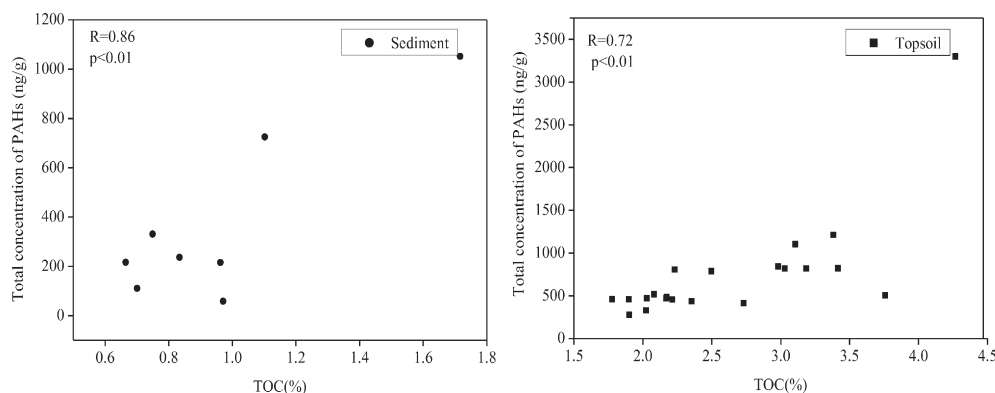


Fig. 5. Relationship between total concentration of PAHs in sediment and topsoil and TOC.  $p$  is the significance of the relationship,  $R$  represents coefficient of correlation.

washing could produce wastewater containing gasoline and diesel, which could be discharged into low lying farmland and sinkholes, and then be transported into the underground river through leaching or water and soil erosion processes.

### 3.5. TOC affecting the content of sediment and topsoil PAHs

Soil organic matter is an important factor for PAHs levels (Boehm et al. 2002). In topsoil, TOC was significantly correlated with 15 species of PAHs (except Nap) and the total concentration of PAHs (Fig. 5,  $R = 0.72$ ,  $p < 0.01$ ), indicating that PAHs contamination in soil might be primary controlled by soil organic matter. These results were similar to those of Shao et al. (2014) and Tang et al. (2006). In addition, a higher correlation coefficient between TOC and HMW PAHs than TOC and LMW PAHs was found. This could be related to the high concentration of TOC and the strong adsorption of HMW PAHs (Hinga 2003; Shao et al. 2014) in topsoil. Another non-exclusive reason might be the higher vapor pressure and greater water solubility of LMW PAHs lead to more rapid volatilization and migration from the topsoil.

Shi et al. (2007) reported that components and species of organic matter would influence the behavior and fate of sediment associated PAHs. Other studies have found a strong correlation between PAHs and TOC (Shi et al. 2007; Yan et al. 2009). Sediment associated PAHs linearly correlated with organic carbon content and were primarily controlled by TOC (Shi et al. 2007). However, Wu et al. (2003) found no correlation between TOC and PAHs. In sediment from G2, TOC was positively correlated with 13 species of PAHs (except InP, DaA and BgP) and

total concentration of PAHs (Fig. 5). This suggests that TOC was an important factor affecting sediment associated PAHs. There may be other factors involved such as clay mineral content and pH value (Shi et al. 2007). When TOC content is low, the partitioning of PAHs into sediment can be determined by both the organic carbon content and the inorganic matrix, such as clay minerals (Maskaoui et al. 2002). TOC content in G2 sediment was low, ranging from 0.67% to 1.7%. A significant positive correlation was found between the pH value of the sediment and InP, DaA and BgP indicating that the pH value was likely a factor influencing PAHs concentrations (Fig. 6).

## 4. Conclusions

1. PAHs levels in water and topsoil of this study were not high, contrasted with the results of other studies PAHs contamination in sediment were greater than other study (see section 3.1).
2. LMW PAHs predominated in soil, water and sediment. The percentages of M-HMW PAHs to total PAHs in soil and sediment were higher than those in water samples. This finding illustrates the different properties of LMW PHAs and HMW PAHs.
3. The higher concentration and different composition of PAHs in water and sediment at G1 compared to G2, indicated that HMW PAHs can accumulate and persist for a long time in the underground river sediment. Similar PAHs composition profiles among G1, G2 and topsoil suggested that the sediments at G2 mainly come from the transport of upstream water and surface soil.
4. Source apportionment of PAHs suggested a mixed origin of PAHs. Vehicle emissions, coal combustion sources, and petrogenic sources appear to be the dominant sources for PAHs in topsoil.
5. TOC was the most important factor affecting the concentration of PAHs in sediment and topsoil.

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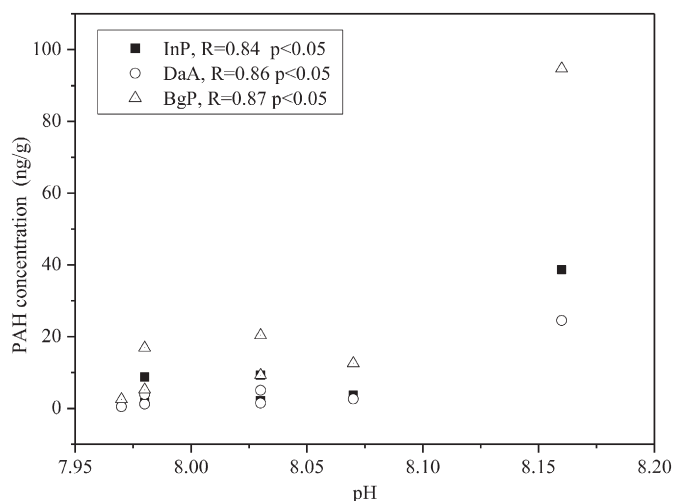


Fig. 6. Relationship between InP concentration and pH, DaA and pH, BgP and pH in sediments.  $p$  is the significance of the relationship,  $R$  represents coefficient of correlation.

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