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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.

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 LRUS; quantify the main sources of PAHs in the system; and understand the effect of karst hydrogeology on PAHs contamination ofthe 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^2, with about 11 km^2 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_2. Hexamethylbenzene was added to the samples for GC–MS analysis.

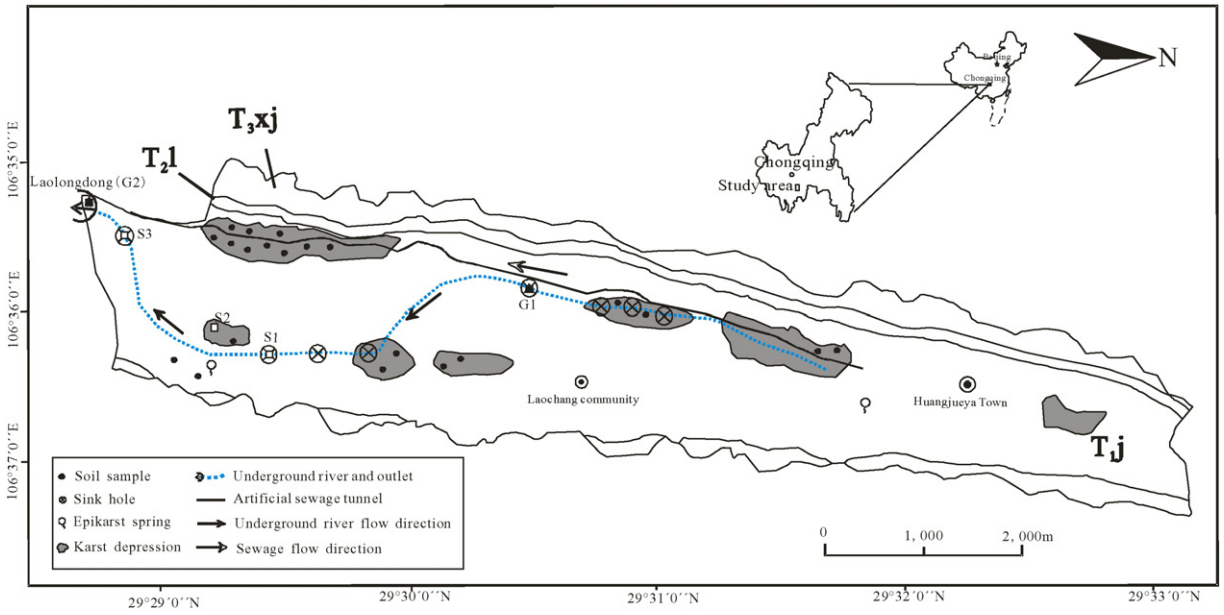

Fig. 1. Study area and sampling locations in the Laolongdong underground river system, Chongqing Province, southwestern China. G1, G2 — groundwater, S1, S3 — waste water discharged into sinkholes, S2 — surface water in a kaste depression.