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ADSORPTIVE BEHAVIOUR OF ARSENIC IN A KARST SUBTERRANEAN STREAM AND PRINCIPAL COMPONENTS ANALYSIS OF ITS INFLUENCING VARIABLES: A CASE STUDY AT THE LIHU SUBTERRANEAN STREAM, GUANGXI PROVINCE, CHINA

ADSORPCIJSKO OBNAŠANJE ARZENA V KRAŠKIH PODZEMNIH TOKOVIH IN ANALIZA GLAVNIH KOMPONENT SPREMENLJIVK, KI VPLIVAJO NANJ: PRIMER PODZEMNEGA TOKA LIHU, PROVINCA GUANGXI, KITAJSKA

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Abstract UDC 551.444:546.19(510)

Yang Hui & Zhang Liankai: Adsorptive behaviour of arsenic in a karst subterranean stream and principal components analysis of its influencing variables: A case study at the Lihu subterranean stream, Guangxi province, China

Arsenic (As) pollutants are serious threat to water ecological security and human health, especially in karst areas because of their unique hydrogeological characteristics. Physical-chemical analyses of karst water and its sediments at the Lihu subterranean stream, southwest China, were conducted by ICP-MS and XRF to elucidate the reaction mechanisms of arsenic in karst subterranean streams. The results show that inorganic arsenic comprise most of the total arsenic, while organic arsenic including monomethylated arsenic (MMA) and dimethyl arsenic (DMA) are not detected or infinitesimal. The reducing environment in the subterranean stream makes As(III) dominant and accounts for 53 % of the inorganic species. Adsorptive behaviour of arsenic occurred and the removal rates of As, As(III) and As(V) in the Lihu subterranean stream are 51 %, 36 % and 59 % respectively after a 25.6 km underground distance. To find out the main influencing factors on arsenic adsorptive process in this underground river, principal component analysis in SPSS and Minitab were applied. Seven main factors, i.e. sediment Fe (Fe_{sed}), sediment Al (Al_{sed}), sediment Ca (Ca_{sed}), particulate organic matter (POM), sediment Mn (Mn_{sed}), water Ca^{2+} (Ca^{2+}) and water HCO_3^- (HCO_3^-) are extracted from thirteen indicators. The rank of those factors for total arsenic and As(III) is $Ca_{sed} > Fe_{sed} > Ca^{2+} > POM > Mn_{sed} > Al_{sed} > HCO_3^-$, while it is $Fe_{sed} > Ca_{sed} > Ca^{2+} > Mn_{sed} > POM > Al_{sed} > HCO_3^-$ for As(V). Of these seven factors, Fe_{sed}, Al_{sed}, Ca_{sed}, POM, Mn_{sed} and

Izvleček UDK 551.444:546.19(510)

Yang Hui & Zhang Liankai: Adsorpcijsko obnašanje arzena v kraških podzemnih tokovih in analiza glavnih komponent spremenljivk, ki vplivajo nanj: primer podzemnega toka Lihu, provinca Guangxi, Kitajska

Arzen (As) je nevaren onesnaževalec, ki ogroža ekološko stanje voda in zdravje ljudi; še posebej v krasu zaradi njegovih edinstvenih hidrogeoloških značilnosti. Z namenom pojasnitve reakcijskih mehanizmov arzena v kraških podzemnih tokovih so bile z uporabo ICP-MS in XRF opravljene fizikalno-kemijske analize kraške vode in sedimentov v podzemnem toku Lihu na jugozahodu Kitajske. Rezultati kažejo, da večino skupnega arzena predstavlja anorganski arzen, organski arzen, vključno z monometil arzenovo kislino (MMA) in dimetil arzenovo kislino (DMA), pa ni bil zaznan. Zaradi redukcijskega okolja v podzemnem toku prevladuje As(III), ki predstavlja 53 % anorganskega tipa. Pojavilo se je adsorpcijsko obnašanje arzena in deleži As, As(III) in As(V) so se zmanjšali za 51 %, 36 % in 59 % na 25,6 km dolgem podzemnem toku Lihu. Z namenom določitve najpomembnejših faktorjev, ki vplivajo na procese adsorpcije arzena v tej podzemni reki, je bila uporabljena anliza glavnih komponent v SPSS in Minitab. Sedem glavnih faktorjev, to so Fe v sedimentu (Fe_{sed}), Al v sedimente (Al_{sed}), Ca v sedimentu (Ca_{sed}), suspendirana organska snov (POM), Mn v sedimentu (Mn_{sed}), Ca^{2+} v vodi (Ca^{2+}) in HCO_3^- v vodi (HCO_3^-), je bilo povzeto iz trinajstih indikatorjev. Zaporedje teh faktorjev za skupni arzen in As(III) je $Ca_{sed} > Fe_{sed} > Ca^{2+} > POM > Mn_{sed} > Al_{sed} > HCO_3^-$, za AS(V) pa $Fe_{sed} > Ca_{sed} > Ca^{2+} > Mn_{sed} > POM > Al_{sed} > HCO_3^-$. Od teh sedmih faktorjev Fe_{sed}, Al_{sed}, Ca_{sed}, POM, Mn_{sed} in Ca^{2+} spodbujajo adsorpcijo, HCO_3^- pa

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Ca^{2+} are promoting factors for arsenic adsorption while HCO_3^- is an inhibiting factor. Calcium and bicarbonate turn out to be the main influencing factors for water arsenic adsorption in the study area, largely because the high calcium and alkaline values in karst water. This finding is an obvious distinction compared with the research findings at a non-karst area.

Keywords: karst subterranean stream, sediment, arsenic, influencing factors, principal component analysis.

jo zavira. V vodah proučevanega območja sta kalcij in hidrogenkarbonat glavna faktorja, ki vplivata na adsorpcijo arzena, predvsem zaradi visoke vsebnosti kalcija in alkalnosti v kraških vodah. Ta ugotovitev je značilna razlika v primerjavi z raziskovalnimi rezultati za nekraško območje.

Ključne besede: kraški podzemni tok, sediment, arzen, faktorji vpliva, analiza glavnih komponent.

INTRODUCTION

As an ubiquitous element in the environment, arsenic (As) is a carcinogen to both humans and animals. The arsenic contamination for water, air and soil is a significant environment health concern because of its toxicity (Ng *et al.* 2003). Arsenic mine drainage, a common type of pollution that forms at non-ferrous metal mining districts, is one of the most important anthropogenic arsenic sources. Gross arsenic discharged by mining activity has reached up to 72.6 % of man-made sources in the world (Han *et al.* 2003).

The arsenic storage in China is rich and it accounts for about 70 % of the world's total storage (Xiao *et al.* 2008). Guangxi province, located in southern China, reserves 41.5 % of China's total arsenic (Wei & Zhou 1992). Arsenic pollutants produced by mining, mineral processing and metal chemical process in this area have polluted the soil, vegetation, surface water and groundwater through runoff, leaching and wind transportation (Segura *et al.* 2006, Li & Su 2001, Li *et al.* 2010, Zhai *et al.* 2008). Jian *et al.* 2012 has reported that the arsenic concentration in sediments of the Diao River in northern Guangxi hit 1000 mg/kg (67 times more than the background level).

The total area of the karst globally is about 22 million km^2 and covers 15 % of the Earth's land surface (Nguyet & Goldscheider 2006). Guangxi province is just located in the world's largest karst contiguous distribution area (Li & Luo 1983). Karst aquifers are becoming an increasingly important resource in many countries and currently contribute one quarter of world-wide drinking water supply (Nguyet & Goldscheider 2006), predicted to rise to almost 50 % in the near future (Kollarits *et al.* 2006). Karst systems are more complicated than sand and gravel aquifers, because of the strong karst development, slow soil forming process, substantial uplift in Cenozoic (in China), and the duplex structure in surface and underground (Yuan & Cai 1988). Karst problems such as rock desertification, soil erosion, and soil degeneration cause loss of natural protective and filtration layer and therefore, the groundwater is vulnerable to being polluted (Ford & Williams 1989). Many studies on the geochemical behavior of arsenic in closed basin groundwater or surface water have been conducted by scholars (Ahmed *et al.* 2004, Bissen & Frimmel 2003, Guo *et al.* 2003, Guo *et al.* 2008, Guo *et al.* 2011, Jay *et al.* 2005, Redman *et al.* 2001, Savage *et al.* 2000, Segura *et al.* 2006, Smedley & Kinniburgh 2002, Smedley *et al.* 2002, Wang *et al.* 2010). Compared with those homogeneous aquifer systems, karst subterranean streams have special geological background, spatial structure, hydrodynamic conditions and water chemical characteristics, i.e. the carbonate rock geological background, uneven distribution of underground spatial structure, the strong karst dynamic process and unique hydrochemical characteristics. These features would affect the migration of arsenic in groundwater. Unfortunately, few studies have been done in this field. In-depth research is needed and it is also conducive to reveal the arsenic environmental geochemical behavior in this well-known fragile environment.

STUDY AREA AND METHODS

SITE DESCRIPTION

The Lihu subterranean stream catchment, with the karstification of 31.67 %, is located in NW Guangxi province, southwest China (Fig.1). This river originates from Layi village and Guanxi village, wherein the peak cluster, peak forest and uvala are the main physiographic

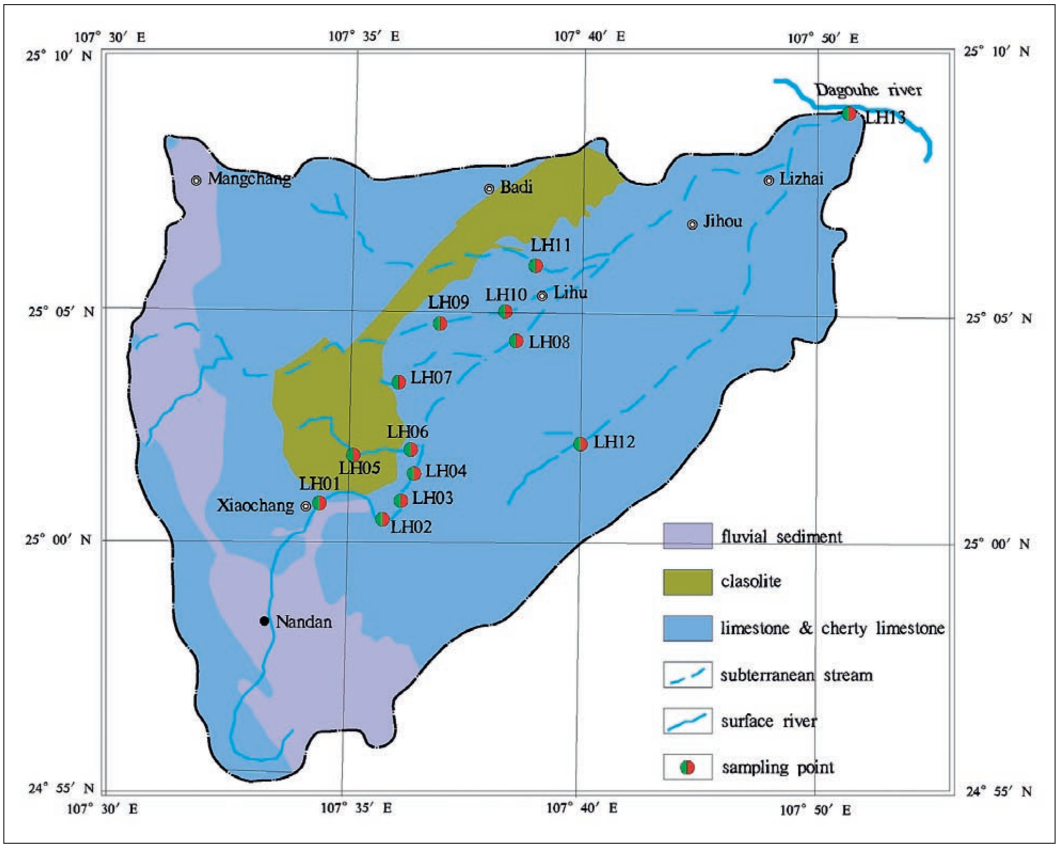

Fig.1: Location of study sites and the geological background of Lihu subterranean stream catchment.

types. It discharges at a steep cliff of the Dagouhe River after flowing through 25.6 km of limestone hills and depressions. The basin area is 517.4 km^2, and the average water flow is 4594 L/s in rainy season (June to August), while 3340 L/s in dry season (December to February). There are three tributaries in this underground river, i.e. Lizhai, Jihou and Badi subterranean streams. The mean annual precipitation in study area ranges from 1261 mm to 1628 mm. Geologically, The Lihu subterranean stream basin consists of various rocks from Carboniferous, Permian, Triassic, to Quaternary fluvial sediments. Cherty limestone is widely distributed in this basin. Geography and geological background of the study area are shown in Fig. 1.

SAMPLES AND EXPERIMENT

The river surface sediments (0 to 5 cm) and water samples were collected in June 2012. Three to five equally spaced distributed samples were obtained on each sampling point. Branches, leaves, roots and other debris were picked out. Collected sediment was put into polyethylene bags that were rinsed with HNO_3 (5 %) and preserved in a refrigerator (at approximately 4 °C) instantly, then freeze dried in laboratory and sieved with 2 mm nylon mesh after being triturated in agate mortar. Concentrations and speciation of arsenic were measured by inductively coupled plasma mass spectrometer (ICP-MS) and inductively coupled plasma-atomic emission spectrometer (ICP-AES) at National Research Center for Geoanalysis, Beijing, China. The contents of major elements (Fe, Mn, Ca, Mg and Al) in sediment samples were determined by X-ray fluorescence spectrometer (XRF, Axios X). Water anions and cations were monitored by plasma spectrometer (IRIS Intrepid II XSP) at the karst geology resources environment supervision and inspection center, Ministry of Land and Resources, PRC. In situ measurement of pH, redox potential (Eh), temperature and electrical conductivity were performed by portable probes (Multi 3420 Set, Water Test Meters). All apparatus and beakers utilized throughout the study were cleaned using acid reagents and deionized water and chemicals in the analysis were of analytical grade.

DATA PROCESSING

Principal component analysis and correlation analysis were performed by SPSS 13.0 software. Maps were generated by ArcGIS 9.0, and Patero diagram was drawn by Minitab 15 software.

MULTIVARIATE STATISTICAL ANALYSIS

There are many influential factors such as sediment physical-chemical properties, coexisting ions, etc., that could affect the migration and transformation of arsenic in groundwater (Singh *et al.* 1999, Su *et al.* 2009). In order to clarify the reaction mechanisms of arsenic in karst underground river, water chemical characteristics and sediment physical-chemical properties were measured in this study. Multivariate statistical analysis methods were also applied to the correlation analysis and principal component analysis (PCA). The aim was to identify the main hydrogeological factors on arsenic adsorption in karst subterranean stream.

PRINCIPAL COMPONENT ANALYSIS

Impact factors, i.e. sediment iron (Fe_{sed}), sediment aluminum (Al_{sed}), sediment magnesium (Mg_{sed}), sediment calcium (Ca_{sed}), particulate organic matter (POM), sediment manganese (Mn_{sed}), water potassium (K^+), water sodium (Na^+), water calcium (Ca^{2+}), water magnesium (Mg^{2+}), water chloride (Cl^-), water sulfate ion (SO_4^{2-}), water bicarbonate ion (HCO_3^-) and sediment arsenic (As_{sed}, $As(III)_{sed}$, $As(V)_{sed}$) were selected in this research for PCA. The contents of those indicators were listed in Tab. 1. To ensure their comparability among these different dimensions of data, dimensionless normalization was used in data processing before PCA. Through normalization processing, a new 16 × 17 matrix were attained. The weight in each column of the new matrix is the same, with a mean value of 0 and standardized deviation of 1. SPSS 13.0 software was then used for correlation analysis. The results are listed in Tab. 2. Most indexes have high Pearson correlation coefficient ($r > 0.3$, $p < 0.05$), indicating a suitable factor analysis and extractable common factors from the matrix.

In PCA, rotated eigenvalues that are higher than 1 were chosen as explanatory variables according to the total variance interpretation instead of without varimax rotation. Accumulative variance contribution of the first four principal components (PC1-PC4) that were extracted from the PCA was 76.4 % (Tab. 3). Namely, most of the information of the total variance of the original variables has been explained by the top four common factors. Correlation of common factors and the original variables before rotation are shown in Tab. 4. The correlations of the first four common factors are not statistically significant. In order to distinguish the relationship between various factors clearly, initial factor loading matrix was rotated in SPSS software. After rotation, the original variables variances were redistributed with the accumulative variance invariably. The changing of variance contribution makes common factors clear and easy to explain.

As can be seen from Tab. 4, seven variables i.e. As_{sed}, $As(III)_{sed}$, $As(V)_{sed}$, Fe_{sed}, Al_{sed}, Ca_{sed}, POM, Mn_{sed}, Ca^{2+} and HCO_3^- have high load on the first common factor PC before and after rotating, illustrating the high intercorrelation between those seven variables. Those seven main influencing variables that impact arsenic contents and its speciation in karst groundwater were drawn from thirteen indicators.

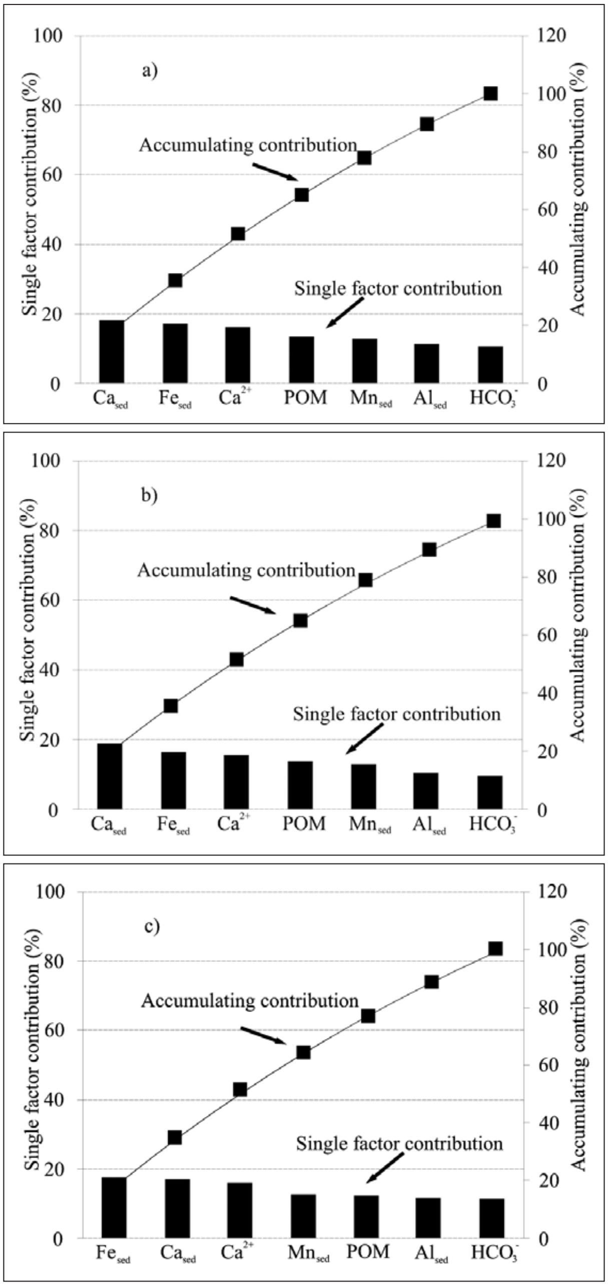

Fig. 2: Pareto sorts of influencing variables on a) total As; b) As(III); c) As(V).

Tab. 1: Sediments physical-chemical properties and water hydro-chemical characteristics in Lihu and Longzhai subterranean stream.

		Sediments									**Water (mg/L)**					
Sampling points	***No.***	***Fe (%)***	***Al (%)***	***Mg (%)***	***Ca (%)***	***POM (%)***	***Mn (μg/g)***	***As (μg/g)***	***As(III) (μg/g)***	***As(V) (μg/g)***	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Xiaochang	LH01	10.39	5.25	0.56	5.33	5.05	363.00	98.40	39.73	58.67	0.10	1.46	41.57	6.34	3.22	22.16	132.20
Layi cave	LH02	13.00	4.87	0.51	6.89	7.35	518.00	113.40	67.08	46.32	1.44	1.28	65.68	6.74	1.25	30.75	147.76
Layi Karst window	LH03	8.73	5.09	0.53	0.95	1.49	356.00	23.72	9.82	13.90	1.58	0.14	10.02	3.32	2.33	49.62	152.43
Liangfeng Cave	LH04	9.21	5.12	0.52	1.72	3.97	277.00	48.26	19.71	28.55	1.49	0.60	34.40	5.85	3.11	25.33	150.88
Qiaocun	LH05	10.97	5.85	1.25	2.33	1.09	378.00	49.70	12.92	36.78	1.06	1.52	48.60	1.41	1.89	35.21	122.88
Ganhe spring	LH06	9.91	9.14	0.51	3.85	5.33	419.00	38.66	15.86	22.80	0.74	1.51	31.90	5.70	4.35	53.62	158.65
Bachuanhe	LH07	7.89	8.33	0.23	2.64	2.64	330.00	38.20	22.30	15.90	2.64	1.74	38.80	6.09	6.47	60.78	125.99
Gantianba	LH08	8.47	5.52	0.39	4.53	1.72	304.00	45.80	29.10	16.70	1.73	1.22	33.70	6.40	5.67	37.22	152.43
Jihou	LH09	6.58	5.29	0.91	3.31	3.31	444.00	43.50	16.80	26.70	1.56	1.15	46.70	6.69	1.65	40.22	155.21
Hongxinghe	LH10	6.03	4.82	0.29	3.16	3.16	249.00	14.94	4.34	10.60	1.44	1.01	45.80	6.27	3.88	29.88	208.42
Badi	LH11	11.30	8.14	0.39	8.56	4.53	494.00	121.60	63.20	58.40	0.72	0.69	62.30	3.81	1.29	17.26	149.32
Lizhai	LH12	4.95	2.67	0.22	1.69	1.69	223.00	9.64	3.65	5.99	0.58	1.28	36.10	8.82	2.53	22.87	213.42
Xiaolongdong	LH13	6.91	3.46	0.38	3.88	2.30	281.00	9.33	5.12	4.21	0.19	1.24	13.94	1.57	1.34	39.87	236.42
Xiaolongdong	LH13	6.91	3.46	0.38	3.88	2.30	281.00	9.33	5.12	4.21	0.19	1.24	13.94	1.57	1.34	39.87	236.42

Tab. 2: Correlation analysis among influencing factors.

	Fe_{sed}	Al_{sed}	Mg_{sed}	Ca_{sed}	POM	Mn_{sed}	As_{sed}	$As(III)_{sed}$	$As(V)_{sed}$	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Fe_{sed}	1															
Al_{sed}	0.655(**)	1														
Mg_{sed}	0.520(*)	0.272	1													
Ca_{sed}	0.696(**)	0.565(*)	0.124	1												
POM	0.471(*)	0.290	−0.045	0.581(**)	1											
Mn_{sed}	0.670(**)	0.463(*)	0.409	0.516(*)	0.472(*)	1										
As_{sed}	0.820(**)	0.546(*)	0.296	0.871(**)	0.640(**)	0.622(**)	1									
$As(III)_{sed}$	0.778(**)	0.506(*)	0.136	0.890(**)	0.657(**)	0.618(**)	0.967(**)	1								
$As(V)_{sed}$	0.802(**)	0.548(*)	0.450	0.783(**)	0.573(*)	0.580(**)	0.960(**)	0.856(**)	1							
K^+	0.114	0.302	0.053	−0.132	−0.127	0.106	−0.033	0.064	−0.137	1						
Na^+	0.125	0.235	0.155	0.228	0.133	−0.072	0.132	0.120	0.135	0.029	1					
Ca^{2+}	0.639(**)	0.492(*)	0.363	0.747(**)	0.501(*)	0.420	0.770(**)	0.744(**)	0.738(**)	0.156	0.358	1				
Mg^{2+}	0.314	0.400	0.004	0.411	0.326	0.035	0.366	0.380	0.323	0.245	0.260	0.564(*)	1			
Cl^-	−0.059	0.262	−0.224	−0.222	−0.076	−0.076	−0.237	−0.197	−0.262	0.475(*)	0.142	−0.171	0.230	1		
SO_4^{2-}	−0.026	0.406	0.032	−0.177	−0.175	−0.055	−0.256	−0.219	−0.277	0.363	0.215	−0.206	0.024	0.237	1	
HCO_3^-	−0.629(**)	−0.498(*)	−0.481(*)	−0.302	−0.161	−0.316	−0.510(*)	−0.457(*)	−0.529(*)	−0.376	−0.257	−0.549(*)	−0.255	−0.047	−0.210	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed). *n=13*

Tab. 3: Eigenvalues, variances and cumulative contribution rate of principal components before and after rotation.

Principal components	***Before rotating***			***After rotating***		
	Eigenvalues	***Variance contribution (%)***	***Accumulating contribution (%)***	***Eigenvalues***	***Variance contribution (%)***	***Accumulating contribution (%)***
PC1	7.07	44.16	44.16	6.34	39.65	39.65
PC2	2.43	15.20	59.36	2.26	14.14	53.79
PC3	1.54	9.62	68.99	2.13	13.29	67.08
PC4	1.18	7.37	76.35	1.48	9.27	76.35

Tab. 4: Factors loading matrix before and after rotation.

Variables	***Common factors before rotating***				***Common factors after rotating***			
	PC1	***PC2***	***PC3***	***PC4***	***PC1***	***PC2***	***PC3***	***PC4***
Fe_{sed}	0.89	0.09	–0.22	0.11	0.78	0.15	0.47	–0.02
Al_{sed}	0.67	0.51	0.00	0.13	0.57	0.56	0.28	0.14
Mg_{sed}	0.41	0.12	–0.74	–0.28	0.13	–0.05	0.89	0.03
Ca_{sed}	0.87	–0.19	0.23	–0.03	0.89	–0.12	0.05	0.20
POM	0.64	–0.23	0.38	0.16	0.76	–0.08	–0.22	0.05
Mn_{sed}	0.68	–0.05	–0.30	0.44	0.67	0.12	0.34	–0.41
As_{sed}	0.96	–0.19	0.04	0.06	0.95	–0.10	0.22	0.06
$As(III)_{sed}$	0.92	–0.16	0.16	0.14	0.95	–0.03	0.09	0.04
$As(V)_{sed}$	0.92	–0.21	–0.10	–0.04	0.87	–0.17	0.36	0.08
K^+	0.08	0.76	0.00	0.29	0.01	0.81	0.09	–0.02
Na^+	0.24	0.34	0.21	–0.72	0.06	0.08	0.17	0.84
Ca^{2+}	0.85	0.03	0.12	–0.27	0.75	–0.01	0.25	0.42
Mg^{2+}	0.46	0.32	0.55	–0.19	0.46	0.31	–0.21	0.55
Cl^-	–0.14	0.67	0.36	0.29	–0.10	0.76	–0.31	0.07
SO_4^{2-}	–0.12	0.72	–0.14	0.00	–0.27	0.64	0.23	0.13
HCO_3^-	–0.39	–0.35	–0.62	–0.21	–0.61	–0.44	0.33	0.15

SORTING ANALYSIS

Pareto diagram is a queuing method in some scientific statistical work. Minitab 15 software was applied to sort the seven variables mentioned at “Principal component analysis” section. The results were shown in Fig. 2. The influence degree of each factor on the arsenic shows a gradient descent. This suggests none of the factors occupy a dominant position. Arsenic in the sediment was affected by the coactions of those seven variables. The impact on As(III) and total As decreased in the order $Ca_{sed} > Fe_{sed} > Ca^{2+} > POM > Mn_{sed} > Al_{sed} > HCO_3^-$; for As(V), the order is $Fe_{sed} > Ca_{sed} > Ca^{2+} > Mn_{sed} > POM > Al_{sed} > HCO_3^-$. What should be noted about these seven variables is that HCO_3^- has negative relationships with total As, As(III) and As(V). The correlation coefficient of HCO_3^- with total As, As(III) and As(V) are –0.51, –0.46 and –0.53, respectively as shown in Tab. 2.

ARSENIC ADSORPTIVE PROCESS IN KARST SUBTERRANEAN STREAM

The concentrations of total arsenic, As(III) and As(V) in the Lihu subterranean stream are listed in Tab. 5. Most of the sampling points’ arsenic content were rich and exceed 10 μg/L (the guideline concentration for drinking water set by the World Health Organization) (Ahmed *et al.* 2004). The average value is 35.76 μg/L, slightly above the value 20.71–27.05μg/L in the Diaojiang river sediment detected by Jian *et al.* (2010) near study area. Mining and metallurgy processes upstream are the main causes of arsenic pollutants. Field investigation completed by our group found that there is a small quarry and a coal mine running into the Layi and Badi cave inlet, respectively, which make the arsenic content of these two points higher than that of other’s (Tab. 5). So the arsenic content in the underground river is closely related to human activities. Due to high dissolved oxygen and high Eh in surface rivers, As(V) is dominant in inorganic arsenic at surface points. The average is 76.3 %. At karst under-

Tab. 5: The concentration of total As, As(III) and As(V) in Lihu subterranean stream.

Sampling points	***No.***	***Total As /µg·L^{-1}***	***As(III) /µg·L^{-1}***	***As(V) /µg·L^{-1}***
Xiaochang	LH01	42.32	15.10	27.22
Layi cave	LH02	86.30	25.89	60.41
Layi Karst window	LH03	35.15	19.28	15.87
Liangfeng Cave	LH04	15.93	7.50	8.43
Qiaocun	LH05	33.60	6.32	27.28
Ganhe spring	LH06	12.50	6.00	6.50
Bachuanhe	LH07	17.22	11.05	6.17
Gantianba	LH08	25.26	15.25	10.01
Jihou	LH09	32.51	12.60	19.91
Hongxinghe	LH10	16.45	5.68	10.77
Badi	LH11	126.19	1.76	124.43
Lizhai	LH12	22.06	3.80	18.26
Xiaolongdong	LH13	15.60	7.33	8.27

Tab. 6: Average content of elements in parent material and soil (Cao & Yuan 2005, Chen et al. 1999) (Wb /10^{-6}).

Elements	***Mean value in Earth's crust***	***Limestone parent material (Qingxudong Fm)***	***Dolomite parent material (Aoxi Fm)***	***Yellow soil (basalt)***	***Red soil (basalt)***	***Calcareous soil***
Al	84100	700	3600	121700	140100	88500
Fe	70700	670	2100	170500	170200	59900
Mn	1400	160	300	1400	600	700
Ca	52900	390400	234600	700	700	16600
Mg	32000	3300	102100	2700	100	8900

ground rivers, Eh may decrease and thus the reducing environments formed, so As(V) is reduced to As(III). The average percentage of As(III) in whole underground river system reaches up to 53 %.

The line chart shown in Fig. 3 represents the changes of arsenic along the main streams of Lihu subterranean stream. Arsenic concentrations from upstream to downstream manifested a declining trend, except for LH02 point, which is influenced by quarry waste residue. The decline of arsenic contents in the subterranean stream implies a water self-purification process in karst groundwater.

For example, the concentration of total As, As(III) and As(V) in sample point LH01 are 42.32 µg/L,

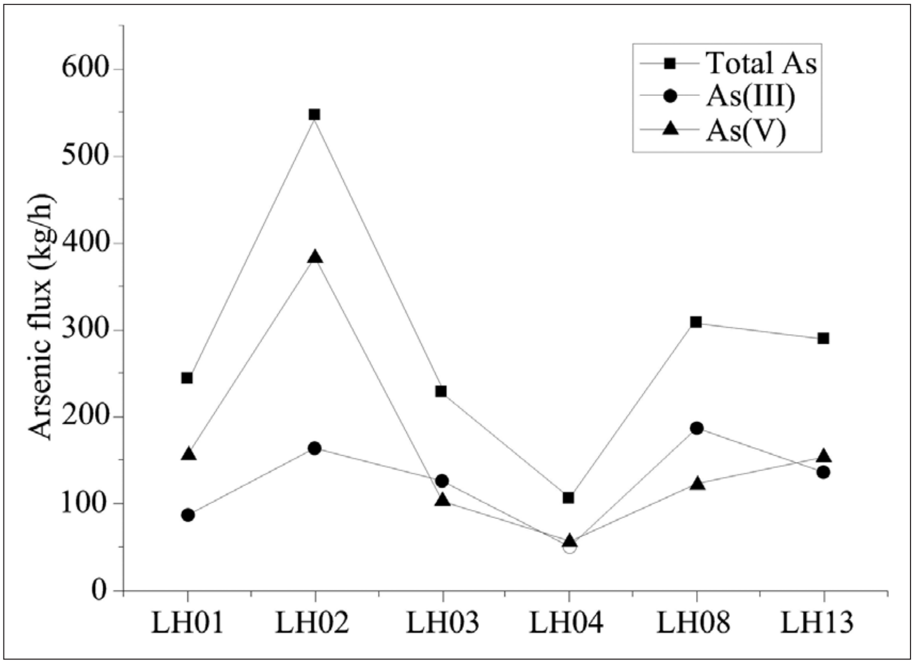

Fig. 3: Variation of inorganic arsenic along the Lihu subterranean stream.

15.10 µg/L and 27.22 µg/L, respectively. Those values are 2.7, 2.0 and 3.2 times higher than that of LH04, and 2.7, 2.1 and 3.3 times higher than that of LH13. The sum fluxes of total As, As(III) and As(V) at upper reaches of LH11, LH10, LH12 and LH08 (Fig. 1) are 589 kg/h, 212 kg/h, 377 kg/h and the fluxes at outlet of Xiaolongdong (LH13) are 290 kg/h, 136 kg/h and 154 kg/h, respectively. The concentrations of those three forms arsenic decreased by 51 %, 36 % and 59 % respectively after a 25.6 km distance in subterranean stream.

DISCUSSION

Compared to the research findings at a non-karst area, calcium and bicarbonate turned out to be the main influence factors for water arsenic adsorption largely because the high calcium and alkaline value in karst water. Therefore, the discussion is mainly focus on those two factors.

CALCIUM FOR ARSENIC ADSORPTION

Generally speaking, the cations such as Fe, Al, Mn have a strong As retention ability and show a remarkable correlation relationships with arsenic (Manning & Goldberg 1997). The Ca can also form complexes with arsenic and then be adsorbed to the sediments surface. Calcium has a promoting effect on arsenic sorption according to Goh and Lim (Goh & Lim 2005). With those ion concentration increases, the sorption function gradually strengthens. Calcium was the most sensitive cations because it can enhance electropositivity at the adsorbent surface. Thus, it strengthens the electrostatic interactions between the arsenic anion, causing more arsenic to be adsorbed. The coexistence of cations consolidate this process (Goh & Lim 2005). Previous research results indicated that the main species of arsenic in water deposits around the Lihu subterranean stream are Fe-As and Ca-As besides residual arsenic (Res-As). The proportion of Ca-As is higher than Al-As and Fe-As (Jian *et al.* 2010), which is different from fluvial sediment in the non-karst area (Cui & Liu 1988, Wei *et al.* 1999). The main lithologic chemical composition in karst area is $CaCO_3$. Carbonate rock can react with arsenic in weak alkaline environment and generate calcium arsenate which precipitates within the stream bottom sediments over time (Bhumbla & Keefer 1994, Jekel & Nriagu 1994).

Compared with the average chemical composition of the Earth's crust, Fe, Al and Mn contents in limestone and dolomite are significantly lower than average crustal elements (only 0.8 % to 21 % of the crustal median). However, the level of calcium and magnesium in karst area is 319 %~738 % of mean value of crust (Tab. 6). Moreover, Fe, Al, Mn contents in calcareous soil is only 0.35 to 1.2 times of red and yellow soil derived from basalt. Yet the corresponding Ca, Mg contents is 3 ~ 89 times higher than that corresponding basalt soil. This may be the reason for increased Ca activities in karst area, and hence it can explain the Ca elements become one of the most important factors on arsenic migration in karst subterranean stream.

BICARBONATE FOR ARSENIC ADSORPTION

The previous research revealed that bicarbonate (HCO_3^-) has a negative relationship with arsenic concentration (Anawar *et al.* 2004, Jay *et al.* 2005, Smith *et al.* 2002, Su *et al.* 2009). They thought that anions such as Cl^-, F^-, SO_4^{2-}, HCO_3^-, $H_2PO_4^-$ and SiO_3^- have prohibitive function on arsenic adsorption, and this prohibitive function would be amplified with the anions concentration increasing (Jay *et al.* 2005, Smith *et al.* 2002; Su *et al.* 2009).

The inhibitional effect of bicarbonate for arsenic adsorption is mainly caused by the competitive adsorption between bicarbonate and arsenic. The higher competitive ability, the more restraining performance. The carbonate weathering by atmospheric CO_2 at karst areas lead to the high bicarbonate concentration in water. The HCO_3^- can be chelated with adsorption sites and consequently hinder arsenic from being adsorbed (Smith *et al.* 1999). Meanwhile, the alkaline environment would slowdown the arsenic adsorption. That is why arsenic concentration in the study area expresses a negative relationship with bicarbonate.

CONCLUSIONS

There are some reasons for arsenic adsorption in karst subterranean stream. According to the study, cations (Fe, Al, Mn, and Ca) and organic matter have acceleration effect on arsenic adsorption, which could separate the arsenic from water and reduce the risk of arsenic contamination. Anions (Cl^- SO_4^{2-} and HCO_3^-), especially HCO_3^-, have inhibitory effect on arsenic removal. Calcium and bicarbonate in karst terrain revealed an important role during arsenic transportation and transformation. Therefore, the unique characteristics of karst should be considered during arsenic treatment in karst underground water.

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