



## Review

## Review of arsenic geochemical characteristics and its significance on arsenic pollution studies in karst groundwater, Southwest China

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## ABSTRACT

As a metalloid element, Arsenic (As) is widely distributed in the natural environment. Its ingestion can cause cancer, deformities, and mutations. Therefore, it has become an important environmental problem in recent years. There are large amounts of arsenic ore and coal with high arsenic content in Southwest China, a karst area. There, arsenic occurs in wastewater from mines contaminate soil, vegetation, and surface water. Karst underground aquifers are also contaminated through pipes, cracks, scuttles, and sinkholes, leading to a more serious arsenic pollution problem than in non-karst areas due to the unique karst hydrogeological conditions. To prevent and curb karst underground water contamination and guarantee water resource security and public health, a review on the arsenic contamination in the karst area is necessary. This paper discusses the progress of geochemical studies on arsenic. Through an analysis of the hydrogeology of karst areas, this paper proposes that studies on arsenic pollution in karst regions should be combined with the spatial distribution and redox characteristics of groundwater. More attention should be paid to chemical compositions of water, soil, and rocks as well as adsorption–desorption processes between water and sediment when conducting arsenic geochemical research in karst groundwater.

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**1. Introduction**

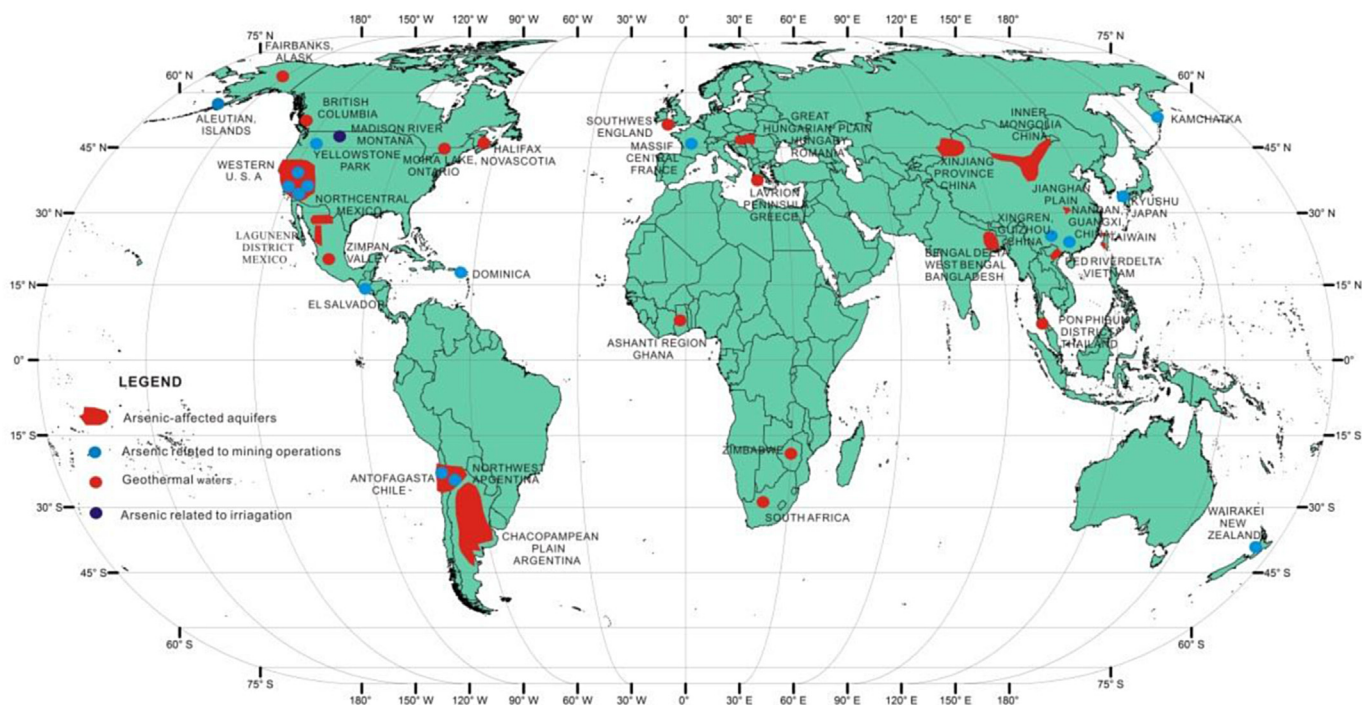
Arsenic (As) is a metalloid element that is widely distributed in the natural environment and is known to be carcinogenic, causing deformities and mutations (Norra et al., 2006). Arsenic and its compounds accumulate in animals and plants and spread via food chains, harming the ecological environment and humanity (Cullen and Reimer, 1989). There two ways of arsenic pollution, i.e. the natural release of arsenic from high-arsenic underground water (Smedley et al., 2003) and human emissions (Zhang et al., 2014), including mine exploiting and concentrating (Wei and Zhou, 1992), irrigation (Norra et al., 2005) and pesticide usage (Alam et al., 2015), etc. In Southwest China, arsenic ore deposit distributes a large area (Xiao et al., 2008). Therefore aquifers in southwestern China are contaminated by arsenic-containing wastewater that with unreasonable treatment. Arsenic from mine can be released and desorbed from minerals when the environmental conditions change, causing a regional arsenic pollution. Arsenic containing wastewater enters underground rivers through pipes, cracks, scuttles, and sinkholes directly, which leads to serious arsenic pollution (Zhang et al., 2014). With population growth and industrial development, this problem is becoming increasingly serious. A number of large aquifers in various parts of the world are identified as problematic, with As concentrations above 50 µg/L (Fig. 1) (Smedley and Kinniburgh, 2002). Also underground rivers, which are widely distributed in karst areas in Southwest China, are reported to be repeatedly contaminated with arsenic. This poses a significant threat to the ecological safety of the water and to the health of local

residents (Ma et al., 2003). Therefore, it is important to conduct a review on arsenic contamination in karst areas.

**2. Advances in arsenic geochemical studies**

*2.1. Bioavailability and toxicity of arsenic*

Many studies indicate that the bioavailability and toxicity of arsenic were determined by the forms of inorganic arsenic. Arsenic is a valence-variable element, and its valence varies from 0 (As), -3 (such as AsH<sub>3</sub>), to +3 (such as As<sub>2</sub>O<sub>3</sub>) or +5 (such as Na<sub>3</sub>AsO<sub>4</sub>) (Liang, 2007). The forms of As in water are mainly soluble compounds, which are closely related to redox potential (Eh) and pH of water bodies. Generally, the surface water has a moderate Eh (200–600 mV) and the pH is neutral. In this case, arsenious acid (H<sub>3</sub>AsO<sub>3</sub>) is the largest component in water. When there is a high Eh, over 600 mV in oxygen-enriched water bodies, the arsenic acid ion (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup>) becomes the largest component (Mandal and Suzuki, 2002). Yuan and Le (2009) suggest that Eh and pH are the major factors controlling the form of arsenic in natural water. Therefore, in oxidizing environments, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> is predominant when the pH is less than 6.9, and HAsO<sub>4</sub><sup>2-</sup> is predominant when the pH is higher than 6.9. In reducing environments, arsenic exists mainly in the form of electroneutral H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> if pH is less than 9.2. Arsenic that stays in sediment is mainly in an inorganic state, and the main valences are As(III) or As(V), of which As(V) is predominant (Wang et al., 1993). The valence can change when the external environment varies in terms of oxidation–reduction



**Fig. 1.** Examples for the distribution of well known arsenic pollution incidences of aquifers and environmental caused by mining and geothermal waters. Information collected from Azcue and Nriagu (1995); Nimick (1998); Smedley and Kinniburgh (2002); Li et al. (2010); Guo et al. (2012); Tao et al. (2012); Zhang and Yang (2013); Gan et al. (2014).

(Manning and Suarez, 2000) (Fig. 2).

Toxicities of arsenic vary with its forms; for example, the toxicity of As(III) is over 60 times greater than that of As(V) (Smedley et al., 2002). For organic arsenate is non-toxic (Rahman et al., 2006), the existing form of inorganic arsenic determines the bioavailability or toxicity of arsenic (Pongratz, 1998). Lin and Tang (1999) tested the  $\text{As}^{3+}$  and  $\text{As}^{5+}$  of 226 water samples in the arsenic-contaminated areas of Inner Mongolia in North China. Results indicated that the specific values of  $\text{As}^{3+}/\sum\text{As}$  in drinking water within the contaminated areas were 0.01–1.0. It is noteworthy that the value is 0.11 in villages with mild arsenic poisoning, 0.55 in villages with serious conditions, and 1.0 in villages with extra-serious conditions. It could explain why few people suffer from arsenicosis in areas with high arsenic content, while many people contract arsenicosis in areas with low arsenic content (Ma et al., 2003).

## 2.2. Adsorption–desorption process of arsenic in sediment–water interface

Sediments are regarded as a buffer zone for water pollutants. Within the sediment–water interface, complex physical, chemical, and biological processes occur, including adsorption, desorption, and flocculation or precipitation or both (Zou, 2004). Sediments, therefore, accumulate pollutants and conversely, become the source of pollutants under certain conditions (Jin et al., 2001). Generally, arsenic accrues negative colloids (such as  $\text{Sb}_2\text{S}_3$ ,  $\text{H}_2\text{SiO}_3$  et al.) and then easily be agglomerated with positive colloids in water. Due to the adsorption process, arsenic transfers from aqueous phase to solid phase quickly and deposited to sediment on the water bottom (Anawar et al., 2004; Rahman et al., 2006). With the environmental conditions changing, the arsenic in sediments would be re-released again, which affects the water quality (Tang, 2006). Therefore, the adsorption–desorption process within sediment–water interface has a significant effect on arsenic migration.

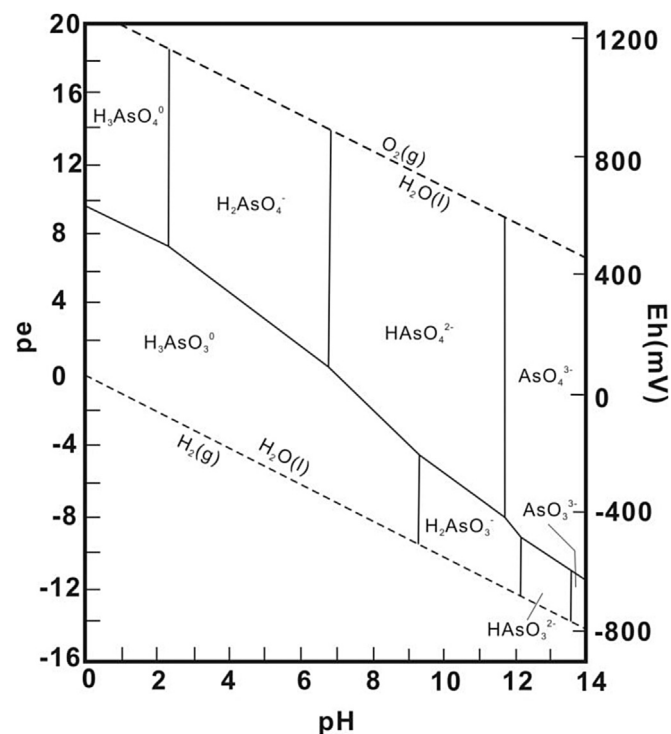


Fig. 2. pH-pe-Eh diagram of arsenic in water at 25 °C (Kumaresan and Riyazuddin, 2001).

Through lab experiments and field observations, Chen and Li (1998), and Gong et al. (2006) studied the adsorption–desorption of arsenic in sediment–water interface under hydraulic disturbance. The results showed that sediments and water were closely correlated: when arsenic is released from sediments to water, there is a greater possibility of arsenic pollution in surface water. During dry seasons, the arsenic in sediments has a weak capability of re-suspension; therefore, arsenic is hardly transport downstream. In the wet season, flood disturbs the balance between sediments and water, enabling the re-suspension of arsenic, leading to downstream transport of pollution.

## 2.3. Arsenic adsorption affected by hydrogeochemical characteristics and physicochemical properties of sediment

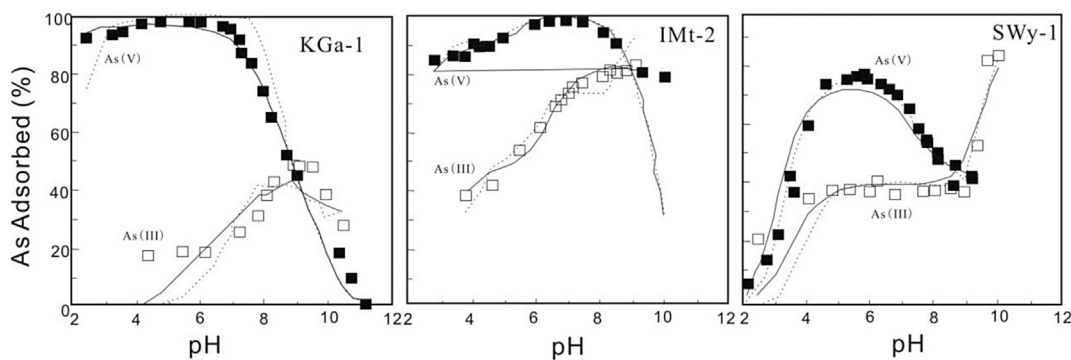
### 2.3.1. pH

Previous research has found that variations of pH affect the charge of colloids, affecting their adsorption ability. Arsenic in sediment exists in the suspended colloid, and it is easily extracted by alkaline aqueous solutions (Smedley et al., 2002) due to the colloid charge, which changes according to variations in the pH (Sadiq, 1997). According to Manning and Goldberg (1997a,b), the arsenic adsorption capacity by kaolinite reaches its maximum when the pH is 5.0, but it drops sharply when the pH is over 6.5. For illite, the suitable pH is 6–8, and it is 5–6 for montmorillonite (Fig. 3). Anawar et al. (2004) tested the release rate of As from pore water in sediment, and found that arsenic begins desorption when the pH reaches 9. The release capacity reaches its peak when the pH reaches 12. To calculate the pH dependency of the adsorption of arsenious acid ( $\text{As}^{5+}$ ) and arsenic acid ( $\text{As}^{3+}$ ) by hydrous ferric oxide (HFO), Johnston and Sarker (2007) relied upon the double diffusion model and cited the database by Dzombak and Morel (1986). The result showed that the adsorption quantity of arsenic drops sharply when the pH over 8.5. Furthermore, studies on the adsorption process of arsenic by sediment in the West Lake and canals east of China, Jin et al. (2001) found that sediment adsorbed the greatest quantity of arsenic when the pH was 6–8.

Pierce and Moore (1982) studied the adsorption of arsenic acid and arsenious acid on hydroxides of iron and found that a great amount of As(V) adsorbed onto hydroxides of iron when the pH is 4–10 and that more As(V) is released into the water when the pH increases. In addition, Gupta and Chen (1978) found that the As(V) is easily adsorbed by hydroxides of aluminum when the pH is within 4–7, and strong adsorption occurs when the pH is over 7.0. There was no obvious change in the adsorption rate when the pH was within 4–9. Wei et al. (1999) found that acidic environments deliver superior environmental conditions for the adsorption of As(V). Furthermore, Li et al. (2011) conducted a comparative analysis of the adsorption of arsenic in sediments in the sea outside the estuary of the Yingkou River in Liaodong Bay, North of China and in the interior reach of the estuary; the result indicated that alkaline conditions favor the adsorption of As(III) and acidic conditions favor the adsorption of As(V).

### 2.3.2. Co-existing ions

Co-existing ions in water bodies inhibit or facilitate the adsorption of arsenic. Some anions in water bodies—such as  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SiO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ —can increase the arsenic content in groundwater (Smith et al., 2003; Smedley et al., 2005). As a result of the competitive effect between anions and As(III) anions, the adsorption of As(III) is inhibited to various degrees. The inhibiting effect becomes stronger when concentrations of anions increase. In this respect,  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{SO}_4^{2-}$  have a particularly strong inhibiting effect on the adsorption of As(III) (Livesey and Huang, 1981). However, for As(V), new adsorptive sites are



**Fig. 3.** Adsorption of As(III) (□) and As(V) (■) on kaolinite (KGa-1), illite (IMt-2), and montmorillonite (Swy-1) with constant capacitance model outputs using the mononuclear (—) and multinuclear (...) assumptions (Manning and Goldberg, 1997a).

formed when ions such as  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  combine with sediment, facilitating the adsorption of As(V) (Goh and Lim, 2005).

Cations in water bodies, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ , can facilitate the adsorption of As(III) and As(V), and this facilitation becomes stronger when the cation concentrations increase. That is because cations are able to attach to the surface of the adsorbent, thereby increasing its electropositivity and strengthening its direct electrostatic force with arsenic anions. This has the effect of attracting a larger number of arsenic anions to attach onto the surface of the adsorbent; thus, any increase in the cations concentration would strengthen this process (Smith et al., 2002).

Smedley et al. (2003) studied the relationship between arsenic content and ion concentration in Huhhot Basin, Inner Mongolia. Results showed that high concentrations of Fe, Mn,  $\text{NH}_4$ ,  $\text{HCO}_3$  and P are a common feature of reducing high-As groundwater. But the highest As concentrations tend to be found in groundwater with low  $\text{SO}_4$  concentrations and indicate that As mobilisation occurs under strongly reducing conditions, where  $\text{SO}_4$  reduction has been an active process. In addition, Seddique, et al. (2008) investigated the chemical characteristics and hydrological conditions of a high arsenic groundwater area in Sonargaon (mid-east Bangladesh), showing that the main hydrochemical type of high arsenic groundwater is  $\text{Ca-Mg-HCO}_3$ . Finally, Deng, et al. (2011) conducted a study on the geochemical process of high arsenic groundwater on Hetao Plain in Northern China, revealing that the hydrochemical types of the high arsenic groundwater include  $\text{HCO}_3\text{-Cl}$ ,  $\text{Cl}$ ,  $\text{HCO}_3$ , and  $\text{Cl-HCO}_3$ .

### 2.3.3. Physicochemical properties of sediment

Oxides (such as of iron, aluminum, and manganese) and organic matter are the main substances affecting the adsorption of As(III) and As(V) by sediments. Through complex surface reactions, the oxides of iron, aluminum, and manganese are able to adsorb both As(III) and As(V) in particles, thereby forming indissoluble arsenic compounds and strengthening the ability of the sediment to adsorb arsenic. According to Moenke (1956), 80% of arsenic in the water precipitates into sediments that contain ferrate in high arsenic water (pH = 5.1). Oscarson et al. (1983) and Wang et al. (2010) considered that iron and manganese compounds show a strong adsorption ability to As(V) and As(III).

In addition, Li et al. (2011) studied the distribution of arsenic content inside and outside an estuary. They reported that as a result of high contents of organic matter and metals such as iron, manganese, and aluminum, the sediments in the estuary had a larger adsorption quantity of As(III) and As(V) than the sediments outside the estuary. Meanwhile, the adsorption quantity of As(III) to sediments is greater than that of As(V). Furthermore, Gao et al. (2010),

Uddin and Lundberg (1998) conducted a correlation analysis on the content of main chemical elements and arsenic in sediments and found that As had a positively correlated relationship with both Al and Fe.

Organic matter particles contain various types of functional groups, such as carboxyl, phenolic hydroxyl, alcoholic extract hydroxyl, ether, and amides. These functional groups are able to coordinate with arsenic, giving sediments greater adsorption ability (Wang and Mulligan, 2006). Moreover, organic acid colloids have a large specific surface area and adsorption ability; thus, they are able to adsorb a large amount of arsenic. In addition, they have a protective colloid effect in relation to colloid iron oxides, thereby facilitating the migration and enrichment of arsenic on colloid iron oxides (Ding et al., 2007).

Although most research results have proven that the content of organic matter in sediment is directly proportional to the adsorption quantity of arsenic (Wang and Mulligan, 2006), several studies have indicated that the presence of organic matter is related to the release of arsenic. Yang et al. (2008) noted that in the groundwater of the Hetao Plain, a high pH and a reducing environment rich in organic matter facilitates the migration, enrichment, and transformation of arsenic. This is because microbes decompose organic matter under consumption of oxygen. It facilitates the formation of a reducing environment and resulting in the release of As in the sediment, ultimately resulting in groundwater with high arsenic content. Through geochemical studies on the arsenic environment on the Hetao Plain in Inner Mongolia, Tang et al. (1996) showed that a depositional environment rich in organic matter is an important factor contributing to high-arsenic groundwater.

### 2.3.4. Two common isothermal adsorption models

To date, there have been limited studies relating to an isothermal model for the adsorption of arsenic by aquatic sediment. However, there are two main models used in existing literature: the Langmuir type (L type) and the Freundlich type (F type) (Kundu and Gupta, 2006).

Jin et al. (1986) conducted studies on the adsorption characteristics of arsenic using suspended sediment in the water system of Xiangjiang River in the south of China; the result indicated that arsenic has different adsorption characteristics in the presence of cation pollutants such as cadmium and copper. To fit the isotherm formulas of selected samples, they used the isotherm of both the F type and the L type. The results showed that the F type has a better fitting degree and a higher correlation coefficient than the L type. Jin et al. (2001) studied the adsorption isothermal formula of sediment to arsenic in the West Lake and the Grand Canal; the result indicated a good fit with the F type formula. Su et al. (2009)

conducted studies on the adsorption of arsenic by sediment and influential factors in the arsenic-poisoned area of the Datong basin in northern China. The results indicated that the adsorption of arsenic by sediment fits the F type adsorption isothermal model and that the adsorption quantity depends on the following factors: the size of the sediment particles, the mass fraction and the type of clay mineral, the mass fraction of iron and aluminum oxides, and the mass fraction of arsenic in the sediment.

### 3. Arsenic pollution in the karst area of southwest China

Arsenic ore resources are distributed unevenly throughout the world. However, 70% of global explored arsenic reserves are located in China (Wei and Zhou, 1992). Of all of the explored arsenic resources in China, 2.5 million tons are found in the southwestern region, accounting for 61.6% of the total explored amount throughout the country (Guo, 2006; Xiao et al., 2008) (Fig. 4). With which 95% of the extracted arsenic of China are found in Guangxi, Hunan and Yunnan, SW China.

Groundwater in the karst area of Southwest China is heavily polluted because of arsenic exploitation and smelting. Wastewater containing As derived from industrial activities, including mine tailings and industrial waste residue, contaminates underground

aquifers through pipes, cracks, scuttles, and sinkholes (Xuan, 1998; Zhou et al., 2005). Vast regions, such as the southeast of China (Li and Su, 2001), experience extreme contamination of groundwater and soil. Monitoring of the Xiaojiang River (a secondary tributary of the Pearl River) revealed an arsenic concentration of over 1000 mg/kg in the river bed sediment, which far exceeds the maximum effect reference value of aquatic sediment, both in China and internationally (Ortega et al., 2008; Jian et al., 2010). Ma (2011) measured arsenic in the groundwater of Nandan County, Guangxi, China, showing that in many parts of the region, groundwater is significantly polluted by arsenic. The monitoring results of Zhang et al. (2014) in 2012, relating to the underground river watershed of Lihu Lake, showed the average arsenic content to be 35.76  $\mu\text{g/L}$ , which is 3.6 times higher than the permissible level. In the Jiaole Coal Mine in Xingren County of Guizhou Province, the arsenic concentration of the epikarst water was found to be 676  $\mu\text{g/L}$ , and the arsenic content of the groundwater was 510  $\mu\text{g/L}$  (Sun et al., 2009; Sun et al., 2013).

Because of the large amounts of arsenic processed in mineral mines, arsenic contamination accidents by industrial and mining enterprises in the southwestern region of China are frequently reported. A summary of the accidents over the last 10 years is listed in Table 1.

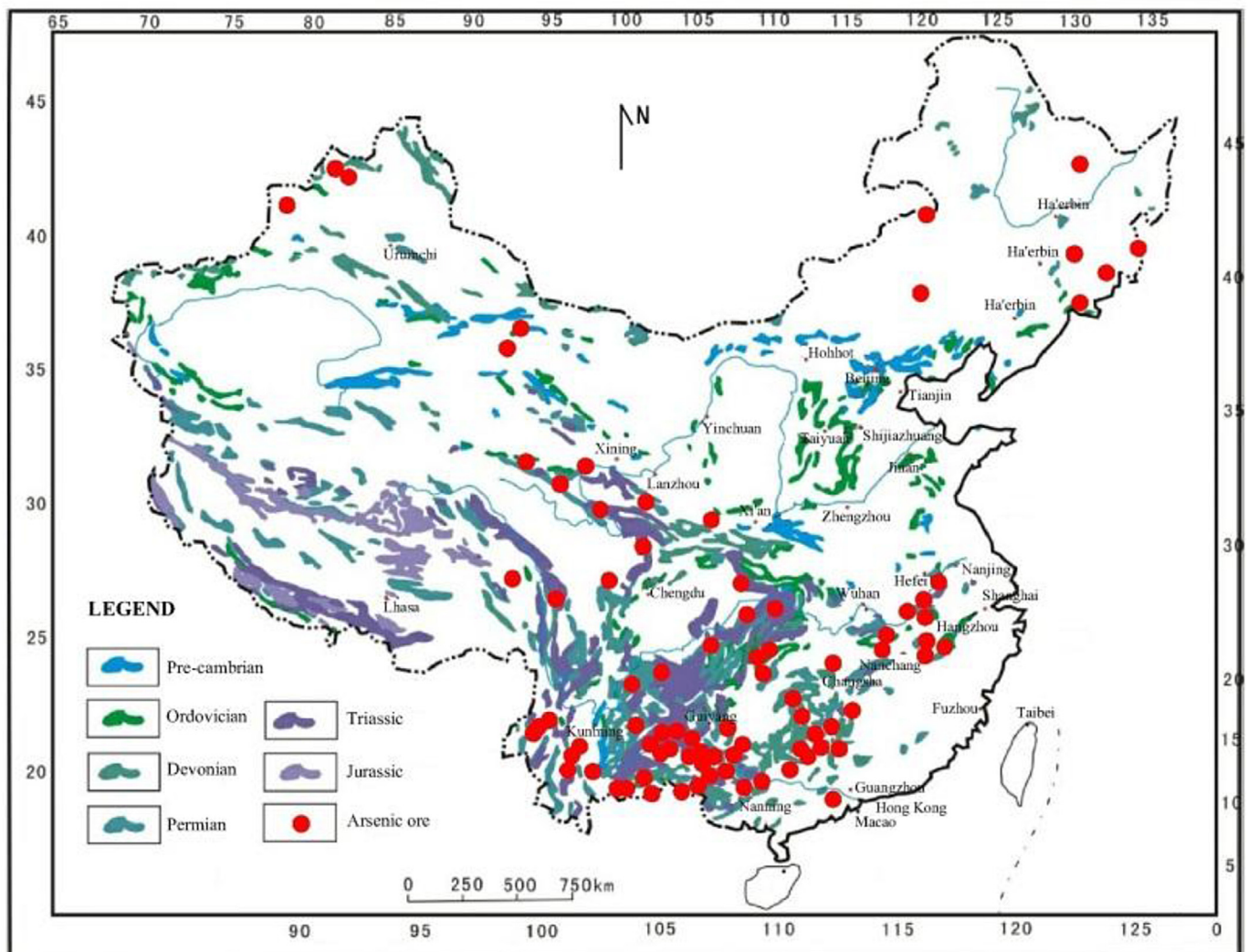


Fig. 4. Karst (different colors represent different strata) and arsenic ore distribution on the Chinese Mainland (Xiao et al., 2008; Cao et al., 2012).

#### 4. Karst hydrogeological background and its impact on arsenic geochemical behavior

Globally, carbonate rock is present in 12% of the Earth's rocks. However, karst groundwater provides 25% of the world's drinking water (Ford and Williams, 1989). China has the largest karst area—the total area of carbonate rock reaches  $3.44 \times 10^6$  km<sup>2</sup> and covers 33% of China's total territory (Li and Luo, 1983) (Fig. 4). In Southwest China, karst groundwater is important for public consumption, irrigation, farming, and industry. In some areas, karst groundwater is the sole water source (Cao et al., 2003). According to statistics (Yuan et al., 2007), there are a total of 2836 rivers in Southwest China's karst area, with a total length of 13,919 km, and a total flow rate of  $467 \times 10^8$  m<sup>3</sup>/a during the dry season (similar to that of the Yellow River). If this region is protected and developed scientifically, the water source problem in the region could be solved efficiently.

However, karst aquifers are extremely vulnerable environmental systems (Goldscheider, 2005). In karst areas, a large-scale bareness of the bedrock and the serious problem of rocky desertification developed because: 1) the ability to create deep soils is limited; 2) carbonate rocks from the Cenozoic era are raised substantially; and 3) the bi-layer structure of the surface and underground is fragile (Fig. 5) (Hu et al., 2008). In karst areas, there is not enough of a soil layer to offer natural protection and to enable filtration (Yuan, 1993; Wang et al., 2001); therefore, pollutants enter the karst underground river system directly and easily through sinkholes, silos, and fissures, and then pollute the groundwater. Additionally, the karst system has high heterogeneity and anisotropism (Nguyet and Goldscheider, 2006). Once this vulnerable environment is destroyed, there is less opportunity for karst areas to recover as compared to non-karst areas.

The karst hydrological system is a three-dimensional entity with uneven spatial distribution, large underground spaces, and broad water areas. In this system, karst windows, grikes, vertical shafts, underground blue holes, underground lakes, and cave systems connect structural groupings such as cracks and pipelines (Fig. 5) (Williams, 1983). The water in karst areas flows very fast. The exchanges between the Earth's surface and the underground occur readily; therefore, particles from the Earth's surface are deposited very easily and reach a thickness of several meters, while sediment does not deposit very easily in areas with narrow pipelines.

Migration and transformation of arsenic into the groundwater is affected by the heterogeneity of the internal structure of underground rivers and the resulting anisotropy of the internal hydraulic connection of the karst hydrological system (Yuan, 1988).

##### 4.1. Karst groundwater is an open system

Protogenic high-arsenic groundwater generally forms within inland or closed basins such as those found within arid or semi-arid areas as well as in flat and low-lying groundwater stagnant zones. These types of aquifers renew and alternate very slowly, providing favorable conditions for arsenic enrichment in groundwater (Guo et al., 2007). However, in karst underground space, the drainage networks are comprised of a vague interface combination of rock, soil, water, and air. In this system, surface water, rainfall, and groundwater are closely connected; thus, water transforms very quickly and flows fast. The groundwater system is easily affected by rainfall, surface water, and human activity and shows a very strong geochemical vulnerability (He et al., 2010). Because of the uneven distribution of rainfall throughout the year in monsoon regions, there is a clear response from groundwater to the seasonal geochemical composition on the Earth's surface, where water quantity, quality, and level are different all year round, resulting in significant dynamic changes in the karst hydrological system (Liu et al., 1999). Moreover, external conditions can easily disturb the dynamic geochemical equilibrium of a karst area within an unsaturated zone (Jiang and Yuan, 1999). For the above reasons, the migration and transformation process of arsenic in karst groundwater is likely to be affected by the open characteristics, which should be considered in the study of arsenic geochemistry behavior.

##### 4.2. Unique chemical compositions of water, soil, and rock in karst area

Most of the karst area in Southwest China is formed on ancient and rigid Triassic carbonate rocks (Pu et al., 2010). Therefore, the relative positions, minerals, and chemical components of carbonate rocks and the developmental characteristics of karst affect the structure and operational laws of the karst ecosystem (Cao et al., 2004). Compared to silicate areas, the karst area of Southwest China has a relatively low content of Fe, Al, and Mn, which account

**Table 1**  
Overview of arsenic pollution events reported in the karst areas of southwestern China.

Year	County/ region	Province	Population exposed	Description of arsenic contamination incidents	Reference
2000	Dengjiatang	Hunan	226 people were poisoned	Individual arsenic smelters discharged pollutants for a long time. Urine test results show that arsenic concentration was four times higher than the local standard.	(Net, 2001; Cao, 2007)
2001	Nandan	Guangxi	193 people were affected	Wastewater containing arsenic discharged from the Wuxu Dressing Plant, approximately 2189 times higher than the permissible level.	Li and Yang (2005)
2006	Yueyang	Hunan	100,000 people's drinking water are threatened	Wastewater containing arsenic was illegally discharged to Xinqiang River by Haoyuan Chemical Co., LTD for a long time. Arsenic concentration exceeded standards by 10 times.	(Cao and Zhang, 2006)
2007	Dushan	Guizhou	20,000 people affected, 17 were poisoned	The arsenic content in the Maqiu River and the Duliujiang River in Dushan County exceeded local standards.	Chen (2008)
2008	Hechi	Guangxi	Over 450 people developed symptoms of arsenic poisoning	A major arsenic poisoning accident occurred due to metallurgy enterprises discharging arsenic wastewater through karst pipelines without permission.	(Wang, 2008)
2008	Yangzong Lake	Yunan	Affecting 20,000 people	Arsenic concentration rose continually after June 2008, and reached 134 µg/L by Sep 2008, which caused the water quality to be far beyond the national standard and unable to be used as a potable water source as before.	(Wang et al., 2011; Zhang et al., 2012)
2009	Linyi	Shandong	More than 500,000 people's health were affected	27,000 tons As-containing wastewater were discharged to Nansu River from an illicit enterprise.	(Anon., 2009)
2013	Huangshi	Hubei	118 people urinated arsenic and 49 were poisoned	Several small arsenic plants discharged arsenic wastewater illegally, causing approximately 240 times above the limit.	(Tao and Yang, 2014)

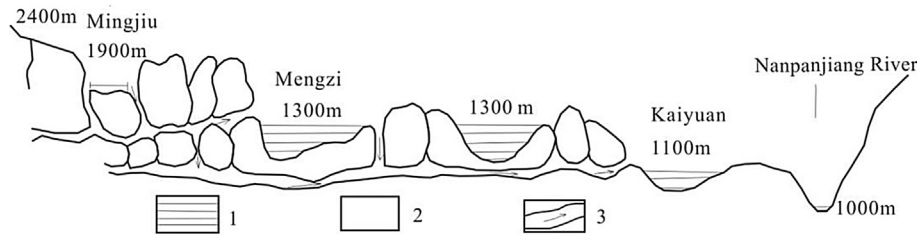


Fig. 5. A typical bi-layer structure diagram of karst area: a case of underground river in Yunnan, China. Symbol 1 is Cenozoic impermeable layer; 2 is Triassic limestone; 3 is underground river system and its direction (Yuan et al., 2007).

for 0.8–21% of its mean value on earth, but its Ca and Mg contents are 3–7 times higher than that on earth's crust (Table 2). The content of Fe, Al, and Mn in the soil (developed from carbonate rocks) is only 0.35–1.2 times that of soil developed from basalts, while for the Ca and Mg, the multiple is 3–89 (Chen et al., 1999; Cao, 2005).

Calcium is predominant in calcareous soil. According to former studies, the migration and transformation of As is affected by both Ca and metallic elements, including Fe, Al and Mn. Jian et al. (2010) indicated that arsenic is found mainly in the form of Fe–As and Ca–As in river sediments. In addition, the proportion of Ca–As is high and the proportions of Al–As and Org–As are relatively low (Jian et al., 2010). Our previous studies (Zhang and Yang, 2013) on the underground rivers in Lihu Lake, Guangxi, found that Ca in both water bodies and sediments has a correlative relationship with arsenic in the sediment.

The sediments in the karst aquifer are mainly comprised of surface soil, gravel, and silt, all of which are carried by flood, mud, and eroded stone. The secondary sediments have  $\text{CaCO}_3$  as their main component, and these include adarce, stalagmites, cave flowers and stalactites, as well as bioaccumulated substances such as the remains of dead plants and animal feces. Sediments with different components have different adsorption processes and adsorption abilities on arsenic (Manning and Goldberg, 1997a). Shi et al. (2007) and Winkel et al. (2013) found that the adsorption process of arsenic is affected by the type, composition, crystalline state, and surface area of the mineral substances present.

#### 4.3. Redox environments of karst aquifers

The redox conditions of karst aquifers are different from either the strong reducing environment of closed basins ( $-153 \sim +98$  mV,  $-33$  mV on average) (Yang et al., 2008), or the oxidation environments of surface water ( $+200 \sim +400$  mV, an oxygen-enriched water is  $> +600$  mV) (Levy et al., 1999; Mandal and Suzuki, 2002). There is a weak reducing environment of karst aquifers between these two environments. This fact has been demonstrated by Zhang et al. (2014) in karst underground rivers, and the 34 Eh samples values were found to be  $-168$  mV  $\sim +120$  mV, and  $-15$  mV, on average. Eh should also be considered as an important influencing factor for arsenic species and arsenic migration (Fig. 2) when

conducting arsenic geochemical research in karst areas.

## 5. Conclusions

Researchers have performed numerous studies related to the morphological characteristics and adsorption laws of arsenic in water and have acquired a number of promising conclusions:

- (1) The pH value is an important factor affecting the form and adsorption of arsenic: the adsorption quantity of arsenic decreases when the pH increases. However, there have been conflicting results on the most suitable pH value for arsenic adsorption. Different, even conflicting, conclusions have been made regarding the optimum environmental conditions for the adsorption of As(III) and As(V) in relation to the pH.
- (2) Co-existing anions in water bodies inhibit the adsorption process of arsenic, while cations facilitate the process.
- (3) The Fe, Mn, and Al content of sediments facilitates arsenic adsorption, and the minerals have a positive correlative relationship with arsenic content. However, controversy remains in relation to the adsorption process of arsenic by organic matter.

Most studies have focused on oceans, lakes, and surface rivers, few have been conducted in relation to karst groundwater. Karst is widespread, and karst groundwater is a basic water source for human life and industry. The studies cited here laid the groundwork for arsenic pollution research in karst areas, but due to the special hydrogeological background and fragile groundwater system of karst areas, as described earlier, some scientific problems still need to be further discussed and addressed. Three suggestions might be useful for addressing arsenic pollution and furthering scientific research in the karst area of Southwest China:

- (1) It is extremely detrimental for arsenic pollutants to discharge into the aquifers through pipelines, cracks, scuttles, sinkholes, etc. Enterprises should strengthen their processing of surface water to control source pollution.
- (2) There is an urgent need to study the adsorption characteristics and migration laws of the underground rivers in the

Table 2

The average content of soil parent material and soil elements (Chen et al., 1999; Cao and Yuan, 2005) ( $10^{-6}$ ).

Elements	The earth's crust element (Clark value)	Qingxu group limestone ( $E_1$ )	Aoxi group dolomite ( $E_2$ )	Yellow soil (basalt)	Red soil (basalt)	The average content in lime soil
Al	84,100	700	3600	121,700	140,100	88,500
Fe	70,700	670	2100	170,500	170,200	59,900
Mn	1400	160	300	1400	600	700
Ca	52,900	390,400	234,600	700	700	16,600
Mg	32,000	3300	102,100	2700	100	8900

karst area to further evaluate arsenic adsorption theories and to prevent and curb the contamination of these water systems. It is necessary to integrate the studies on the migration actions of arsenic in karst groundwater with the studies on the spatial distribution characteristics of karst groundwater as well as the studies on the redox characteristics and chemical compositions of water, soil, and rocks.

- (3) It is essential to pay particular attention to the adsorption-desorption process of the water-sediment interface, which is a key aspect involved in controlling the migration and transformation of arsenic.

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