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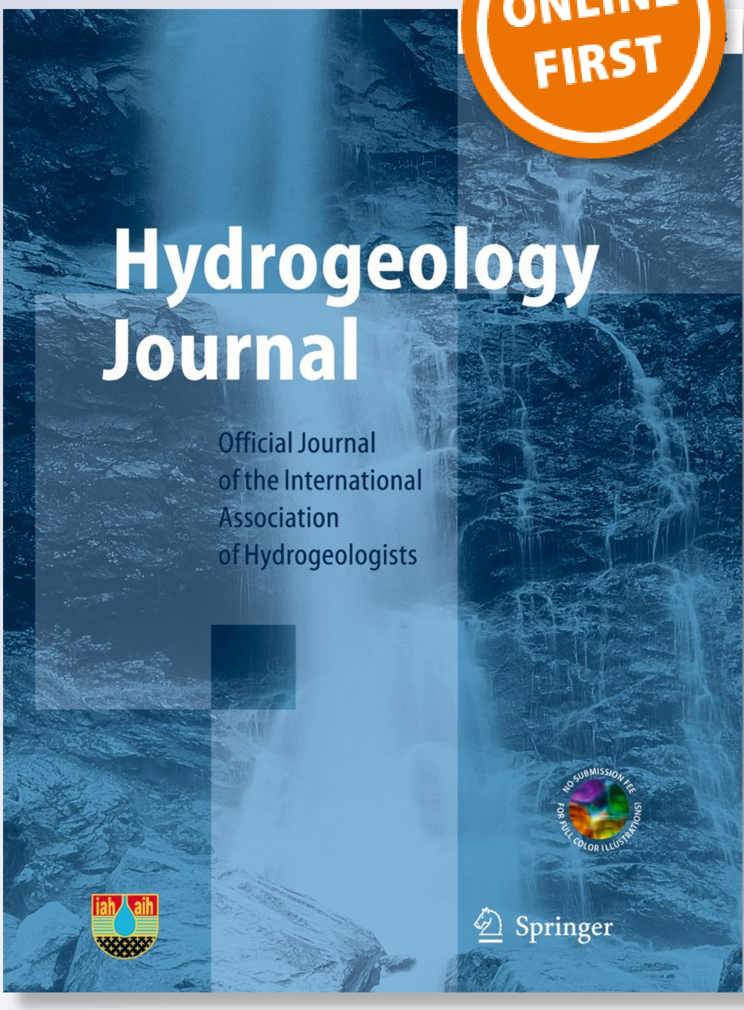

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PAPER

Hydrogeological characterization and environmental effects of the deteriorating urban karst groundwater in a karst trough valley: Nanshan, SW China

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Abstract

The unique hydrogeology of karst makes the associated groundwater respond quickly to rainfall events and vulnerable to anthropogenic pollutions. In this study, high-frequency monitoring of spring discharge, temperature, electrical conductivity (EC) and pH, along with monthly hydrochemical and microbial analyses, was undertaken at the outlet of Laolondong karst underground river in Nanshan, southwestern China. The aim was to explore the environmental effects of the catchment's urban area on the karst groundwater resources. The monitoring data of a tracer test and the response of discharge to rainfall events demonstrate that conduits and narrow fissures coexist in the Laolongdong karst aquifer. The EC, Na^+, Cl^- and SO_4^{2-} values (840 μS/cm, 33.7, 38.6 and 137.2 μg/L, respectively), along with high concentrations of fecal coliform bacteria, at the outlet indicate considerable urban pollution in this area. The contaminants sulfate and nitrate showed different relationships with discharge and EC in different stages of a rainfall event. This behavior provided information about aquifer structure and the influence of transport properties. Meanwhile, the hydrological processes of groundwater flow could be modified by urbanization and result in increasing magnitude of urban floods in the underground river. In addition, sulfuric and nitric acids introduced by urbanization not only impact the karst groundwater quality, but also result in a significant perturbation to the carbon cycling system in the karst area.

Keywords Urban groundwater · Contamination · Hydrochemistry and microbial characteristics · Karst · China

Introduction

Groundwater in karst aquifers is one of the major fresh water sources for the world's population; however, these aquifers are considered highly vulnerable to contamination due to their unique geological and hydrological structure, which results in rapid transport of pollutants in their conduit systems (Yuan 1997; Ford and Williams 2007; Pronk et al. 2009). Hydrochemical analysis of karst water (at the outlet of the system) has been used to reveal karst flow properties and further understand the vulnerability of this natural resource under anthropogenic influence (Grasso and Jeannin 2002; Doctor 2008). A number of studies have been carried out using different parameters—hydraulic, chemical, physical, microbial and isotopic—to explore the karst systems and structural information and to quantify water resources (Valdes et al. 2007; Li et al. 2010). Among them, tracers are almost always used to gain information on the physical, chemical and biological processes controlling the fate and transport of contaminants in karst. These tracers can be naturally occurring, e.g. isotopes (Katz et al. 2001; Jiang et al. 2009), specific conductance (Ryan and Meiman, 1996) and suspended sediment (Massei et al. 2002; Pronk et al. 2006), or artificially made and injected into the aquifer, e.g. dye (Quinlan 1989; He et al. 2010).

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There are three types of water flow (diffuse flow, conduit flow and fissure flow) in a karst system. The temporal variations of dissolved solids, EC and water temperature depend largely on the relative proportion of these three flow components. Diffuse flow has better and longer contact with rock matrix, thereby stabilizing water temperatures and chemical compositions (Ford and Williams 2007). Not only water and solutes, but also different types or organic particles and colloids can be transported through karst systems (Pronk et al. 2009). The complex and ever-changing urban environments make it difficult to identify individual recharge sources and pathways, and to estimate their contributions to the overall groundwater balance (e.g. Barret et al. 1999). Modern city construction includes paving roads/parking lots and buildings and these can decrease groundwater recharge by lessening the percolation areas (Kondoh and Nishiyama 2000), or there can be increasing recharge through park irrigation as well as leaking water-supply and sewage networks (Schot and van der Wal 1992).

This study aims to investigate whether some characteristics (e.g. EC, hydrochemistry, microbial contamination) of the karst groundwater can be largely changed under the influence of natural processes and urbanization, to investigate the temporal variations of discharge and water chemistry in response to recharge events. To achieve these goals, monthly sampling through a hydrological year took place between 2015 and 2016 (samples for microbial analysis were taken in 2014) at the outlet of Laolongdong karst underground river in southwestern China. The response of natural parameters to a storm event at the outlet in July 2015 was also monitored.

The study area

The area of Chongqing Municipality is about 82,400 km^2, 36.5% of which is covered by carbonate rocks where karst groundwater supplies 73% of the total groundwater resources (Pu et al. 2009). Laolongdong karst catchment (LKC) is located between 106°34′15″ and 106°36′29″ E, 29°28′28″ and 29°34′30” N, at the center of Chongqing, with an area of 12.6 km^2 (Fig. 1). The catchment is in the subtropical warm,

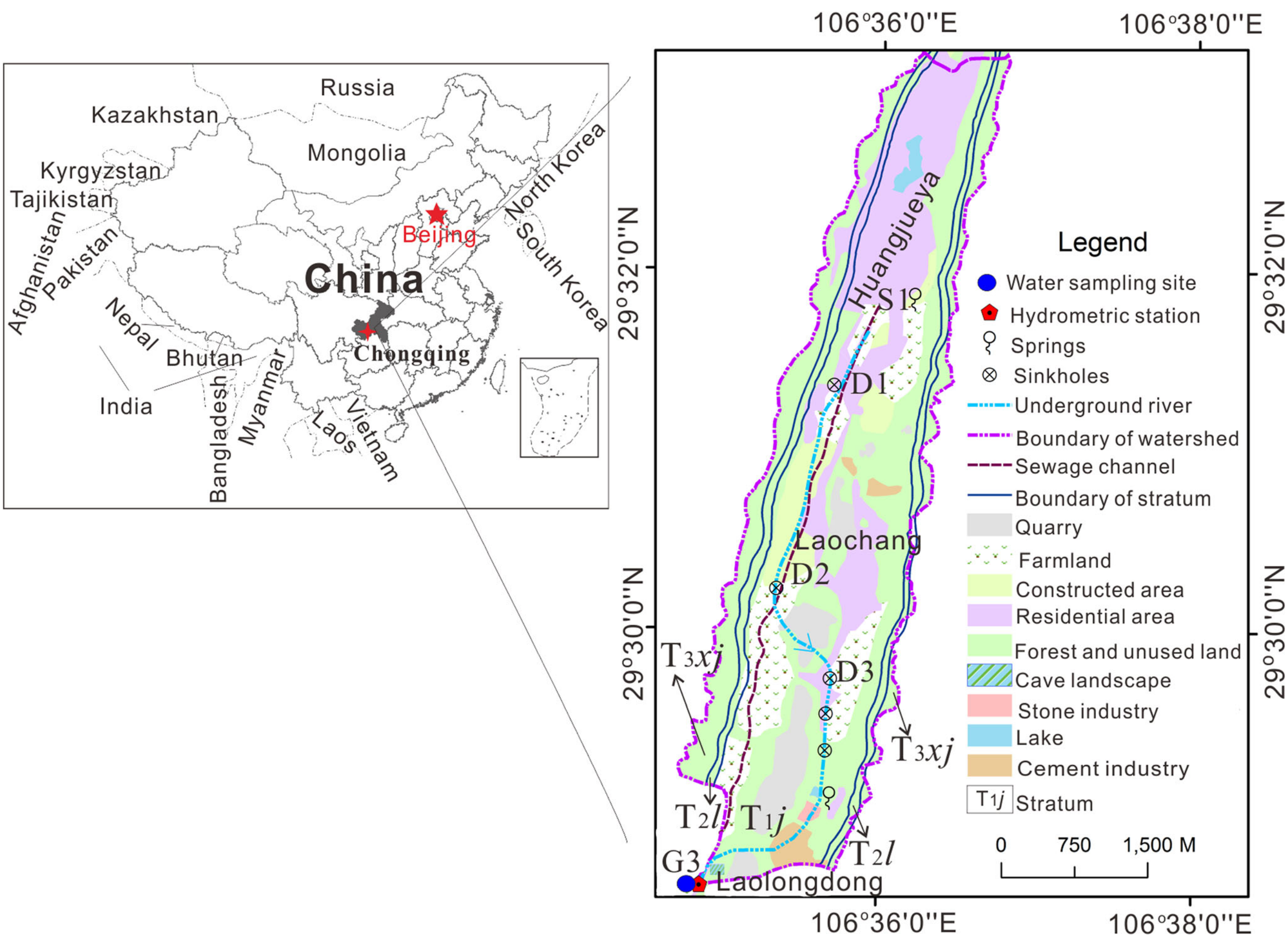

Fig. 1 The location, geology, land use and sampling/test sites in Laolongdong karst catchment

moist climatic zone, affected by the Asian monsoon. The average annual precipitation is 1,100 mm, and the average annual air temperature is 18.5 °C. Rainfall in the wet season (from May to September) accounts for 80% of the total annual precipitation. The evergreen wide-leaf forests dominate the vegetation cover.

The LKC is located on the Nanwenquan anticline, a typical karst valley that extends towards the north–south. Regional bedrocks are Middle and Lower Triassic Jialingjiang Formation (T_1j) and Leikoupo Formation (T_2l), light gray to dark gray limestone and dolomite (Fig. 1), which comprise the main karst aquifer. Additionally, on either side (the western and eastern wing) of the LKC is Upper Triassic Xujiahe Formation (T_3xj) containing feldspar-quartz sandstone, siltstone, mudstone and thin coal layers that overlie carbonate strata according to the geological survey (Fig. 2). In the anticline core, many vertical patulous fissures are developed in the Triassic carbonate rocks, providing basic conditions for the development of karst depressions, fissures, shafts and sinkholes where rainwater and surface water quickly drain through to the karst aquifer with minimal filtration (Pu et al. 2014).

The Laolongdong karst underground river flows towards the south and has a length of 6 km, with the elevation of the outlet at 379 m above sea level in air-filled Laolongdong Cave. The multi-annual mean discharge is approximately 50–80 L/s, with the maximum 13 m^3/s and the minimum 0.6 L/s. The percentages of land use in 2016 were 41.7% for urban, 16.8% for industry, 22.1% for agriculture and 19.4% for forest, respectively. The population in the LKC is densely distributed, approximately 60,000 in total, 60% of which is concentrated near the upstream depression area. Leaking or overflowing sewage from the surface channel often drains rapidly through sinkholes, fissures or shafts into the karst aquifer with little or no filtration. Groundwater from karst aquifer in LKC was the main water supply for local people, and it served as drinking water until the early 1990s. By the end of the 1990s, the surface ecosystems of the catchment were greatly disturbed by human activities such as the urban construction and quarrying operations; consequently, the karst groundwater had degraded rapidly. A series of investigations on the karst hydrological structure, hydrochemical characteristics (Pu et al. 2014), metal pollution (Ren et al. 2015), organic pollution (Xie et al. 2016) and microbial pollution (Lan et al. 2014; Zhang et al. 2016) have been carried out in the LKC over the last 9 years, showing a serious contamination problem in the study area. A channel for sewage collection and treatment was built in the upper part of catchment to lower the threat of contamination in 2014. However, the dumping of raw sewage from some local residential areas still scattered in the catchment, in addition to leaking sewage from the channel, is leading to continuous deterioration of groundwater quality.

Sampling and methods

The continuous monitoring of precipitation, groundwater temperature, EC, pH and water level (precision: 0.1 mm, 0.01 °C, 1 μS/cm, 0.01 pH, and 0.1 cm) occurred during June and July 2015 with a frequency of 15 min. The discharge was obtained according to regression equation:

$$Q = 1.085 \times L^2 - 7.589 \times L - 5.675 \left(R^2 = 0.922, p < 0.001\right) \quad (1)$$

where Q is discharge (L/s); and L is monitored water level (cm).

The Laolongdong karst underground river developed along the north–south valley that constrains the boundary of the catchment (Fig.1). Tracer tests were carried out in May and July in 2012. The tracers (uranine and Tinopal CBS-X) were injected at sites D1, D2, D3 (swallow holes) and recovered at site G3 using a flow-through field fluorimeter (GGUN-FL30) with a frequency of every 5 min (Fig.1). The precision for uranine and Tinopal CBS-X analyses were 0.01 and 0.02 μg/L, respectively. The tracers were carried by natural flowing water to the active conduits and received at the outlet of Laolongdong karst underground river (G3).

Groundwater samples for investigating the hydrogeochemical characteristics were collected monthly during 2015–

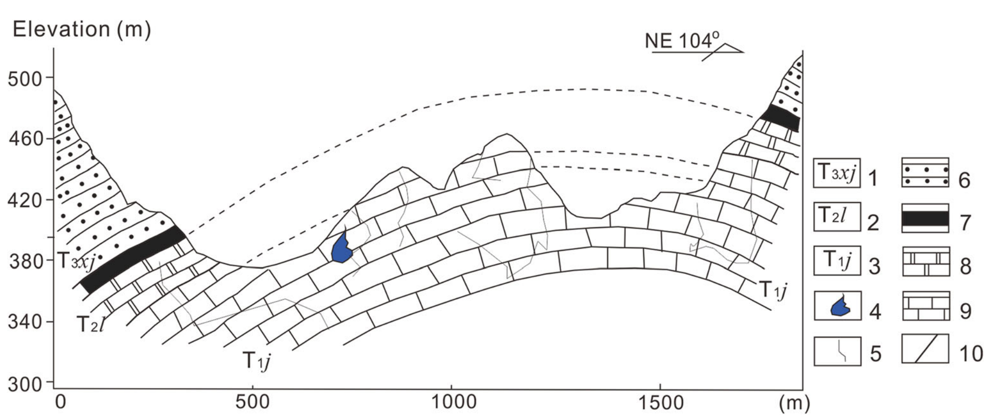

Fig. 2 Cross-section of Laolongdong karst catchment: 1 = T_3xj, 2 = T_2 l, 3 = T_1j, 4 = caves, 5 = fissures, 6 = sandstone, 7 = coal, 8 = dolomite, 9 = limestone, 10 = boundary of strata

2016 at G3, and rainwater samples from the rainy season (April to September 2015) were collected from a meteorological station fixed on the roof of a building at G3. The researchers also monitored hydrochemical parameter changes responding to a rainstorm at G3 in the LKC catchment during 22–26 July 2015. Environmental parameters—water temperature, EC, pH, dissolved oxygen (DO)—were measured in the field using a HQ340d multi-parameter measurer. The precision was 0.1 °C, 1 μS/cm, 0.01 pH, and 0.1 μg/L, respectively. Water was sampled and filtered through 0.45-μm cellulose acetate membrane filters. Samples for cation analysis were placed in 50-ml polyethylene bottles and 1:1 HNO_3 added. Anion samples were also collected in 50-ml polyethylene bottles. All samples were stored in a fridge at 4 °C before pretreatment and instrumental analysis. HCO_3^- and Ca^{2+} with a precision of 0.1 mmol/L and of 2 μg/L were titrated in the field using a portable testing kit produced by Merck KGaA Co. (Germany). Other major cations (K^+, Na^+ and Mg^{2+}) were measured by ICP-OES (Optima 2100DV, Perkin-Elmer Co., USA) and other major anions (SO_4^{2-}, Cl^-, NO_3^- and PO_4^{3-}) were measured using ion chromatography, following US Environment Protection Agency (EPA) standard methods. Precision for all anion and cation analyses was 0.01 μg/L. These analyses were completed in Chongqing Key Laboratory of Karst Environment, China.

The water samples (100–400 ml) for microbial analysis were taken in 2014, underwater and without air, using microbial sampling bags (Labplas, Canada) and stored at 4 °C. Bacterial inoculation and cultivation (fecal coliform, total coliform, fecal streptococcus and total bacteria) took place in the laboratory on the same day, followed by the number counting 24 h later. The cultivated media were MFC (Microbial Fuel Cell), Fuchsin Basic Sodium Sulfite Agar, KF and R2A, separately. The temperature was set at 42.7 °C for fecal coliform cultivation, and 37.4 °C for the remaining bacteria.

Results

Hydraulic connection of the Laolongdong karst underground river and the discharge response to rainfall events

About 10–100 h after the injection, the concentrations of tracers started to increase simultaneously and the peak for each site stayed for about 3–80 h before going back to the previous level. The graph of tracer concentration vs. duration time obtained from site G3 demonstrates a discrete flow (mixture of conduit flow and fissure flow) path and hydraulic connections among these sites (Lan et al. 2014), with remarkably little retardation, providing proper conditions for transporting solutes and contaminants rapidly in the underground river.

The biggest flood caused by rainfall occurred in June to July 2015. During these 2 months, the river discharge responded fast to rainfall events, leading to a high amount of discharge in the catchment, e.g. during a rainstorm on 22 July, the discharge increased rapidly from baseflow (<100 L/s) to ~2,000 L/s in several hours and reduced gradually to the normal flow in the following 5–10 days (Fig. 3).

During rainstorms, rainwater went into the karst system and dissolved carbonate rocks. In response, the river discharge increased rapidly in a short time and EC reduced due to higher velocity and the least duration of water–rock contact (Fig. 3). This phenomenon is commonly found elsewhere, i.e. Liangdiantang Spring (Li et al. 2008) and Gihon Spring (Amiel et al. 2010). As shown in Fig. 3, the responding discharge was at its maximum 3.5 h behind the maximum amount of rainfall. It showed a rapid increase of discharge when the rainfall event began, indicating hydrodynamic characteristics of conduit flow. During the storm event, the EC values began to fluctuate within 8 h and then continued to decrease as pulses of rain entered into the system. The difference between the initial and minimum EC in response to the storm was 150 μS/cm. The lowest EC troughs occurred 27–30 h after the beginning of the rainfall event, and they were delayed compared with the discharge peaks, confirming the delayed arrival of the new recharge water. This phenomenon could be attributed to the "older water" that existed as preceding baseflow and the EC/temperature/pH only began to decrease with the delayed arrival of the new recharge water that was less mineralized due to the flow's short residence time. After the rainfall events, the EC gradually returned to its previous state, the duration and strength of which could be partially explained by the degree of karstification in the aquifer, the temporal variations of rain intensity, spatial rainfall uniformity and lapse time between storms (Amiel et al. 2010). This pattern was characterized in double porosity aquifers that consisted of large karstified conduits and narrow fissures (Bakalowicz 2005; Amiel et al. 2010).

The flow moved fast with reducing temperature during the rainstorm, resulting in more fluctuated temperature variations, and the low temperature values only lasted for a short time due to the small area of the open-system catchment (Figs. 1 and 3). The following increase of water temperature after rainfall appeared to be associated with the temperature of surrounding rocks.

The storm event not only implied that the highly efficient transport of recharge through the aquifer was by the conduit system, but also the contaminants that were released from the aquifer matrix were delivered to the spring as the discharge increased. The variations of sulfate in the underground river showed response to the storm similar to the EC curve (Fig. 3). The nitrate variations in the underground river were largely different to the discharge or EC variations, which might be

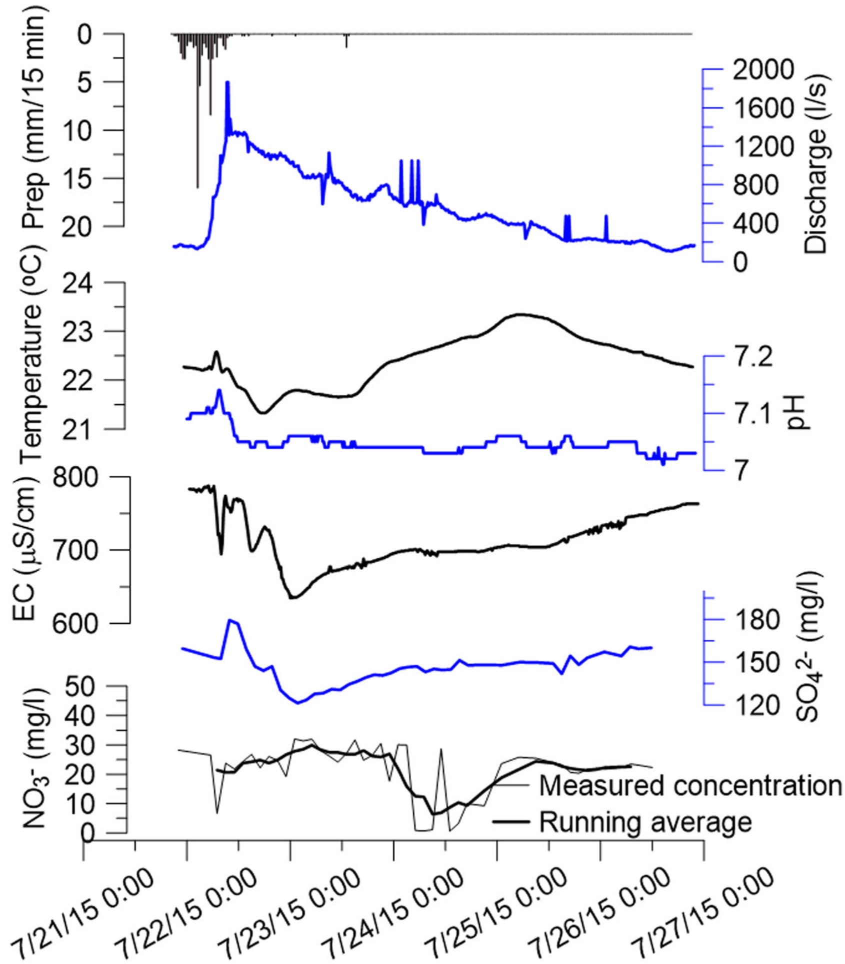

Fig. 3 Results of the high-frequency sampling for hydrochemical parameters in Laolongdong underground river during a rainstorm in July 2015

related to changes of transport conditions as the rainwater entered the underground river.

Hydrogeochemical properties

The mean monthly water temperature ranged between 17.6 and 22.8 °C with a mean value of 20.0 ± 1.0 °C, with less fluctuation compared with air temperature (18.5 ± 7.2 °C). This indicates the effect of rock structure and formation, which moderate the changing magnitude of groundwater temperature based on rock temperature, aquifer structure and residence time. The pH ranged from 6.9 to 7.4, mean 7.1 ± 0.1. EC ranged from 750 to 996 µS/cm with a mean of 894 ± 67 µS/cm. The highest EC peaks occurred in winter, while the minimum appeared in September (Table 1; Fig. 4).

In the sampling year, the dominant dissolved ions are Ca^{2+} (117 ± 5 µg/L), followed by Na^{+} (33.7 ± 15.4 µg/L), Mg^{2+} (16.2 ± 2.7 µg/L) and K^{+} (13.5 ± 3.7 µg/L). The main dissolved anions are HCO_3^{-} (5.0 ± 0.8 mmol/L), SO_4^{2-} (137.2 ± 25.9 µg/L), followed by Cl^{-} (38.6 ± 10.6 µg/L), NO_3^{-} (16.0 ± 9.7 µg/L) and PO_4^{3-} (1.1 ± 0.8 µg/L). Thus, the hydrochemical type of the groundwater is HCO_3-SO_4-Ca. Ca^{2+}, Mg^{2+} and HCO_3^{-} are mainly from carbonate rock dissolution in natural karst system (White 1988). Water samples had nitrate concentration exceeding background concentrations for groundwater around the world (2–3 µg/L) reported by Madison and Brunett (1985). Meanwhile, as shown in Fig. 4, the concentrations of NO_3^{-} and SO_4^{2-} in groundwater tended to increase in the rainy season, showing reverse trend to the variations of Cl^{-}, PO_4^{3-}, DO and EC (Fig. 4).

As shown in Table 1, rainwater had lower pH values, ranging from 5.1 to 5.5, typically characterized by acid rain. Concentrations of SO_4^{2-} and NO_3^{-} in rainwater ranged from 5.1 µg/L to 15.4 µg/L with a mean of 9.1 µg/L, and 1.3 µg/L to 6.3 µg/L with a mean of 3.4 µg/L, respectively. Other ion concentrations were very low in rainwater.

Microbial contamination

In the Laolongdong karst underground river, the total bacteria (TB) fluctuated from 3760 to 2.92×10^7 (mean 2.85×10^6) CFU/100 ml, and the total coliform (TC) ranged from 540 to 2.65×10^5 (mean 2.70×10^4) CFU/100 ml. The fecal coliform and fecal streptococcus (FC and FS) concentrations were

Table 1 The hydrogeochemical characteristics of groundwater and rainfall in LKC

Time (year.month)	Temp (°C)	DO (μg/L)	pH	EC (μS/cm)	K^+ (μg/L)	Na^+ (μg/L)	Ca^{2+} (μg/L)	Mg^{2+} (μg/L)	HCO_3^- (mmol/L)	SO_4^{2-} (μg/L)	NO_3^- (μg/L)	Cl^- (μg/L)	PO_4^{3-} (μg/L)	SIc
Groundwater														
2015.3	18.7	0.0	7.3	996	20.1	66.0	114	21.0	6.7	91.8	4.4	52.9	2.9	0.38
2015.4	19.2	2.2	7.1	885	18.7	52.1	122	19.3	4.7	156.5	17.5	38.2	0.6	0.21
2015.5	20.0	1.4	7.0	885	18.5	54.2	116	19.1	4.8	169.3	10.6	47.0	1.0	−0.06
2015.6	21.3	2.7	7.0	791	14.0	26.8	124	17.0	3.7	174.1	27.5	29.8	0.3	0.23
2015.7	22.3	2.4	7.1	788	13.0	24.4	112	17.5	4.3	159.5	28.3	29.4	0.5	0.47
2015.8	22.8	3.4	–	717	13.4	21.6	108	15.4	5.9	154.6	22.2	24.8	0.1	−0.13
2015.9	20.5	2.8	6.9	783	10.8	21.7	118	15.8	4.2	141.5	30.9	26.4	0.5	−0.17
2015.10	20.7	2.2	7.0	783	9.0	18.9	122	12.5	4.5	137.7	15.7	29.7	0.7	0.03
2015.11	20.2	0.3	7.1	848	10.2	28.1	115	13.2	5.3	103.6	2.1	52.7	2.2	0.24
2016.1	18.5	0.0	7.1	900	11.3	34.9	112	13.5	5.8	104.7	0.9	52.7	2.1	0.39
2016.2	17.6	1.3	7.0	876	n.d	n.d	120	n.d	5.6	125.4	14.3	46.2	0.9	0.15
2016.3	17.8	1.6	7.4	799	9.7	21.8	126	13.4	5.0	127.7	17.7	33.0	0.9	0.28
Mean	20.0	1.7	7.1	838	13.5	33.7	117	16.2	5.0	137.2	16.0	38.6	1.1	0.33
Standard error	1.0	1.1	0.1	72	3.7	15.4	5.0	2.7	0.8	25.9	9.7	10.6	0.8	0.16
Rain water														
2015.4	16.4	8.5	–	71	0.4	0.4	10	0.2	–	13.0	4.0	0.2	0.0	–
2015.5	19.2	8.9	5.3	54	0.5	0.6	10	0.3	–	9.8	6.3	2.2	1.8	–
2015.6	21.2	8.3	5.5	39	1.4	0.5	4	0.2	–	5.1	3.6	1.7	0.4	–
2015.7	22.4	8.2	5.1	17	1.0	0.4	1	0.0	–	5.7	3.1	1.1	0.0	–
2015.8	22.6	8.0	–	17	1.6	0.4	1	0.0	–	5.3	1.3	0.4	0.2	–
2015.9	16.9	7.7	–	21	0.34	0.4	2	0.1	–	15.4	2.2	5.3	0.2	–
Mean	19.8	8.3	–	36.5	0.9	0.4	4.7	0.1	–	9.1	3.4	1.8	0.4	–

much lower, ranging from 25 to 2300 (mean 686) CFU/100 ml and from 2 to 280 (mean 69) CFU/100 ml, respectively. FC content was overloaded in every month (the national standard <0.00 CFU/100 ml). No seasonal trends of microbial variations were observed in an annual cycle of 2014 (Table 2; Fig. 5).

Discussion

Urban contributions to the hydrogeochemistry and microbial contamination of Laolongdong underground river

Table 3 compares the values of groundwater hydrochemistry between Laolongdong and Qingmuguan groundwater (20 km NW of LKC) which has similar geologic and climatic background to LKC, but with different dominant land-use type (agriculture and forest land in Qingmuguan karst catchment). The obvious differences in groundwater hydrochemistry between Laolongdong and Qingmuguan groundwater were observed, of which Laolongdong groundwater showed higher temperature, EC, K^+, Na^+, SO_4^{2-}, PO_4^{3-} and Cl^- than those in Qingmuguan groundwater.

Concentrations of K^+, Na^+, SO_4^{2-}, Cl^- and PO_4^{3-} in Laolongdong groundwater were three times more than those in Qingmuguan groundwater, indicating that the high solute concentrations in Laolongdong groundwater are attributed to anthropogenic pollution in the urbanized area. The high Na^+ and Cl^- contents in Laolongdong groundwater, compared with those from Qingmuguan carbonate aquifers, should not be attributed to marine salt, because of the long distance from the coast and low amount of salt in rainfall (Table 1), which also explained the lower concentration of Cl^- in groundwater in the rainy season (Fig. 4). Urban anthropogenic pollution such as the use of salt in restaurants and laundry detergent, are the most likely origin of Cl^- in the LKC. The high concentration of SO_4^{2-} in Laolongdong groundwater, compared with Qingmuguan groundwater, could be attributed to urban anthropogenic pollution (i.e. laundry detergent and human waste) and acid rain. While agricultural activities (the use of nitrogen fertilizers) are likely to be responsible for the relatively high NO_3^- concentration in Qingmuguan groundwater. However, this is not saying that nitrate contamination is less serious in Laolongdong groundwater, where the changes of

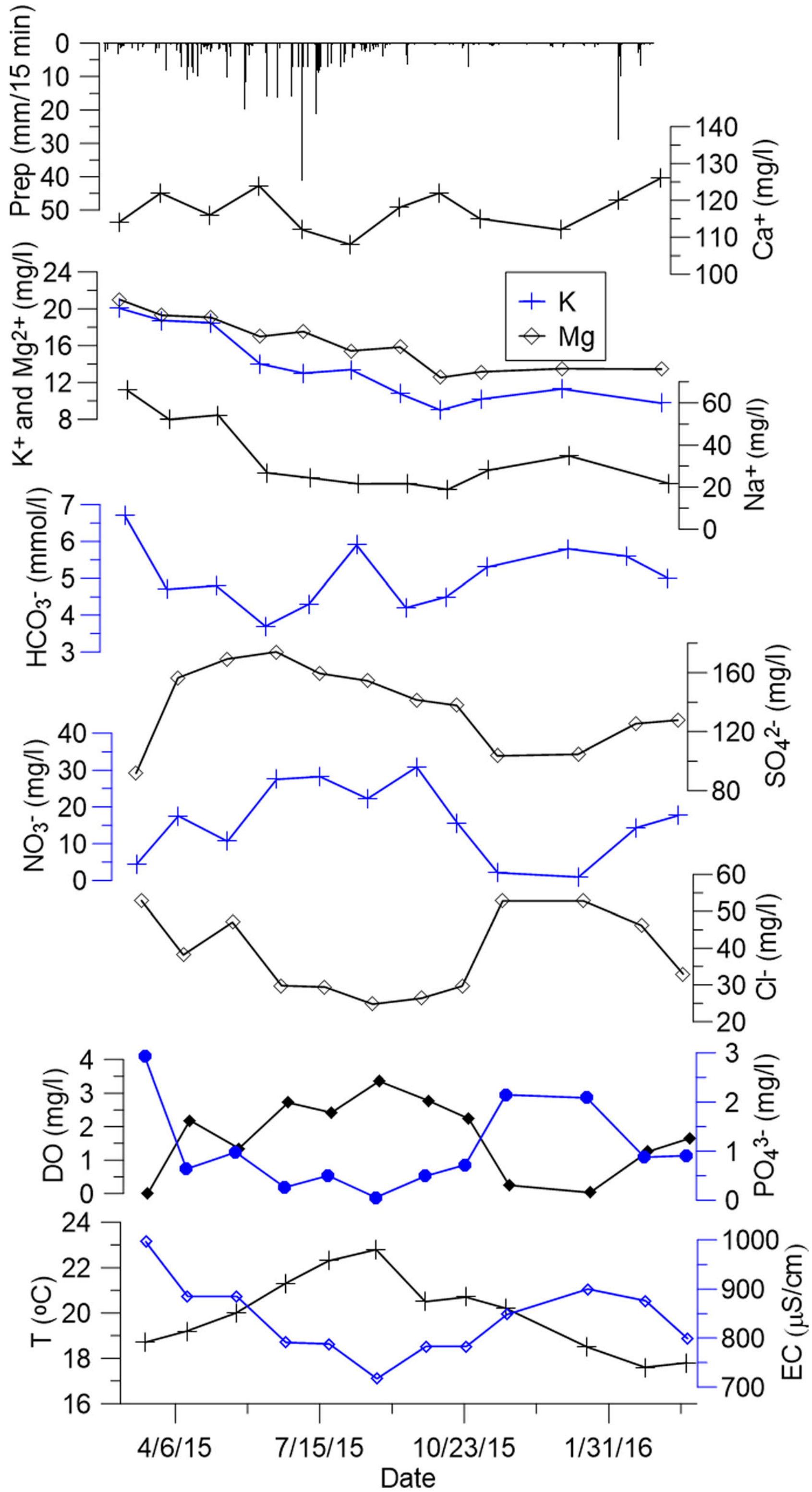

Fig. 4 Monthly variations of the hydrogeochemical characteristics of groundwater

redox conditions (lower DO concentrations) have resulted in reduction of nitrate. As shown in Fig. 3, with the increase of discharge, the NO_3^- concentration of groundwater increased rapidly from 22 to 30 μg/L in a short time during a rainstorm, suggesting that the higher NO_3^- concentration of groundwater might be attributed to sewage and animal feces that had been stored in the aquifer but released into the groundwater with the rainwater infiltration. In addition, changes of environmental

Table 2 The microbial contamination and source indicator in LKC

Time (year.month)	Total bacteria (CFU/ 100 ml)	Total coliform (CFU/ 100 ml)	Fecal coliform (FC) (CFU/ 100 ml)	Fecal streptococcus (FS) (CFU/ 100 ml)	FC/ FS
2014.1	45,800	7,900	4,380	15	288.9
2014.2	3,760	540	45	3	18.0
2014.3	573,000	2,200	150	33	4.5
2014.4	325,000	550	27	6	4.2
2014.5	1,650,000	20,000	100	8	12.8
2014.6	1,192,500	3,000	45	8	5.8
2014.7	13,900	1,135	151	12	12.2
2014.8	29,200,000	265,000	2,300	98	23.5
2014.9	65,500	11,825	525	120	4.4
2014.10	758,250	2,828	25	280	0.1
2014.11	220,000	3,100	144	116	1.2
2014.12	122,250	6,700	345	124	2.8

conditions, e.g. the increased temperature and DO content could prevent denitrification, a process by which the microbes convert nitrate in the water into nitrogen gas, which is then released into the atmosphere. Thus, the nitrate contamination should not be ignored in the Laolongdong underground river.

Concentrations of total bacteria and total coliform in the Laolongdong karst underground river reached 2.92×10^7 and 2.65×10^5 CFU/100 ml, respectively, showing serious microbial contamination. The FC/FS ratio was proposed to distinguish fecal sources (Gourmelon et al. 2007; Ahmed et al. 2013): ≥4 is human feces; ≤0.7 is from warm-blood animals; 2 < FC/FS < 4 is mixed sources in which human feces dominates; 0.7 < FC/FS < 1 is mixed sources in which animal feces dominate. The results of this study show that Laolongdong groundwater was mainly contaminated by human feces most of the year with high FC/FS ratios due to the influx of human sewage (>4 from January to September; Table 2). In contrast, the less serious contamination from October to December might be due to reduced frequency and strength of rainfall as well as the preliminary effects of sewage treatment in the recharge area of Laolongdong karst underground river.

Effects of urbanization on the hydrological processes of groundwater

In LKC, the Jialingjiang Formation (T_1j) and Leikoupo Formation (T_2l) are the main aquifers that receive groundwater recharge (Fig. 2). The relatively slow recession curves demonstrate that Laolongdong karst underground river is likely to be in an aquifer containing large conduits and narrow fissures (Fig. 3). As the population grows and the road networks and housing develop, urbanization not only impacts the groundwater quality, but also contributes to changes in the hydrological cycle. The increase in area of impervious or hard surfaces could decrease the amount of water that soaks into the groundwater system and increase the amount of surface runoff. Thus, the peak flows of storm water could be larger and arrive earlier, and result in increasing magnitude of urban floods in the underground river (Fig. 3). In the rainy season, surface flow through sink holes could be the main groundwater recharge mechanism. However, in the dry season, the sinkholes might contribute less to the discharge and the water could stay in the soil and fissures for a long time before being

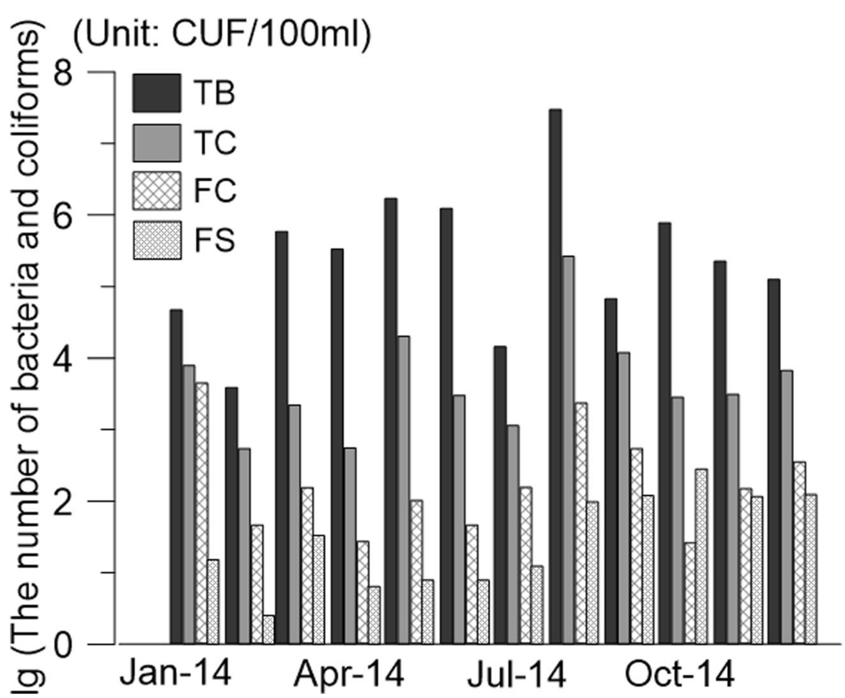

Fig. 5 Monthly variations of the fecal microbial indicators in groundwater

Table 3 The mean values of groundwater hydrochemistry at Laolongdong and Qingmuguan

Spring name	Temp (°C)	DO (μg/L)	pH	EC (μS/cm)	K^+ (μg/L)	Na^+ (μg/L)	Ca^{2+} (μg/L)	Mg^{2+} (μg/L)	HCO_3^- (mmol/L)	SO_4^{2-} (μg/L)	NO_3^- (μg/L)	Cl^- (μg/L)	PO_4^{3-} (μg/L)
Laolongdong	20.0	1.7	7.1	838	13.5	33.7	117	16.2	5.0	137.2	16.0	38.6	1.1
Qingmuguan*	18.6	7.6	7.3	611	3.2	5.2	125	16.7	5.2	47.9	22.2	8.5	0.4

*The data of Qingmuguan groundwater cited from He et al. 2010

transported into the underground river. A rainfall event occurred in 2011 and was monitored by Cao (2012); this showed that the response curve of the water level of the underground river to rainfall was generally ladder-shaped. In contrast, the discharge fluctuation curve was pyramid-shaped with a long tail (Fig. 3). On one hand, the different shapes reflected different flow patterns, for example, the flood in 2015 reflected conduit flow that responds fast to rainfall and the flood in 2011 revealed fissure and diffuse flow that was developed from a less karstified area and responded slowly to recharge water (Felton and Currens 1994; Zhou 1995). On the other hand, the sharp and fluctuated discharge curve in 2015 might be related to increased runoff in the urbanized area; however, it is difficult to distinguish how much the runoff from the urbanized area actually contributed to the underground river because the amount of rainfall in 2011 was just a half of that in 2015, which might also be responsible for the difference of discharge fluctuations. As indicated by some studies, groundwater depletion has been reported as a global problem in the last 100 years, and the groundwater level has gone down in some cities (Wada et al. 2010; Haque et al. 2013); however, in the case of the carbonate aquifer system in LKC, in a humid climate where recharge is mainly precipitation and discrete flow is dominant. Groundwater depletion or increased runoff through sinkholes due to urbanization are not markedly observed or just masked by heavy rainfall. More studies have to be done to reveal the hydrological process of the underground river under the influence of urbanization in the future.

Meanwhile, the temperature of Laolongdong groundwater was 1.4 °C higher than that in Qingmuguan groundwater (Table 3) even though both groundwater temperatures were mainly controlled by atmospheric temperature, indicating that waste water (i.e. from the catering industry) with a higher temperature in the urbanization area could result in an increase of the groundwater temperature. Also, the impervious surfaces of urbanization can collect and accumulate pollutants and then those pollutants could be carried by runoff directly into the underground river through a series of sinkholes and result in deterioration of the groundwater quality.

Other implications

Urbanization brings inorganic and microbial contamination, and also induces acids (nitric and sulfuric acids) to take part in dissolving carbonate rocks in karst areas, which results in changes to the hydrochemical characteristics of the groundwater. In a natural karst system, if only carbonic acid takes part in dissolving carbonate rocks, the molar ratio of $[Ca^{2+}+Mg^{2+}]/[HCO_3^-]$ is close to 0.5 in theory (Eq. 1). However, most of the studies in recent years have shown that nitric and sulfuric acids originate from agricultural and industrial activities, which interfere with this natural process and this has resulted in changes of the $[Ca^{2+}+Mg^{2+}]/[HCO_3^-]$ ratio (Jiang 2013). The molar ratios of $[Ca^{2+}+Mg^{2+}]/[HCO_3^-]$ of groundwater samples are deviated from 0.5, and close to 1, indicating other acids (such as nitric and sulfuric acids, Eqs. 2 and 3) besides carbonic acid have dissolved the carbonate rocks (Fig. 6)—for example, high NO_3^- and SO_4^{2-} concentrations in the groundwater during rainy season (Table 1) indicate that nitric and sulfuric acids from rainfall might be one of the important sources of NO_3^- and SO_4^{2-} in the karst underground river. This assumption is confirmed by the fact that groundwater samples collected during the rainfall event were located closer to the 1:1 line (Fig. 6),

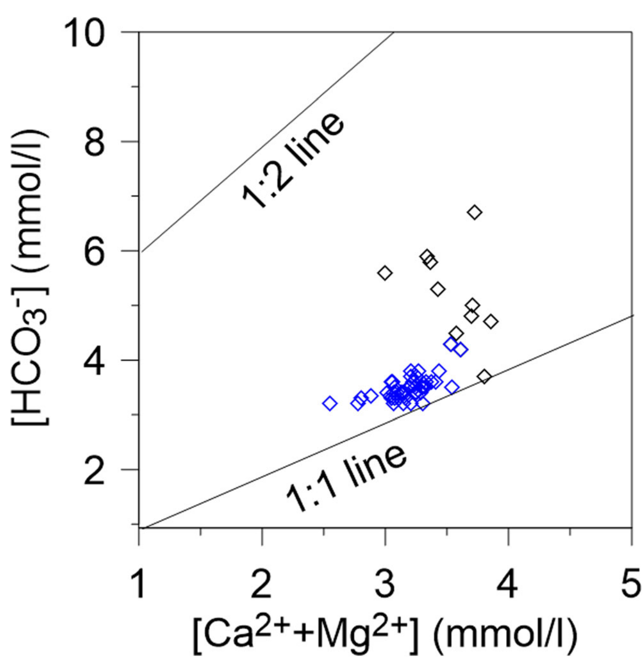

Fig. 6 The covariation of $[Ca^{2+}+Mg^{2+}]$ vs. $[HCO_3^-]$ in groundwater during 2015–2016. (The samples marked in blue were collected during the rainstorm)

and there is much closer correlation between SO_4^{2-} and NO_3^- ($R^2 = 0.64$, $p < 0.05$, Table 3).

$$Ca_{(1-x)}\,MgCO_3 + H_2O + CO_2 \rightarrow (1-x)\,Ca^{2+} + xMg^{2+} + 2\,HCO_3^- \quad (2)$$

$$\left(Ca_{(1-x)}\,Mg_x\right)CO_3 + HNO_3 \rightarrow (1-x)\,Ca^{2+} + xMg^{2+} + NO_3^- + HCO_3^- \quad (3)$$

$$2\left(Ca_{(1-x)}\,Mg_x\right)CO_3 + H_2SO_4 \rightarrow 2\,(1-x)\,Ca^{2+} + 2xMg^{2+} + SO_4^{2-} + 2HCO_3^- \quad (4)$$

Conventionally, the DIC in karst groundwater is mainly derived from carbonate dissolution by carbonic acid, which forms from the reaction of soil or atmospheric CO_2 with water, and is believed to be a major control on atmospheric carbon dioxide (CO_2) concentrations over geologic time, because half of DIC in groundwater is derived from the soil or atmospheric CO_2. The data in this paper indicated that carbonate was dissolved by sulfuric and nitric acids introduced by urbanization and resulted in a significant increase in the export of DIC, rather than from the CO_2 sequestration within a karst underground river system. These increasing DIC concentrations were related in large part to land disturbance activities as opposed to variations in geology. Furthermore, when the carbonate was attacked by protons (sulfuric and nitric acids), the nitrate and sulfate concentrations in the karst groundwater could be elevated. Urbanization is fairly widespread and elevated nitrate and sulfate concentrations are found frequently in karst systems, and therefore it is likely that these observations can be applied to most karst systems, suggesting that urbanization results in a significant perturbation to the cycling and export of inorganic carbon and groundwater quality. As a consequence, the amount of soil or atmospheric CO_2 consumed by carbonate weathering is reduced when sulfuric and nitric acids are involved, and thus the drawdown of CO_2 by carbonate weathering could be overestimated by previous research in karst areas.

Conclusions

In the karst aquifer of Laolongdong, a tracer test and rainfall-induced discharge observations indicate that large conduit flow and narrow fissure flow coexist in this catchment, and karst waters can travel swiftly through the aquifer with few filtering processes. Thus, the groundwater becomes particularly vulnerable to urban contamination. The urbanized recharge catchment of the Laolongdong groundwater greatly affects the hydrogeological characteristics of this karst river. The dominant dissolved ions found in the Laolongdong karst underground river, along with high concentrations of SO_4^{2-}, NO_3^-, fecal coliform bacteria and high electrical conductivity, point to the significant impact of anthropogenic activity in the spring catchment on the groundwater quality. The results also showed that Laolongdong karst underground river was mainly contaminated by human feces most of the year. The hydrochemical facies of the groundwater, resulting from urbanization, were characterized by HCO_3-SO_4-Ca type in the LKC. Meanwhile, urbanization could modify the hydrological processes of groundwater and result in the increasing magnitude of urban floods from the underground river; however, further studies are needed to reveal the effects of the urbanized area on the hydrological processes due to the complicated karst system. It is difficult to distinguish the scale of changes in the groundwater system caused by natural processes (rainfall) or urbanized areas (surface runoff through sinkholes). A more important finding is that sulfuric and nitric acids introduced by urbanization not only impact the karst groundwater quality, but also result in a significant perturbation to the carbon cycling in karst areas.

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