A review of high arsenic groundwater in Mainland and Taiwan, China: Distribution, characteristics and geochemical processes

Huaming Guo a,b,*, Dongguang Wen c, Zeyun Liu b, Yongfeng Jia a,b, Qi Guo a,b

ABSTRACT

China is a typical high-As region, where 20 provinces have high As groundwaters among 34 provinces. These groundwaters usually occur in both arid–semiarid inland basins and river deltas. In the inland basins, mainly distributed in the northwest of China, shallow groundwaters usually have high As concentrations in alluvial lacustrine or lacustrine sediment aquifers, while high As groundwater mainly occurs in fluvial–marine sedimentary aquifers in the river deltas, which have been affected by transgression. In both the inland basins and the river deltas, high As groundwaters, mainly occurring in reducing conditions, are characterized by high Fe and Mn concentrations, high pH and HCO_{3}^{-} concentration, and relatively low NO_{3}^{-} and SO_{4}^{2-} concentrations. Although As contents are well correlated to Fe/Mn contents in the aquifer sediments, groundwater As concentrations are generally independent of sediment As contents. Redox processes, microbe-related reduction, and desorption processes are the major geochemical processes for As enrichment in groundwaters. In reducing conditions, both reductive dissolution of Fe oxides and reductive desorption of As are believed to result in As mobilization, which would be catalyzed by indigenous microbes. Although decomposition of the low-molecular weight organic matter during microbe metabolization would also release the colloid-bound As into groundwater, the cycling of colloid-bound As still needs to be further investigated during redox processes. Besides, high pH and high HCO_{3}^{-} lead to As desorption from adsorption sites in the aquifer systems. However, the contribution of competitive desorption to high As concentrations is still unknown and remains to be discovered, relative to reductive dissolution of Fe oxides, especially in the inland basins.

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1. Introduction

Arsenic is a ubiquitous element in the earth's crust, which has notoriously been known as a toxicant and carcinogen for the general population. It has been ranked among the top 20 most hazardous, high priority substances by the Agency for Toxic Substances and Disease Registry (ATSDR, 2005), which can cause acute and chronic health effects on human (Gray et al., 1988; WHO, 1996; Saha, 2003). Acute poisoning symptoms include gastrointestinal discomfort, vomiting, coma and even death, which usually occur within 30 min of ingestion, while the chronic effects commonly include skin diseases (pigmentation, dermal hyperkeratosis, and skin cancer), many other cardiovascular, neurological, hematological, renal and respiratory diseases, skin cancer, and other internal cancers (Morton and Dunette, 1994).

Elevated As levels of aqueous environment have resulted from both natural processes and anthropogenic activities (Bissen and Frimmel, 2003). Most As problems are the result of mobilization under natural conditions, including weathering reactions, biological activities and volcanic emissions (Smedley and Kinniburgh, 2002). Arsenic concentration in the earth’s water is up to 50 mg/L (Ellis and Mahon, 1977), while natural groundwaters in As-rich provinces have high As concentration of 1500 μg/L (Guo et al., 2008a). Ingestion of high As drinking water is a major pathway for As to enter the human body, and therefore poses the significant threat to human health. High As concentrations have widely been found in potable groundwaters, which have received much concern from both governmental and scientific levels (Guo et al., 2007a). In order to protect public health, the World Health Organization has set a provisional guideline limit of 10 μg/L for As in drinking water (WHO, 1996), which has been subsequently adopted by the European Union (European Commission, 1998), the United States (EPA Office of Groundwater and Drinking Water, 2002), and China (Ministry of Health of PR China, 2006). However, although China is seeking to reduce its limit in line with the WHO guideline value, the guideline is still set to the 50 μg/L in rural areas because of lack of adequate testing facilities for lower concentrations and high cost of water treatment for As removal.

South and Southeast Asia is a typical high-As region, where the occurrence of As in the alluvial/lacustrine aquifers of many inland basins and deltaic systems has become a well-known problem (Winkel et al., 2008). Hundreds of millions of people are suffering from chronic As poisoning in Bangladesh, India, China, Pakistan, Nepal, Cambodia, and Vietnam (Bissen and Frimmel, 2003; Smedley and Kinniburgh, 2002). The groundwater As is of geogenic origin and considerably patchy on a local scale or a regional scale (Harvey et al., 2002; Ng et al., 2003; van Geen et al., 2003; McArthur et al., 2004; Guo et al., 2008a). Hydrogeological and biogeochemical studies showed that source of dissolved organic carbon, microbial diversity, sedimentation sequences and groundwater hydraulics are the major contributors for spatial and temporal variation in As concentrations (Harvey et al., 2002; van Geen et al., 2003; McArthur et al., 2004, 2011; Guo et al., 2012, 2013b; Fendorf et al., 2010).

Among these high As groundwater countries, China is one of the largest countries, where high As groundwaters have been found in both inland basins experiencing an arid/semiarid continental climate, and river deltas experiencing a humid tropical climate (Guo et al., 2008a; Chen, 1998). In the Mainland of China, high As groundwaters (>10 μg/L) have been found in 19 provinces. These provinces include Anhui, Beijing, Gansu, Guangdong, Hubei, Henan, Hubei, Inner Mongolia, Jilin, Jiangsu, Liaoning, Ningxia, Qinghai, Shandong, Shanxi, Shaanxi, Sichuan, Xinjiang, and Yunnan (Jin et al., 2003). Estimation based on a statistical risk model shows that 19.6 million residents are at risk from being affected by the consumption of high As groundwater throughout China (Rodríguez-Lado et al., 2013). The number of residents at risk may be underestimated since the model mainly considers the alluvial sediments aquifers. According, the results must be confirmed with additional field investigations.

This paper summarizes distribution and chemical characteristics of high As groundwater, hydrogeological settings of high As groundwater aquifers, and systematically reviews geochemical processes controlling As distribution in typical areas of China.

2. Distribution of high As groundwater

High As groundwaters (>10 μg/L) have been widely found in China (Fig. 1). Generally, there are two types of areas where high As groundwater naturally occurs. One is the arid–semiarid inland basins. The other is the river deltas. The former mainly includes the Yinchuan basin, the Hetao basin, the Huanghe basin, the Datong basin, the Yuncheng basin, the Songnen basin, the Guide basin and the Dzungaria basin. The Yinchuan basin (7300 km²), the Hetao basin (10,000 km²), the Huanghe basin (4800 km²), the Datong basin (7440 km²), and the Yuncheng basin (4950 km²) lies along the Yellow river from the west to the east. The Songnen basin is located in the west of Jilin province, and the Dzungaria basin in the north of Xinjiang province. The delta areas mainly include the Yangtze river delta, the Yellow river delta, and the Pearl river delta.
concentrations (Fan et al., 1993). High As concentrations up to 1860 \( \mu g/L \) have been found in shallow dug wells to tube wells (usually 15–30 m in depth) with hand pump or electric motor pump in many locations in Inner Mongolia (Guo et al., 2008a). Li and Li (1994), Tang et al. (1996), Guo et al. (2008a), Jin et al. (2003), Gao, 1990), Tang et al. (1996), Smedley et al. (2003). While in the basins of Hetao and Huhhot it has been generally believed to occur naturally in later Pleistocene–Holocene alluvial–lacustrine aquifers (Ma et al., 1995; Smedley et al., 2003). Aquifer sediments hosting high As groundwater are usually deep grey in color, while sediments with low As groundwater are yellow (Zhang et al., 2000).

The Hetao basin is located to the west of the Huhhot basin, which is a typical sedimentary basin hosting high As groundwater. Although the Yellow river lies to the south of the basin and its water is used for farmland irrigation, groundwater is the major source of drinking water. Before 1980s, every village had 2–4 dug wells (3–5 m in depth) for producing drinking water. Since the water usually has high total dissolved solid (TDS)>1000 mg/L, local residents have changed their drinking water resources from dug wells to tube wells (usually 15–30 m in depth) with hand pump since the early of 1980s (Tang et al., 1996). These groundwater generally have lower TDS relative to dug well waters, while contain high As concentration (>50 \( \mu g/L \)). The transformation of drinking water resources has led to endemic As poisoning since 1990 (Fan et al., 1993). Saline groundwaters have been found in the shallow aquifers in parts of the region as a result of evaporative concentration and many have high F– concentrations, although the F– does not generally correlate with As (Smedley et al., 2003). Aquifer sediments hosting high As groundwater are usually deep grey in color, while sediments with low As groundwater are yellow (Zhang et al., 2000).

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<td>–</td>
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</tbody>
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naturally under reducing conditions. In contrast, Zhang et al. (2002) suggested that the As in groundwater of the Hetao Basin should be released from high elevations, where mining had been carried out for a long time, and then transported from the mining district down-gradient.

2.1.2. The Datong basin, the Taiyuan and the Yuncheng basins of Shanxi province

Shanxin province is severely affected by high As groundwater. Endemic arsenism was firstly confirmed in 1994 in the Datong basin (Cheng et al., 1994; Jin et al., 2003). High As groundwater was firstly reported in 1997, with As concentrations between 1 and 660 μg/L (Wang, 1997). Recently, groundwater As data obtained show that tube well waters in the Taiyuan basin and the Yuncheng basin also contain As concentration >50 μg/L (Wang et al., 2007a; Currell et al., 2011).

The Datong basin is located in the northern part of the Shanxi Province. In this basin, every village had 3–5 dug wells for drinking water supply before the middle of 1980s. Those wells had depths between 8 and 10 m. Since 1985, groundwater level has declined, which caused no water in those dug wells during dry seasons. Local residents changed their drinking water resources from dug wells to tube wells (between 20 and 40 m in depth) with hand pump. Wang et al. (1998) found that As concentrations range between 2.0 and 1300 μg/L in groundwaters (Table 1). A recent investigation shows that 54.4% of the tested 3083 wells have As concentration exceeding 50 μg/L (Wang et al., 2003b). High As groundwater is characterized by high pH between 7.1 and 8.7 (mean 8.2, n = 15), high HPO$_4^{2-}$ contents up to 12.7 mg/L (mean 1.45 mg/L, n = 15), low SO$_4^{2-}$ concentrations generally less than 2.0 mg/L (Wang et al., 2004a). The affected groundwater has been found in alluvial–lacustrine aquifers containing relatively high organic matter (up to 1.0% organic carbon). Arsenic is mainly present as inorganic As(III), accounting for 55–66% of total As, in the reducing aquifers (Guo et al., 2003).

The Taiyuan basin, lying in the center of the Shanxi province, hosts high As groundwater in the sedimentary aquifers. High As groundwaters are mainly distributed along the Ciyao river and the Wenyu river in the flat plain with an area around 800 km$^2$. Population exposed to high As groundwater (>50 μg/L) was about 23,600 (Wang et al., 2004b). Depths of wells producing high As groundwater mainly range between 50 and 200 m. Arsenic concentration has the range from 0.1 to 116 μg/L (Zhang and Guo, 2007). High As groundwater areas are generally consistent to the regions with groundwater levels less than 4.0 m below land surface (Guo et al., 2007c; Zhang and Guo, 2007).

Being located in the southern part of the Shanxi province, the Yuncheng basin has also been found to host high As groundwater. Population exposed to high As groundwater (>50 μg/L) was around 156,000. High As groundwaters were mainly observed in Yanhu district and Yongji city (Jin et al., 2003), neighboring Yanhu lake and Wuxing lake, respectively. Groundwater chemistry is generally characterized by high F$, NO_3^-$ and SO$_4^{2-}$ (Currell et al., 2011). Arsenic concentration ranges between 0.1 and 500 μg/L (Table 1). High As groundwater mainly occurs in the northern Sushui River basin.

2.1.3. The Songnen basin of Jilin province

High As groundwater has been found in the southwest of the Songnen basin of Jilin province in the late 19th century (Liu et al., 2002). In this area, arsenicosis was first reported in 1995 (Wang et al., 2006). Around 1964, residents changed their drinking water resources from shallow wells (4–10 m) (F$^-$ concentrations >1.0 mg/L) to deep wells (20–40 m) to avoid F$^-$ endemic poisoning. However, the deep wells mostly have high As concentration >10 μg/L (Lu et al., 2000), which is the major cause of endemic As diseases (Bian et al., 2012). In Tongyu county and Taonan city,
residents have severely been affected by high As groundwater (Lu et al., 2004). Around 3800 residents were exposed to high As groundwater (>50 µg/L) (Table 1). The basin is a Mesozoic–Cenozoic Collapsed basin with thick fluvial–lacustrine aquifers. High As groundwater mainly occurs in confined aquifers at depths between 50 and 80 m below land surface (Tang et al., 2010). Arsenic concentrations range between <1.0 and 360 µg/L (Tong et al., 2004).

2.1.4. The Yinchuan basin of Ningxia province

The Yinchuan basin is located to the southwest of the Hetao basin, where the Yellow river passes through. Arsenicosis was firstly recognized in 1995 in the basin (Hu et al., 1999). Arsenic-affected areas generally exist as two strips in the flat plain in the north of the basin, being parallel to the Yellow river (including Pingluo county, Huimin county, and Helan county), with length of 350 km and width between 10 and 60 km. One is located at the front of alluvial fans in the north, and the other near the Yellow river in the southeast (Zhang et al., 2010a). Arsenic concentration is up to 105 µg/L in the southeastern strip (Guo and Guo, 2013), while in the northwestern strip between <0.1 and 200 µg/L (Tan et al., 2006). Vertically, high As groundwater mainly occurs in alluvial–lacustrine aquifers at depths between 10 and 40 m (Han et al., 2010). Around 36,000 residents were at risk (Tan et al., 2006), being exposed to high As groundwater. Prevalence of arsenicosis in the north of the basin was up to 11.7% (Hu et al., 1999).

2.1.5. The Dzungaria basin of Xinjiang province

The Dzungaria basin is located in the north part of Xinjiang province. Arsenic-affected areas mainly lie in the southwestern part of the basin, with an area of 1200 km² (Wang et al., 1995). Before 1960s, surface water (including river water and melting snow) was used for drinking. Due to water pollution of the rivers, local residents changed their drinking water resources from surface water to groundwater after 1960s. Those groundwaters were usually pumped from confined aquifers (Huang, 1983), which normally have high As concentrations. Wang (1984) found As concentrations up to 1200 µg/L in groundwaters. Luo et al. (2006a) reported As concentrations between 70 and 830 µg/L in deep artesian groundwaters (>200 m in depth) in the south of the Dzungaria basin to the north of the Tianshan Mountains. It was observed that As concentration increases with increasing well depth (Wang, 1994). In the north of the basin, groundwater concentration has the range between 100 and 140 µg/L at depth around 200 m, which increases to 300–400 µg/L at the depth around 300 m (Hong, 1983). Arsenic-affected areas are mainly distributed between Aibi Lake (in the southwest of the Dzungaria basin) and Manasi River, parallel to the Tianshan Mountain (Wang et al., 2002). Shallow groundwaters usually have As concentrations between <10 and 68 µg/L.

Ingestion of those high As groundwaters for more than 10 years had resulted in chronic As poisoning in the local people (Wang, 1994). In the early 1980s, the cases of As poisoning were firstly recognized in the Dzungaria basin of Xinjiang province. The prevalence of endemic arsenism was up to 40% in 1991 (Liu et al., 1991), and decreased to 9% in 2007 due to the transformation of drinking water resources (Yang et al., 2009).

2.2. High As groundwater in river deltas

2.2.1. The Yangtze river delta of Shanghai and Nanjing

High As groundwater also occurs in the Yangtze river delta (Table 1). Since 1970s, groundwater with As concentrations greater than 50 µg/L has been found in the first confined aquifers along Nantong–Shanghai in the south of the Yangtze river delta (Chen, 1998). Confined groundwater is hosted in reducing aquifers, generally containing high Fe(II) concentration (mostly >10 mg/L) (Chen, 1998; Gu and Zhen, 1995). Arsenic concentration is positively correlated with Fe(II) concentration. Near Nanjing city, As concentration of groundwater near the Yangtze river at the distance <5 km is generally greater than that far away from the river (Yu, 1999). Arsenic concentration in shallow groundwater is generally low (<4.0 µg/L).

2.2.2. The Yellow river delta of Shandong province

The Yellow river is considered as a non-perennial river in the downstream of Shandong province, where high As groundwater has been found. Shallow groundwater has As concentrations between 0.22 and 235 µg/L (Pang et al., 2007). High As groundwater has mainly been hosted in the Weihe group of shallow aquifers, which is distributed in Xiawa, Botou, Shengtuo, Wopu, and Houzhen, near the coastal line. In Zibo city, shallow groundwater generally has As concentrations between 0.2 and 82 µg/L (Li et al., 2012). In Binzhou city around 80 km downstream of Zibo city along the Yellow river, shallow groundwater has higher As concentrations (~20 µg/L) than surface water (~10 µg/L) (Zhang et al., 2010b). An investigation in the north of Shandong plain in the downstream of the Yellow river shows that shallow groundwater has As concentration between <5 and 440 µg/L, and high-As (>10 µg/L) groundwater samples account for 37% of 482 samples taken at depths between 20 and 50 m (Liu et al., 2013). However, no data are available for As concentrations in deep groundwater in the Yellow river delta.

2.2.3. The Pearl river delta of Guangdong province

The Pearl river delta is mainly distributed in the Guangdong province. Arsenic concentrations between 2.8 and 161 µg/L have recently been observed in shallow groundwaters of the Pearl river delta (Table 1) (Huang et al., 2010; Wang et al., 2012). Groundwater generally occurs in reducing conditions, with neutral-weak alkaline pH. It is characterized by high concentrations of NH₄⁺ (~390 mg/L) and dissolved organic carbon (DOC) (36 mg/L) (Jiao et al., 2010), and low concentrations of NO₃⁻ and NO₂⁻ (Wang et al., 2012). Arsenic concentration is independent of salinity. Huang et al. (2010) believed that groundwater As originates from sediment As and anthropogenic As penetrating from sewage water irrigation. However, Wang et al. (2012) suggested that mineralization of organic matter and reductive dissolution of Fe oxyhydroxides should be the major processes for As mobilization.

2.2.4. The Chianan alluvial plain of Taiwan

The Chianan alluvial plain is located in the southwest of Taiwan, which is bounded by the Peikang river to the north, the Erjen river to the south, the Taiwan Strait to the west, and the Central Range to the east, with an area of 2400 km². Two major rivers, the Pa-chang and Tsengwen, flow from the northeast to the west through the northern part and the southern part of the plain, respectively. A peripheral vascular gangrene disease, known as the Blackfoot disease (BFD), was first reported in the Chianan plain (Tsong et al., 1961), where many people consumed well waters with high As concentrations in the 1960s (Tsong, 1977).

Around 46–61% of shallow wells in the plain had As concentrations exceeding WHO recommended guideline of 10 µg/L. High As groundwater generally occurs in reducing conditions (Liu et al., 2003; Wang et al., 2011; Nath et al., 2011). Approximately 86–93% of high As water had the redox potential (EH) between −75.5 and −139.7 mV (Agricultural Engineering Research Center, 2008). Arsenic concentrations show a large variation, with the range between 1.0 and 575 µg/L and the mean of 208 µg/L (Nath et al., 2011). Arsenic(III) is the dominant As species (~67% of total As). Iron and Mn concentrations are also variable, with the means of 0.72 ± 1.6 mg/L and 107 ± 187 µg/L, respectively. Besides, organic metallic complexes, which have been considered as the
fluorescent substances (or humic substances), coexist with high As concentrations in the artesian well waters (Liu, 1986). These humic substances have been suspected to be associated with development of Blackfoot disease, as well as high As concentrations (Lu, 1990).

2.2.5. The Lanyang alluvial plain of Taiwan

The Lanyang plain is located in the northeast of Taiwan, which is the alluvial fan formed by the Lanyang river. The area is triangular, with an area of approximately 400 km², bound to the Pacific Ocean in the east and to the Central Mountain in the west (Selim Reza et al., 2011). The main river, the Lanyang River, flows from west to east through the middle of the area (Chen, 2000). Residents in the Lanyang basin had used shallow well water (<40 m deep) for more than 50 years, which is the main source of exposure to inorganic As among local residents (Chiou et al., 2001). Arsenic concentration in the well water ranged from undetectable levels (<0.15 µg/L) to 3590 µg/L, with a wide variation in median values from undetectable (<0.15 µg/L) to 140 µg/L (Yang et al., 2003). Although As distribution in the shallow aquifers is mainly controlled by surface activities, high As groundwater has generally been found in the reducing zone, where As(III) is the major As species in groundwater (Lee et al., 2008). Chen et al. (1985) indicated that As(III) and As(V) represented 87% and 5.8% of total As, respectively. High As groundwater (>50 µg/L) is mainly distributed in six townships, including Jiaosi, Yilan, JhongWet, WuJie, DonShan, and LouDon (Lee et al., 2007).

2.3. Others (mountain areas)

In Qinghai province, high As concentrations have been found in spring waters and deep groundwater at depths between 100 and 400 m (Table 1). An et al. (2006) reported that groundwater As ranges between 2.0 and 308 µg/L, with 22.67% samples having As concentrations >10 µg/L, while As concentrations in spring water lie between 0.1 and 1070 µg/L, with 6.20% samples having As concentrations >10 µg/L. High As groundwater mainly occurs in Guide region and Qilian ranges (Zhang et al., 2009). In Guide region, artesian groundwater in Neogene siltstone usually has high As concentration (Zhang et al., 2010a; Shi et al., 2010). It was suggested that those high As groundwater is affected by geothermal water, due to the good correlation between As concentration and water temperature (Shi et al., 2010). Groundwater is mainly controlled by the NNW and the EW faults (Zhang et al., 2010a). Therefore, groundwater As is believed to have geothermal sources. High As groundwater (>50 µg/L) has also been found in Gansu province, which is mainly distributed in Hezuo, Tianzhu, Huanxian, Zhouqu, Weixuan, and Chengxian (Bai et al., 2007). Arsenic concentration is up to 2160 µg/L (Table 1). Among 210 water samples with As concentration >50 µg/L, 50.48% samples are shallow groundwater, and 36.19% spring water. High As waters mainly occur around the fault-induced ravines (Bai et al., 2007). In the Hezuo city, it was found that river water, spring water and shallow groundwater contain high As concentration, which leads to the occurrence of chronic arsenicosis (Xu et al., 2007). It was confirmed that 126 residents had symptoms of endemic As poisoning in 2007–2008.

In Sichuan province, high As groundwater is mainly distributed in Jinchuan county, Aba county, and Luding county (Table 1). In Jinchuan county, high As concentration with the range between 56 and 287 µg/L was found in spring water (Deng et al., 2004). Although no other chemical data were available, they suggested that weathering of As-containing minerals would be the cause for As enrichment in groundwater. An investigation on water As in Aba county showed that spring water mostly has high As concentration, which was believed to be related to weathering of As-bearing minerals (Qin and Li, 2008). Arsenic concentration between 0.1 and 75 µg/L was observed in spring water and stream water in Luding county (Li and Ni, 2005). There are 59% samples having As concentration greater than 10 µg/L.

In Yunnan province, high As concentrations have mainly been found in geothermal water (Table 1). Arsenic in the hot-springs waters is in the ranges between 43.6 and 687 µg/L in Tengchong area (Liu et al., 2009), where As(III) is the major As species with the fraction up to 91% of total As. The highest As concentration (887 µg/L) was found in the Guming spring in Rehai geothermal field with temperature of 96.0 °C and pH of 8.93 (Guo and Wang, 2012). Besides, shallow groundwater and surface water contain high As concentration in Gengma county and Simao county. Arsenic concentration is up to 200 µg/L in Gengma county, leading to endemic As poisoning (Wang and Kong, 2006). Spring water is the major media hosting high As concentration in Simao county, which was proposed to be related the weathering of bedrock (Luo et al., 2006b).

High As groundwater has resulted in negative effects on human health. Yu et al. (2007) reported that high As concentration (>50 µg/L), being observed in about 5% of tested 445,638 wells in 20,517 villages of 16 provinces from the Mainland China, affected an estimated 0.58 million residences, between 2001 and 2005. The population being at risk by the consumption of As-contaminated groundwater is estimated to be 19.6 million according to a statistical risk model (Rodríguez-Lado et al., 2013). However, this 19.6 million may be underestimated since the model mainly includes As groundwater in alluvial sediment aquifers, excluding the bedrock aquifers in mountain areas. The model showed that the North China plain, the Qaidam basin, the Heihe basin, the Ejina basin, the Tarim basin, and the Northeastern plain are the potential high As basins, although this estimation should be validated by actual geochemical investigation.

3. Hydrogeology of the aquifers

3.1. Sedimentary aquifers

3.1.1. Inland aquifers

High As groundwater mainly occurred in Quaternary sedimentary aquifers in arid–semi-arid inland basins. These inland basins usually have thick sedimentary sequences, up to several kilometers. Several aquifer groups are normally recognized, including shallow aquifers, semi-confined aquifers, and confined aquifers. Shallow groundwaters in alluvial lacustrine or lacustrine sediments usually have high As concentrations. Although affected by the surface water, groundwater usually flows from the piedmont front to the flat plain. Low-lying and flat topography attributes to low hydraulic gradients in the central of the basins. Low permeability of aquifer sediments and low hydraulic gradients cause low flow rates and limited flushing of the aquifers.

3.1.1.1. The Hetao basin and the Huhhot basin. The Hetao basin and the Huhhot basin in Inner Mongolia are formed by extension induced by the Neogene faults (Zhao et al., 1984). The Hetao basin is located between the Yellow river to the south and the Langshan Mountains to the south. There are sediment sequences of 500–1500 m in the southeast of the basin, and 7000–8000 m in the northwest of the basin (Guo et al., 2008a). Affected by palaeo-climate and tectonic movement, the Tertiary sediments occur in oxic conditions and accumulate great amounts of salinity, while the Quaternary sediments have both alluvial and lacustrine sources, with fine clast. The Quaternary sediments are mainly derived from the Langshan Mountains and partly from fluvial deposits of the Yellow river. The Huhhot basin lies between the Daqing Mountains.
and the Yellow river, which has a gentle WSW slope with elevation between 1100 and 980 m. Quaternary sediment sequences of sands, silt and clay occur in the basin, with the thickness around 1500 m (Smedley et al., 2003). The sediments are heterogeneous both spatially and with depth. However, Holocene sediments outcropping at surface are typically coarse-grained in the basin margins and fine-grained in the central parts of the basin. Due to tectonic movement, the rapid uplift of the mountains and the rapid subsidence of the basin result in high sediment accumulation rate in both basins, especially in Middle- and Late-Pleistocene (~0.6 mm/yr) and Holocene (~1.2 mm/yr) (Li et al., 2007).

In the Hetao basin, unconfined or semi-confined aquifers occur in the shallow deposits at depths <100 m with upper Pleistocene–Holocene alluvial–pluvial and alluvial lacustrine sands, while confined aquifers in the deep deposits with middle Pleistocene lacustrine sands occur at depths greater than 100 m (Guo et al., 2008a). High As groundwater is mainly present in the semi-confined shallow aquifers, showing the strip-type spatial pattern. The high As zones correspond to the subsidence centers of the basin (Yang et al., 2008). Shallow groundwater may be heavily affected by drainage channels and irrigation channels (Guo et al., 2011a). The main drainage channel, being located in the piedmont depression of the northern Hetao basin, discharges shallow groundwater from the piedmont area in the north and from the recharge area near the Yellow river in the south (Zhang et al., 2013). Shallow aquifers in the piedmont alluvial–pluvial plain are mostly coarse sands and gravels with hydraulic conductivity up to 20 m/d, and in the alluvial lacustrine flat plain primarily being composed of silt and fine sands with hydraulic conductivity less than 2.2 m/d (Guo et al., 2010). Regions in the piedmont area and near the Yellow river are the high flow rate area with hydraulic gradients >0.8‰, while near the drainage channels the low flow rate area with hydraulic gradients <0.8‰ (Zhang et al., 2013). Therefore, groundwater flow rate in the piedmont with coarse sands and gravels with a hydraulic gradient of 0.8‰ is around 1.6 cm/d, and in the flat plain with silt and fine sands with a hydraulic gradient of 0.8‰ around 0.18 cm/d. On the one hand, the low flow rate leads to long residence time of groundwater in the aquifer, and therefore near equilibrium of water–rock interaction. On the other hand, these flow rates are too slow to flush As out of the aquifer, because it takes thousands of years to flush As over a distance of 1 km in the Gan–Brāmaputra delta with a flow rate of 5.0 cm/d (van Geen et al., 2008). Groundwater is recharged by vertically infiltrating meteoric water in the basin and laterally penetrating fracture water from marble, slate and gneiss along the mountain front, as well as a little leaked water from river and ditches, and irrigation return flow from farmland. Shallow groundwater generally flows from north to south in the northern part and from southwest to northeast in the southern part (Guo et al., 2008a). During irrigation seasons, groundwater table is high in the flat plain irrigated with diverted–Yellow river water and low in the piedmont area irrigated with groundwater, which would alter groundwater flow conditions (Guo et al., 2013c).

In the Huhhot basin, sequences of lacustrine sediments frequently occur in the low-lying central parts of the basin, and alluvial deposits along the mountain foothills. Sandy layers in the upper 40 m form shallow aquifers (Smedley et al., 2003). Deep aquifers exist at depths >100 m. High As groundwater mainly occurs in the transition area between the alluvial fans and the Yellow river fluvial plain, where clayey sands and fine sands are present in the aquifers near palaeo-channels of the Yellow river and lagoons (Li and Li, 1994). Although exact values of water flow rates were not reported, groundwater has higher flow rates in the mountain foothills than those in the low-lying central plain, due to the higher topography and good permeability (Zhang et al., 2000). Groundwater is mainly recharged from the mountain foothill and alluvial fans, and discharged in the low-lying areas via evaporation (Liu et al., 1996).

3.1.1.2. The Yinchen basin. Three geomorphologically distinct units are recognized in this basin, including the piedmont proluvial plain with a gravel aquifer, the alluvial–diluvial plain with a sandy gravel aquifer and the alluvial–lacustrine plain with a sand aquifer (Han et al., 2013). High As groundwater has mainly been found in shallow groundwaters in the north of the alluvial–lacustrine plain (Han et al., 2010), where faulting with resulting paleo-lakes or erosion (paleo-river channel) result in low-lying topographic areas. In the piedmont region of the Helan Mountain and the alluvial–lacustrine plain in the southernmost of the basin, unconfined aquifers mainly occur. In the central and eastern parts of the basin, multi-layers of alluvial and lacustrine deposits form the unconfined shallow aquifer with depth between 10 and 40 m, a first confined aquifer with depths between 25–60 m and 140–160 m, and a second deep confined aquifer with depth between 140 and 240–260 m (Xue, 2011). Regional groundwater flow is generally from the borders of the plain towards the interior of the basin, and from the southwest to the northeast under low hydraulic gradients because of the flat topography (Han et al., 2010; Wang et al., 2013a). The unconfined shallow groundwater is recharged by precipitation and infiltration of irrigation water diverted from the Yellow river, and is discharged by evaporation, drainage canal, pumping, and infiltration to deeper aquifer (Wang and Yu, 2001). The hydraulic gradient of the shallow groundwater in the southern part of the alluvial plain is generally greater than 0.4‰, and less than 0.4‰ in the northern part of the alluvial–lacustrine plain, which is related to the occurrence of high As groundwater (Han et al., 2013). The groundwater renewal rates range from 11% to 15% in the south, while between 0.1% and 6% in the north (Wang et al., 2013a).

3.1.1.3. The Datong basin. The Datong basin is one of the Cenozoic basins of the Shanxi rift system, which produces a series of en-echelon half grabens, as a result of northeast displacement of the Ordos block. Gneiss and basalt of the Hengshan Segment of Wutai Group of Archean occur to the east of the basin, and Cambrian and Ordovician limestone and Carboniferous and Permian sandstone–shale to the west. Thick Quaternary sediments have deposited in the basin, ranging between 200 m in the margin and 2700 m in the center, with a sedimentation rate around 0.24 mm/yr (Wen et al., 2013). The sediments from the basin margin are mostly alluvial–pluvial gravel and sand, and those at the central part of the basin sandy loam and silt, lacustrine and alluvial–lacustrine sandy loam, silt clay and clay with high organic matter contents (Guo and Wang, 2005). The shallow Quaternary aquifer in the center of the basin usually consists of 60 m deposits of gray to blackish lacustrine and alluvial–lacustrine medium–fine sand, silt clay and clay (Wang et al., 2009), which hosts shallow groundwater. Arsenic concentration is high (up to 1930 μg/L) in the reducing groundwater in the central low-lying area (Guo et al., 2003; Guo and Wang, 2005). High As groundwater has mainly been found in the eastern side of the Sanggan river, which suggests that groundwater As would ultimately originate from local source of gneiss and basalt weathering since the higher As contents are found in gneiss and basalt to the east of the basin than in limestone and sandstone–shale to the west of the basin (Guo, 2002). Shallow groundwater is mainly recharged by vertically infiltrating meteoric water in the basin and laterally flowing fracture water in bedrock along the basin margins, as well as irrigation return flow. The general direction of groundwater flow is from the margin to the center of the basin (Guo and Wang, 2005). The velocity of groundwater flow ranges between 0.20 and 0.58 m/d near the mountains (Xie et al., 2009a), but groundwater flow in the flat
and low-lying area in the basin center is very low. Although the hydraulic gradients and the flow rates are not specifically reported, high As concentration is expected to be associated with the low flow rate of groundwater in reducing conditions (Guo and Wang, 2005; Guo et al., 2003; Xie et al., 2012).

3.1.1.4. The Songnen basin. The Songnen basin is a part of Meso-Cenozoic Songliao graben basin, with thick sequences (~5000 m) of inland fluvial–lacustrine sediments (Bian et al., 2012). Vertical tectonic movement leads to depression in the east and uplift in the west, which forms a gentle SE slope with an altitude around 300 m above see level (asl) in the northwest and an altitude around 130 m asl in the southeast. The Daxing'anling Mountains lie to the northwest of the Songnen basin. Upper Neogene strata are characterized by glutenite, sandstone and siltstone with mudstone and silty mudstone of Da'an group in the lower part, and semi-consolidated fluvial–lacustrine deposits (including glutenite, sandstone, siltstone, and silty mudstone) of Taikang group in the upper part. Lower Quaternary sediments are mainly composed of gravel sands, interbeded with fine sands and clay. Middle Quaternary sediments are characterized by clayey silt and silt, while Upper Quaternary sediments by loess, clayey silt, fine sand and middle sand, which are widely distributed in the basin. In Holocene sediments, sequences vary from alluvial sands in the bottom, through alluvial–lacustrine fine sand, silt and silty clay and lacustrine clay and silty clay in the middle, to aeolian silt and silty sand in the uppermost layer (Feng, 2007; Bian et al., 2007).

Groundwater is mainly hosted in Cenozoic sediments. Aquifer systems are divided into the Quaternary porous unconfined and confined aquifers (shallow aquifer and mid-deep aquifer), and the pore-fracture confined aquifers of Upper Neogene Da'an and Taikang groups (deep aquifer I), the Cretaceous fracture-pore confined aquifers (deep aquifer II) (Tang et al., 2010). Shallow groundwater occurs in Holocene alluvial sand aquifer, and Upper Quaternary fine-sand and middle-sand aquifer, with conductivities of 30–50, and 5–15 m/d, respectively. Confined groundwater is mainly hosted in Lower Quaternary gravel sands with the thickness between 10 and 40 m, and in Upper Neogene Da'an and Taikang sandstone and glutenite with the thickness between 20 and 90 m (Bian et al., 2009).

High As groundwater mainly occurs in shallow aquifers at depths <20 m and in Upper Quaternary confined aquifer at depths between 20 and 100 m (Bian et al., 2012). Spatially, As concentration greater than 10 µg/L has been found in the shallow aquifers in the alluvial–lacustrine plain between the distal edge of the alluvial fans and the Huolin river, and confined aquifer in the alluvial–lacustrine plain near Tongyu county. High As concentration may be related to glacial deposits in Upper Quaternary and lacustrine deposits in Holocene.

3.1.2. River deltas

In the river deltas, thick sequences of Quaternary sediments have usually been deposited due to tectonic subsidence. In those areas, marine sediments are interlaced with fluvial deposits, which have normally been affected by transgression. The sediments are relatively young. The flat topography leads to low hydraulic gradients, and therefore low groundwater flow rates. The interbeds of marine and fluvial deposits are mainly composed of silty sand, silt, clayey silt and clay, with high content of natural organic matter. This readily leads to reducing conditions in aquifers.

3.1.2.1. The Yangtze river delta. The Yangtze river delta is located in the south of the Subei depression. During Quaternary, interbeds of marine and fluvial deposits have developed due to tectonic depression, with the average thickness around 200–300 m (Song et al., 2000). Aquifer systems were observed in the Quaternary sediments, including Holocene unconfined aquifers, Middle-Lower Pleistocene confined aquifers, and Lower Pleistocene confined aquifers (Song et al., 2000; Xu, 2002). The Holocene unconfined aquifers are widely distributed, with the interbeds of silty clay, silt and fine sand. Continuous aquifers underlie the unconfined aquifers. There are two confined aquifers in Middle-Lower Pleistocene sediment sequences, including confined aquifers I and II (Chen, 1998; Song et al., 2000; Xu, 2002). Confined aquifer I is characterized by silt and silty sand, which originate from both marine and fluvial deposits, while confined aquifer II by sand, pebbly sand, and middle-fine sand being mainly from the Yangtze river estuarine deposits (Song et al., 2000; Xu, 2002). Normally, the former Yangtze river eroded the upper aquitards of confined aquifers I and II near the palaeo-channels, which makes the hydraulic connection between confined aquifers I and II.

3.1.2.2. The Yellow river delta. The Yellow river delta is located in the southern edge of the Bohai seabasin with an area of 7893 km² and natural slope gradients between 1/8000 and 1/12,000 (Zhang et al., 2005). It has been affected by Laizhou depression, Jiyang depression, and Bozhong uplift (Yuan et al., 2006). Since the Cenozoic era, subsidence movement has been predominated. Continuous subsidence leads to the thick Quaternary sequences, which is up to 400 m. Topographically, it is divided into piedmont plain and alluvial–marine plain (Li et al., 2008). The piedmont plain is located to the south of the Xiaqinghe river, which is mainly deposited by alluvial and fluvial sediments, while the alluvial–marine plain to the north of the Xiaqinghe river (Li et al., 2008; Yao et al., 2002). The alluvial sediments have interlaced the marine sediments in the alluvial–marine plain. Based on buried depths of aquifers and hydraulic connections, three aquifer groups are divided in sedimentation sequences of Quaternary and Tertiary Minghuazhen group, including shallow unconfined and semi-confined aquifers (Aquifer I), middle confined porous aquifers (Aquifer II), and deep confined porous–fissure aquifers (Aquifer III) (Yao et al., 2002). Aquifer I is mainly composed of fluvial and marine silt and clay silt, with the depth of burial less than 60 m (An et al., 2012). During the deposition of Aquifer I, two transgressions had occurred, which leads to the presence of saline water in the alluvial–marine plain. The lower aquitard of Aquifer II lies at depths between 180 and 370 m, which is the upper aquitard of the Aquifer III (Yao et al., 2002). The Yellow river is the natural divide of groundwater systems. In the river delta to the north of the Yellow river, groundwater flows from the south to the north or the northeast, while from the north to the southeast in the river delta to the south of the Yellow river (Li et al., 2008). High As groundwater has mainly been found in the shallow aquifer (Aquifer I) in the alluvial–marine plain, which may be related to the low slope gradients and interbedded marine deposits.

3.1.2.3. The Pearl river delta. The Pearl river delta is located in the south-central of Guangdong province, which is surrounded by mountains to the north, the west and the east, and by the South China Sea to the south. It is formed as a result of uplift of the Tibetan Plateau during the Tertiary and Quaternary Periods (Zong et al., 2009). During the Late Quaternary, active fault systems have led to land subsidence of the Pearl river basin at a rate of 0.2 mm/a (Huang et al., 1986), and therefore sedimentation of terrestrial and marine deposits on Cretaceous–Tertiary sandstones and Mesozoic granites (Huang et al., 1982). The Quaternary deposits mainly
consist of four stratigraphic units: two terrestrial units (T1 and T2) and two marine units (M1 and M2) (Wang et al., 2012). The old terrestrial unit (T2), mainly composed of sand and gravel, had deposited in the last transgression in the late Pleistocene (Wang et al., 2013b). The old silt and clay marine unit (M2), overlying on T2, was formed during the interglacial period (about 130 ka before present) (Zong et al., 2009). A younger terrestrial unit (T1), mainly composed of alluvial sand and clayey silt, was deposited along the palaeo-river channels. During Holocene, a large-scale transgression has resulted in a layer of younger marine sediments (M1) with a thickness of 5–20 m (Wang et al., 2013b). In many places, the old marine unit (M2) and the younger terrestrial unit (T1) are missing. The fine-grained silts and clays of M1 and M2 comprise the aquitards. Accordingly, the old terrestrial unit (T2) is the basal aquifer, and the younger unit (T1), being fluvial sands and clayey silt, is a local intermediate aquifer (Jiao et al., 2010). The general direction of regional groundwater flow in the sand and gravel aquifer follows roughly the major river flow, which is from northwest to southeast (Wang et al., 2012). High As groundwater has mainly been found in the basal aquifers (Wang et al., 2012).

3.2. Geothermal related aquifers

In the Guide basin and the Tengchong area, high As groundwater are closely associated with deep geothermal water. Usually, deep geothermal water recharges the shallow groundwater via faults due to recent tectonic movement. Spatial distribution of As concentration is generally consistent with the occurrence of tension faults.

The Guide basin is a Mesozoic–Cenozoic sedimentary basin, which is controlled by the giant faults occurring in the front of the mountains. The basin belongs to the Qilian–Helan stratigraphic zone and the Zhamashan Mountains sub-region (Gu et al., 1992). Since the Cenozoic era, the basin has continuously subsided, leading to deposition of clast sediments with a thickness around 2000 m (Chen et al., 2010). The Neogene system with a thickness around 1330 m consists of a set of red piedmont fluvi–lacustrine sediments, which unconformably contact with the underlying Proterozoic or Triassic basement. The Quaternary deposits overlie the Neogene system (Gu et al., 1992). Confined aquifer and unconfined aquifer were observed in Neogene and Quaternary deposits, respectively. Quaternary unconfined aquifers are mainly composed of alluvial silt and fine sand, which are mainly distributed in piedmont plains and river valley plains. The Guide group of Neogene deposits is widely distributed in the basin, which consists of middle-grained sandstone, coarse-grained sandstone, and siltstone (Chen et al., 2010). Artesian groundwater normally occurs in the Guide group of Neogene deposits. Groundwater from unconfined aquifer usually has undetectable As (<10 μg/L). However, As concentration of artesian groundwaters from confined aquifer is generally high (between 112 and 319 μg/L) (Shi et al., 2010). Both well water temperature and As increase with increasing the well depths (Zhang et al., 2010a), suggesting that As should be hydrothermally leached from the organic-rich fine lacustrine deposits of the Neogene Guide group.

The Tengchong area belongs to the Yunnan–Tibet geothermal belt of China, a major part of the Mediterranean–Himalayas geothermal belt (Liao and Zhao, 1999). Tectonically, it is situated in the mini-Tengchong block and the eastern collision boundary between the India and Eurasia plates, and develops from a micro continent between Gondwanaland and Eurasia (Du et al., 2005). Since the Late Paleozoic, tectonic activity has become very intense. Quaternary volcanoes and fault structures are presently the most conspicuous features of this region (Shangguan et al., 2005; Zhang et al., 2008). The active faults with strikes of NNE, NS, NW and NE have well developed in the region (Liao and Guo, 1986). The geothermal surface manifestations (e.g. hot springs) have been found on the margins of volcanic rock areas, in correspondence to fault systems (Zhang et al., 1987). In this region, 68 different volcanoes, of which three are Holocene volcanoes (namely Dayingshan, Maanshan and Heikongsan), have been identified, and about 140 sites of hot spring activity have been found (Du et al., 2005). Hot spring waters in the Rehai have been classified into four chemical groups, including Na–Cl–HCO₃ or Na–HCO₃–Cl waters discharged with high temperatures in granite and granitic clastic sedimentary rocks (Group I), Na–HCO₃ waters in areas of metamorphic rocks and granite rocks (Group II), Ca(Mg)–HCO₃ or Ca/Mg–Na–HCO₃ waters with lower temperatures (<40°C) in areas with Ordovician–Silurian slates and basalt and/or andesite (Group III), and Na–HCO₃–SO₄ or Ca–Na–HCO₃–SO₄ waters (Group IV) (Zhang et al., 1987). Spring waters in Groups I and II usually contain high As concentration, which is up to 887 μg/L (Guo and Wang, 2012).

4. Aqueous chemistry of high As groundwater

In this section, we take the Datong basin, the Hetao basin, the Yinchuan basin as representatives of inland arid–semiarid basins, and the Pearl river delta as representative of the river delta for delineating aqueous chemistry of high As groundwater in China. The chemical data of the Datong basin are cited from Guo et al. (2003), Xie et al. (2009a), and Luo et al. (2012), the Hetao basin from Guo et al. (2011a) and Luo et al. (2012), the Yinchuan basin from Smedley et al. (2003) and Mukherjee et al. (2009). The data of the Yinchuan basin are obtained from our investigation in 2012. The data reported in Wang et al. (2012) are used for high As groundwater in the Pearl river delta.

4.1. Major ions

Concentrations of major ions significantly varied in high As groundwaters. Sodium and Cl⁻ concentrations increased from the Datong basin, through the Yinchuan basin, the Huhhot basin and the Hetao basin, to the Pearl river delta (Fig. 2a). In the Datong basin, the Yinchuan basin, and the Hetao basin (the inland basins), Na⁺ concentrations are mostly greater than Cl⁻ concentrations, while groundwater in the Pearl river delta has higher Cl⁻ concentration than Na⁺ concentration. Most groundwater has HCO₃⁻ concentrations between 200 and 2000 mg/L, showing less variation relative to Cl⁻ concentration (mostly between 10 and 20,000 mg/L). Groundwater in the inland basins has generally higher HCO₃⁻ concentration than Cl⁻ concentration, while in the river delta Cl⁻ concentration is higher than HCO₃⁻ concentration (Fig. 2b). Total dissolved solid (TDS) has the values between 200 and 20,000 mg/L. Generally, TDS values in groundwaters of the river delta are greater than those in the inland basins (Fig. 2c). There is a good correlation between Na⁺ concentration and TDS value (Fig. 2c), showing the major contribution of Na⁺ to TDS. There is no significant correlation between Ca²⁺ and SO₄²⁻ (Fig. 2e). In the Pearl river delta, Ca²⁺ concentration is higher than SO₄²⁻ concentration, while groundwaters mostly have higher SO₄²⁻ concentration than Ca²⁺ in the Yinchuan basin, the Hetao basin and the Huhhot basin. The Datong basin generally has the lowest SO₄²⁻ concentration, with Ca²⁺ concentration greater than SO₄²⁻. Additionally, HCO₃⁻ concentration is usually greater than SO₄²⁻ concentration in both the inland basins and the river delta (Fig. 2f).

In the Huhhot basin, concentrations of HCO₃⁻ and Na⁺ are usually high in the shallow groundwaters, which are mostly located in the lower part of the pieper plots, although groundwaters vary in chemical composition both laterally along the flow paths and with depth (Smedley et al., 2001). Along the flow paths, shallow
Groundwaters evolve from Ca–HCO₃ type in the pediment areas along the basin, to Na–HCO₃/Cl or mixed-ion types in the central parts of the basin (Smedley et al., 2003). Mukherjee et al. (2009) showed that the shallow groundwater is generally of a mixed Ca–Na–HCO₃–Cl type. They observed dilute Ca–Mg–HCO₃ and Na–HCO₃ groundwaters with TDS <500 mg/L in the alluvial plains in the north of the basin and in the alluvial fans on the SE side of the Manhan Mountains, and slight saline groundwaters in the alluvial and lacustrine plains downstream the Daheihe river and lacustrine deposits in the foothills of the Manhan Mountains with TDS between 1000 and 3000 mg/L and water types of Na–Mg–HCO₃–Cl, Na–Cl–HCO₃, Na–Cl–SO₄, and Na–Mg–SO₄–Cl. Spatially, high As groundwater mainly occurs in the alluvial–lacustrine plains and near the Hasu Lake (Smedley et al., 2003).

In the Hetao basin, groundwater chemistry evolves from the alluvial fans to the alluvial–lacustrine plain. Shallow groundwater is generally of Ca–HCO₃–SO₄ type with low salinity in the regional recharge area of the alluvial fans, Mg–Ca–HCO₃–Cl in the distal edge of the fans (Guo et al., 2010), and Na–Cl–HCO₃ with high salinity in the central part of the basin (Guo et al., 2008a; Luo et al., 2012).

Fig. 2. Na⁺ vs. Cl⁻ (a), HCO₃⁻ vs. Cl⁻ (b), Na⁺ vs. TDS (c), HCO₃⁻ vs. TDS (d), Ca²⁺ vs. SO₄²⁻ (e), and HCO₃⁻ vs. SO₄²⁻ in groundwaters of the Datong basin, the Hetao basin, the Huhhot basin, the Yinchuan basin, and the Pearl river delta. 

<table>
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<th>Symbol</th>
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<tr>
<td>Red</td>
<td>The Huhhot basin (Smedley et al., 2003)</td>
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<td>Blue</td>
<td>The Hetao basin (Guo et al., 2011)</td>
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<td>Green</td>
<td>The Datong basin (Guo et al., 2003)</td>
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<tr>
<td>Green</td>
<td>The Datong basin (Xie et al., 2009)</td>
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<td>Green</td>
<td>The Huhhot basin (Mukherjee et al., 2009)</td>
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<td>The Hetao basin (Luo et al., 2012)</td>
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<td>The Datong basin (Luo et al., 2012)</td>
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<td>Green</td>
<td>The Pearl River delta (Wang et al., 2012)</td>
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<tr>
<td>Green</td>
<td>The Huhhot basin obtained in this study</td>
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et al., 2012). High salinity in the center of basin is related to evaporation and irrigation losses. The widely-distributed irrigation channels and drainage channels have posed an impact on groundwater chemistry. Near the drainage channels, groundwater is generally of Na–Cl–HCO₃ type with electric conductivity between 1930 and 9500 μS/cm, while of Ca–HCO₃ type near the irrigation channels with electric conductivity between 500 and 900 μS/cm (Guo et al., 2011a). An investigation carried out in Hangjinhouqi in the northwest of the Hetao basin showed that shallow groundwaters are generally of Na–HCO₃ or Na–Cl–HCO₃–Cl type along the Langshan Mountains front and in the south recharged from the Yellow river, while mostly Na–Cl–HCO₃ or Na–Cl type in the flat plain (Deng et al., 2009).

In the Yinchuan basin, groundwater chemistry spatially varies, which is dependent of hydrogeological settings. Shallow groundwater displays increasing trends in TDS, Na⁺, Cl⁻, and SO₄²⁻ along the direction of groundwater flow path from SW to NE (Han, 2013). In the south of the basin which is the recharge area, shallow groundwater is generally of Mg–Na–HCO₃–SO₄ type. In the center of the basin, groundwater is of a mixed Ca–Na–HCO₃–SO₄ or Mg–Na–HCO₃–Cl type. In the north which is the discharge area, the hydrochemical type is mainly of Na–Ca–Cl–SO₄ with elevated TDS (Wang et al., 2013a). In the center-north of the basin, the return flow of irrigation water with low TDS (around 350 mg/L) leads to the scattered distribution of fresh shallow groundwater, although groundwater mostly has high TDS values (1000–3000 mg/L) (Han et al., 2013). High As groundwater has mainly been observed in the north of alluvial-laustrine plain (Han et al., 2013; Guo and Guo, 2013).

In the Datong basin, groundwater is generally of Ca–HCO₃ type in the pediment discharge areas for regional shallow groundwater system, with TDS between 247 and 792 mg/L. In the converging zone between recharge and discharge areas, the major ions are HCO₃⁻, Mg²⁺, Ca²⁺, and Na⁺, plotted at the middle-left of Piper trilinear diagram (Guo and Wang, 2005). In the enrichment zone, immediately downstream of the converging zone, shallow groundwater is generally of Na–HCO₃–SO₄–Cl type with TDS between 440 and 8900 mg/L, plotted at the middle right of Piper trilinear diagram. Shallow groundwater, being located in the discharge area of the regional groundwater system and at the center of the basin, has the water type of Na–HCO₃. High As concentration has mainly been found in the shallow groundwater at the center of the basin (Guo et al., 2003; Xie et al., 2009a). These sodium-rich waters usually have high concentrations of As and Fe³⁺, ranging between 7.9 and 1530 μg/L, and between 0.48 and 7.33 mg/L, respectively (Guo et al., 2003; Wang et al., 2009).

Shallow groundwater has been substantially affected by both paleo seawater and freshwater in the Pearl river delta (Jiao et al., 2010). Groundwater is mostly of Na–Cl type in the southwest of the delta, Ca–HCO₃ or Na–HCO₃ in the northwest, and Na–Cl in the northeast (Wang and Jiao, 2012; Huang et al., 2013). Due to the strong seawater influence, groundwaters close to the sea usually have water type of Na–Cl. Along the regional groundwater flow from the northwest to the southeast, groundwaters evolve from Ca–HCO₃ or Na–HCO₃ type to Na–Cl type (Wang and Jiao, 2012). In this area, groundwater is not only affected by seawater intrusion, but also shows a clear path of hydrogeochemical evolution from Ca–HCO₃, through Ca–Cl, to Na–Cl types (Huang et al., 2013). High As groundwater has been mainly found in the northwest and northeast of the delta, with water types of Ca–HCO₃, Na–HCO₃ and Na–Cl (Wang et al., 2012).

4.2. Redox sensitive species

Either in the inland basins or in the river delta of China, high As groundwater usually occurs in reducing conditions, with ORP mostly <0 mV (Fig. 3a). The groundwater in the Hetao basin has the lowest ORP values, followed by the Huhhot basin, the Datong basin, and the Yinchuan basin. As an effective candidate for electron donor in groundwater systems, dissolved organic carbon (DOC) is normally high, mostly ranging between 5 and 20 mg/L (Fig. 3a). In the Hetao basin, DOC concentration is the highest, with the average of 12.0 mg/L, followed by the Huhehot basin (average 8.3 mg/L), the Yinchuan basin (average 6.0 mg/L), and the Datong basin (average 5.0 mg/L). Generally, there are negative correlations between DOC and ORP of the high As groundwater. It may indicate that DOC is the trigger in developing the reducing conditions in the aquifers (McArthur et al., 2004; Polizzotto et al., 2008).

In the reducing conditions, concentrations of SO₄²⁻ and NO₃⁻ are relatively low (Fig. 3b). Sulfate concentration is the lowest in the Huhehot basin, with the average of 40 mg/L, while the Hetao basin groundwaters have the lowest NO₃⁻ concentration (average 2.3 mg/L). The Yinchuan basin groundwaters have the highest SO₄²⁻ concentration, with an average of 277 mg/L. In the Hetao basin, groundwaters have SO₄²⁻ concentrations between <0.1 and 1260 mg/L (average 230 mg/L). In comparison with the Hetao basin and the Yinchuan basin, the Datong basin and the Huhehot basin have higher concentrations of NO₃⁻ (average 12.5 and 9.2 mg/L, respectively), and lower concentration of SO₄²⁻ (average 61.5 and 65.8 mg/L, respectively). The general low concentrations of NO₃⁻ and SO₄²⁻ imply that denitrification and sulfate reduction occur in aquifers with high As groundwater (Guo et al., 2008a; Deng et al., 2009; Xie et al., 2009a).

Additionally, concentrations of Fe and Mn are generally high. In the Pearl river delta, Fe and Mn concentrations are the highest, with average values of 29 mg/L and 5600 μg/L, respectively, followed by the Yinchuan basin (with averages of 2.10 mg/L and 532 μg/L, respectively) (Fig. 3c). In comparison, the Hetao basin and the Huhehot basin have relatively lower concentrations of Fe (with averages of 0.50 and 0.76 mg/L, respectively) and Mn (with averages of 254 and 201 μg/L, respectively). In the Datong basin, groundwaters have the lowest concentrations of Fe and Mn. Generally, it has been found that Fe concentration is positively correlated with Mn concentration (Fig. 3c). The relatively lower concentrations of Fe and Mn in the Hetao basin and the Huhehot basin with stronger reducing conditions may be due to the coexistence of SO₄²⁻ and S²⁻. Detectable S²⁻ has been found in groundwaters of the Hetao basin (Guo et al., 2010, 2011a), the Huhehot basin (Smedley et al., 2003), and the Datong basin (Xie et al., 2013). In the reducing conditions, the S²⁻ produced from SO₄²⁻ reduction would restrain the accumulation of Fe and Mn in groundwaters (Guo et al., 2013a,b).

Although both Fe and As would preferentially be released in reducing conditions, there is no significant correlation between Fe concentration and As concentration in high As groundwaters (Fig. 3d). In the Hetao basin, groundwaters have high As concentration with an average of 213 μg/L, although Fe and Mn concentrations are relatively low. Arsenic concentration is the highest in the Datong basin, with an average of 308 μg/L, where the lowest Fe and Mn concentrations are observed. The average As concentrations are 28.0 and 173 μg/L in the Yinchuan basin and the Huhehot basin, respectively. In the Pearl river delta with the highest Fe and Mn concentrations, groundwater As concentration is relatively lower, with the average of 33.0 μg/L. Although the reductive dissolution of Fe oxides would release As from solids into groundwater, Fe(II) may be scavenged by means of resorption on the minerals or precipitation of siderite or pyrite (Guo et al., 2013a). Besides, the released As may be co-precipitated with pyrite or adsorbed on Fe minerals. Pathways of Fe and As cycling are expected to be different, and therefore As is decoupled with Fe in high As groundwater systems (van Geen et al., 2004; Burnol et al., 2007).

Both U and Mo are redox-sensitive elements. Their concentrations show big variations in high As groundwaters (Fig. 3e).
Concentration of U ranges between 0.02 and 172 μg/L, with an average of 4.99 μg/L, in the Hetao basin. The average U concentration is the highest in the Huhhot basin (5.55 μg/L with the range between <0.01 and 38 μg/L). In comparison, U concentration is relatively lower in the Yinchuan basin (between 0.04 and 31.0 μg/L, average 2.77 μg/L) and in the Datong basin (between <0.01 and 23.0, average 2.79 μg/L). In general, there is a negative correlation between U and As (Fig. 3e). High U concentrations are associated with low As waters, and vice versa. Uranium is relatively immobile as insoluble U(OH)₄ species in the reducing conditions (Gorby and Lovley, 1992), showing low concentration, while mobile as soluble UO₂(CO₃)²⁻ or UO₂(CO₃)⁴⁻ species in oxic conditions (Moon et al., 2009). Similar to U, Mo shows the highest concentration in the Huhhot basin groundwater, with an average of 7.35 μg/L, followed by the Hetao basin groundwater, the Datong basin groundwater, and the Yinchuan basin groundwater. The Hetao basin groundwater has identical Mo concentrations to the Datong basin, with average values of 5.07 and 6.14 μg/L, respectively. Likewise, Mo concentrations are generally lower in the higher As groundwater (Fig. 3f), since it is readily immobilized as MoO₅SₓC₀⁴ₓ in reducing conditions (Tossell, 2005). The relationships between U and As, and Mo and As support naturally occurrence of high As groundwater in reducing conditions (Xie et al., 2009a).

4.3. Arsenic species

Arsenic species not only control the toxicity of high As groundwater and its impact on human health, but also play an important role in As cycling in groundwater systems. Arsenite (As(III)) and arsenate (As(V)) are two major As species predominantly occurring in natural water (Cullen and Reimer, 1989). The former is about 60 times toxic than the latter (Morton and Dunette, 1994). Furthermore, As(V), mainly being present as oxyanionic forms (H₂AsO₄⁻, H₃AsO₄²⁻) at neutral pH (Smedley and Kinniburgh, 2002), is readily...
captured on the aquifer sediments by means of adsorption and co-precipitation (Dinesh et al., 2007). In comparison, As(III), being predominantly as a neutral species (H₃AsO₃), is quite mobile due to the lack of electrostatic attraction and easily mobilized in the groundwater systems (Ravenscroft et al., 2009). Therefore, data on groundwater As species have usually been provided in recently-published literatures.

Arsenic(III) is the major As species in those high As groundwaters. In the Datong basin, As(III) concentrations range between <1.0 and 1040 µg/L, accounting for 0–92% total As. In average, 73.9% of total As is present as As(III) (<1.0–1430 µg/L) in groundwater of the Huhhot basin. The Hetao basin groundwaters have As(III) concentration between <1.0 and 755 µg/L, accounting for from 0% to 97% total As. Although total As concentrations are relatively low, ratios of As(III) to total As range between 0% and 100% with the average of 73.4% in the Yinchuan basin.

Seventy-seven percent of groundwater samples have ratios of As(III) to the total concentration greater than 50% in the Datong basin, 75% samples in the Huhhot basin, 87% samples in the Hetao basin, and 82% samples in the Yinchuan basin (Fig. 4a). Statistically, ratios of As(III) to total concentration are the highest in groundwaters of the Yinchuan basin, followed by the Hetao basin, the Huhhot basin, and the Datong basin (Fig. 4b). The median values of As(III)/total As are 61.8% and 89.5% in the Datong basin and the Yinchuan basin, respectively. Methylated As species (MMAA, DMAA) was only reported in the Datong basin by Xie et al. (2009a), with concentrations of MMA and DMA between <0.4 and 4.6 µg/L and <0.4 and 5.4 µg/L, respectively. In the other basins, methylated As species are undetectable (<0.4 µg/L). The prevalence of As(III) over As(V) also indicates the reducing natures of high groundwaters (Guo et al., 2008a).

4.4. Colloid particles

In China, particulate and colloidal As has been intensively investigated in the Hetao basin (Gong et al., 2006; Guo et al., 2009, 2011b), although no related data are available in other inland basins and the river delta. Investigation of 583 groundwater samples from 120 wells in the Hetao basin of Inner Mongolia shows that approximately 35% of total As in well water is present as particulate As, which does not pass through 0.45 µm filters (Gong et al., 2006). However, they found substantially less particulate As (10–22% with an average of 16%) by means of on-site filtration and species separation in six well water samples. In order to avoid exposing to air and settling the soluble components, on-site filtration in N₂ atmosphere is necessary.

On-site filtration by progressively decreasing membrane pore size (10, 5, 3, 1, 0.8, 0.45 µm) under N₂ in the Hetao basin shows that 30%–60% Fe is associated with the large particles (>0.45 µm), although As concentrations do not exhibit large variations through the different decreasing pore size cut-offs (Guo et al., 2009). They suggest that Fe complex is the major component of the large-size particles (>0.45 µm), and conclude that a small proportion of As (<15%) is retained in large-size Fe complexing particles in groundwaters saturated with respect to siderite and pyrite.

Later, Guo et al. (2011b) have carried out successive ultrafiltration through a progressively decreasing pore size (0.45 µm, 100, 30, 10, 5 kDa) for 8 well waters in the Hetao basin. They have identified two types of colloids, including large-size Fe colloids and small-size organic colloids. A large drop (~30%) of Fe concentration was observed between 0.45 µm filtrate and 100 kDa ultrafiltrate, showing the presence of Fe as large-size colloids with grain size between 100 kDa and 0.45 µm. However, a large proportion of As is retained in the 5–30 kDa fractions, which is consistent with organic carbon (OC) distribution among the ultrafiltrates (Guo et al., 2011b). It indicates that As would be more likely associated with organic colloids than Fe colloids, which is confirmed by SEM images, EDS analysis and synchrotron XRF analyses. The better correlation between As(V) and OC than As(III) and OC in the 5–10 kDa fraction implies that OC would have a better affinity for As(V) than As(III) (Guo et al., 2011b). This As-NOM colloidal association has also been observed in wetland environments (Langner et al., 2012; Buschmann et al., 2006) and the laboratory experiments (Bauer and Blodau, 2009). Guo et al. (2011b) suggest that the NOM-complexed As would be difficult to be removed from high As groundwater in the Hetao basin by means of ultrafiltration due to the presence of 5–10 kDa colloids. However, distributions of particulate and colloidal As in other inland basins and river deltas are still unknown and remain to be discovered.

4.5. Dynamic variation in As concentration

In the As-affected areas, groundwater As concentrations are quite patchy on a local or regional scale both vertically and
horizontally (Guo et al., 2012; Deng et al., 2009; He et al., 2009; Han et al., 2013; Xie et al., 2009a; Smedley et al., 2003). In local or regional groundwater flow systems, spatial variations in As concentration may lead to temporal dynamics of As concentrations (Guo et al., 2013b). In the Hetao basin, groundwater As mainly ranges between <1.0 and 1000 µg/L over distance from tens of meters to kilometers. A small set of samples (n = 23), obtained in July/August and November 2006 in the low-lying plain with surface water irrigation, show that shallow groundwater generally displays higher As concentration in November than in July, although a larger set of groundwater samples (n = 30), annually collected in July/August from 2006 to 2010, have showed no significant change in As concentration (Guo et al., 2013c). They believe that the higher As concentration is associated with the higher water level in November, during which more reducing condition induced by flooding irrigation leads to more As release via local reductive dissolution of Fe oxides. Further investigation has been carried out based on monthly monitoring of shallow groundwaters, illustrating temporal evolution of groundwater As approximately along the flow path at depths between 5 and 20 m (Guo et al., 2013b). It indicates that high As groundwaters have slight increasing trends at depths around 20 m and 15 m. However, groundwater As keeps relatively constant at depths <10 m, where low As groundwaters are present. It is suggested that variations in groundwater As are not only controlled by redox potentials (or groundwater level), but also by the recharge of neighboring groundwater (Guo et al., 2013b).

In the Yinchuan basin, around four-year monitoring data show that low As groundwater in deep aquifer (around 80 m) has no significant temporal variation in As concentration, while evident variations have been observed in shallow groundwaters (<30 m) with high As concentrations (>70 µg/L) (Han et al., 2013). The increase in water level is not always connected to the increase in groundwater As concentrations. They have proposed that infiltration of irrigation water with more labile carbon would induce reducing conditions and increase As concentration during 2008 to 2009, and suggested that longer-term observation should be needed to confirm variation trends.

In the Datong basin with intensive extraction of groundwater for irrigation over decades, leaching of irrigation return flow, halite dissolution, and evaporation have been recognized using environment isotopes (δ18O and δD) and Cl/Br ratios in groundwaters (Xie et al., 2012). They found that a group of groundwaters with a significant increase in Cl− concentrations and less increase in δ18O values mostly have high As concentration (>10 µg/L), while those groundwaters showing lateral mixing and/or evaporation generally have low As concentrations (<10 µg/L). It is suggested that irrigation return flow would predominantly promote As mobilization, although no temporal variation data are available to support this hypothesis.

5. Mobilization of As in aquifers

5.1. Sources of arsenic

Groundwater As is generally geogenic, which mainly comes from aquifer sediments (Guo et al., 2008a; Wang et al., 2009). High As groundwater generally occurs in aquifers, where sediments do not contain high As contents (Ravenscroft et al., 2009; Fendorf et al., 2010). However, the ultimate source of groundwater As may come from the aquifer sediments, which would release solid As into groundwater by means of (bio)geochemical processes. Chemical data of sediments are used for evaluating the difference in sediment chemistry in the Datong basin (Xie et al., 2009a), the Hetao basin (Guo et al., 2008a), the Huhhot basin (Smedley et al., 2003), the Yinchuan basin (Han et al., 2013), and the Pearl river delta (Wang et al., 2012).

The lowest As contents were observed in the Yinchuan sediments with the range between 3.7 and 18.3 mg/kg and an average of 6.66 mg/kg, followed by the Huhhot sediments (Fig. 5). The lowest As contents in the aquifer sediments would be associated with the low groundwater As concentration in the Yinchuan basin. It indicates that, in the similar conditions, groundwater As would be dependent of sediment As. In the Datong basin, high As groundwater mostly occurs in the eastern side of the Sanggan river (Guo et al., 2003; Xie et al., 2009a), where the granite has high As contents up to 12.4 mg/kg in the Hengshan Mountain (Wang, 1998), while low As groundwater in the left side of the Sanggan river, where As contents range between 0.8 and 3.4 mg/kg in the limestone and the sandstone and shale in the Hongtao Mountain (Guo, 2002).

Although groundwater As concentrations are generally higher in the Datong basin than in the Hetao basin, the Datong aquifer sediments normally have lower As contents with the range between 4.9 and 26.8 mg/kg and an average of 11.8 mg/kg than the Hetao basin sediments with the range between 7.26 and 73.3 mg/kg and an average of 18.9 mg/kg. Moreover, the Pearl river delta has the highest sediment As contents with the range between 5.0 and 39.6 mg/kg and an average of 17.8 mg/kg (Fig. 5), but the lowest groundwater As concentration. Therefore, groundwater As concentrations do not necessarily depend on As contents in the aquifer sediment (Fendorf et al., 2010; Harvey, 2008). The bias of abnormal groundwater As concentration from the sediment As content would be the result of redox processes, microbe-related reduction, and desorption processes occurring in the aquifer systems, which are discussed later.

Good relationships between As and Fe/Mn have been observed in the aquifer sediments (Fig. 6). It indicates that As would be associated with Fe/Mn oxide minerals in the aquifers, which usually have strong affinity for both As(III) and As(V) (Goldberg and Johnston, 2001; Mohan and Pittman, 2007). This is confirmed by sequential leaching experiments (Guo et al., 2008a; Deng et al., 2011; Xie et al., 2009b). Guo et al. (2008a) show that As is mostly bound to Fe/Mn oxides in aquifer sediments of the Hetao basin, although Fe/Mn oxide-bound As is generally higher in

![Fig. 5. Box-Whisker plots of As contents in aquifer sediments of the Datong basin, the Huhhot basin, the Hetao basin, the Yinchuan basin, and the Pearl river delta.](image-url)
low-As groundwater aquifers than in high-As groundwater aquifers. Arsenic strongly adsorbed on and co-precipitated with amorphous Fe oxyhydroxides accounts for 35% and 20% the total As contents in the Hetao sediments, respectively (Deng et al., 2011). Although around 10% sediment As is extracted from pyrite, it is unknown whether this fraction is the sink of groundwater As in the authigenic pyrite. Extraction of 12 sediment samples in the Huhhot basin using 0.2 M acid ammonium oxalate solution shows that up to 30% of sediment As is oxalate-extractable and considered as amorphous Fe oxyhydroxide-bound As (Smedley et al., 2003). In aquifer sediments of the Datong basin, it has been found that Fe oxyhydroxides may be the major source of As in the aquifer, which is based on the fact that concentration of NH$_4$OH–HCl extracted Fe is strongly correlated with that of extracted As (Xie et al., 2009b). Further investigation has found the good correlation between As concentrations and two magnetic parameters (i.e., saturated isothermal remnant magnetization (SIRM) and isothermal remnant magnetization (IRM)), showing that the ferrimagnetic minerals including maghemite and haematite are the dominant carriers for As (Xie et al., 2009c).

5.2. Redox processes

As mentioned above, dissolved organic carbon (DOC) is the trigger for the formation of reducing conditions. High concentrations of DOC provide electrons for electron acceptors, which leads to reduction in the sequence NO$_3^–$, Mn(IV), As(V), Fe(III) and SO$_4^{2–}$ (Stumm and Morgan, 1996; Mukherjee et al., 2012). Most of these species are reduced within the sedimentary aquifers in both the inland basins and the river delta. Coexistence of NO$_3^–$ and NH$_4^+$ has been observed in the Hetao basin (Guo et al., 2011a; Deng et al., 2009), the Huhhot basin (Smedley et al., 2003), the Yinchuan basin (Han et al., 2013; Guo and Guo, 2013), the Datong basin (Xie et al., 2009a), and the Pearl river delta (Wang et al., 2012), showing that NO$_3^–$ reduction usually occurs. The fact that groundwaters with Mn concentration greater than 10 mg/L generally have low As concentration indicates that reductive dissolution of Fe(III) oxyhydroxides universally occurs in the reducing aquifers. During reductive dissolution, As adsorbed onto Fe(III)-oxyhydroxides is released (Nickson et al., 1998; Islam et al., 2004). This is the major mechanism for genesis of high As groundwater in reducing aquifers. Iron(II) produced by Fe(III) reduction would like to be adsorbed on the residual Fe-oxyhydroxides if being present (Appelo et al., 2002; van Geen et al., 2004; Handler et al., 2009), or combined with S$^{2–}$ and HCO$_3^–$ to form pyrite and siderite (Guo et al., 2013b). Iron isotope study in the Hetao groundwater identifies three pathways for Fe and As cycling (Guo et al., 2013a). Light $^{56}$Fe values and high As concentrations reflect the occurrence of Fe(III) oxide reduction in anoxic conditions. In strongly reducing conditions, precipitation of isotopically light Fe-pyrite and/or siderite following Fe-oxide reduction results in enrichment of isotopically heavy Fe in groundwater with both high and low As concentrations. Re-adsorption of Fe(II) following Fe(III) reduction leads to further enrichment of isotopically light Fe and relative low As concentrations in anoxic–suboxic conditions (Guo et al., 2013a). The mixed effect of those pathways controls As and Fe cycling in groundwater systems, which is most likely the cause of the fact that dissolved Fe concentrations are poorly correlated with dissolved As concentrations (Guo et al., 2008a; Deng et al., 2009; Xie et al., 2009a; Han et al., 2013; Wang et al., 2012). In the Pearl river delta, Wang et al. (2012) observed the presence of pyrite in the aquifer sediments, and suggested that coprecipitation of As with authigenic pyrite would significantly scavenge aquatic As in the coastal aquifer–aquitard system. In addition to authigenic pyrite, siderite precipitation would also eliminate As from groundwater in the Hetao groundwater (Guo et al., 2013b).

As redox potential further decreases, SO$_4^{2–}$ reduction would predominate with the production of S$^{2–}$. Sulphide has been detected in most of groundwater samples in the Hetao basin (Guo et al., 2010, 2011a; Deng et al., 2009), the Datong basin (Xie et al., 2009a), and Mn oxides is not directly related to high As concentration in the groundwater systems (McArthur et al., 2004).

Under redox conditions, with As(V) reduction predominated, both dissolved As(V) and adsorbed As(V) are expected to be reduced to As(III) (Mukherjee et al., 2012). The reduction of adsorbed As(V) results in the release of solid As into groundwater, due to the lower affinity of As(III) species to mineral surfaces compared to the As(V) species (Guo et al., 2007b; Manning et al., 1998). The reductive desorption of As increases groundwater As(III) concentration (Smedley and Kinniburgh, 2002), and leads to the fact that As(III) is the predominant As species in the high As groundwaters of the inland basins and the river deltas.

Besides, relatively high concentrations of Fe(II) in high-As groundwater indicate that reductive dissolution of Fe(III) oxyhydroxides universally occurs in the reducing aquifers. During reductive dissolution, As adsorbed onto Fe(III)-oxyhydroxides is released (Nickson et al., 1998; Islam et al., 2004). This is the major mechanism for genesis of high As groundwater in reducing aquifers. Iron(II) produced by Fe(III) reduction would like to be adsorbed on the residual Fe-oxyhydroxides if being present (Appelo et al., 2002; van Geen et al., 2004; Handler et al., 2009), or combined with S$^{2–}$ and HCO$_3^–$ to form pyrite and siderite (Guo et al., 2013b). Iron isotope study in the Hetao groundwater identifies three pathways for Fe and As cycling (Guo et al., 2013a). Light $^{56}$Fe values and high As concentrations reflect the occurrence of Fe(III) oxide reduction in anoxic conditions. In strongly reducing conditions, precipitation of isotopically light Fe-pyrite and/or siderite following Fe-oxide reduction results in enrichment of isotopically heavy Fe in groundwater with both high and low As concentrations. Re-adsorption of Fe(II) following Fe(III) reduction leads to further enrichment of isotopically light Fe and relative low As concentrations in anoxic–suboxic conditions (Guo et al., 2013a). The mixed effect of those pathways controls As and Fe cycling in groundwater systems, which is most likely the cause of the fact that dissolved Fe concentrations are poorly correlated with dissolved As concentrations (Guo et al., 2008a; Deng et al., 2009; Xie et al., 2009a; Han et al., 2013; Wang et al., 2012). In the Pearl river delta, Wang et al. (2012) observed the presence of pyrite in the aquifer sediments, and suggested that coprecipitation of As with authigenic pyrite would significantly scavenge aquatic As in the coastal aquifer–aquitard system. In addition to authigenic pyrite, siderite precipitation would also eliminate As from groundwater in the Hetao groundwater (Guo et al., 2013b).

As redox potential further decreases, SO$_4^{2–}$ reduction would predominate with the production of S$^{2–}$. Sulphide has been detected in most of groundwater samples in the Hetao basin (Guo et al., 2010, 2011a; Deng et al., 2009), the Datong basin (Xie et al., 2009a), and

![Fig. 6. Arsenic contents vs. Fe$_2$O$_3$ (a) and Mn (b) in aquifer sediments of the Datong basin, the Huhhot basin, the Hetao basin, the Yinchuan basin, and the Pearl river delta.](image)
the Huhhot basin (Smedley et al., 2003). In the Hetao basin, molar ratios of SO\textsubscript{4}\textsuperscript{2-} to Cl\textsuperscript{-} show a negative correlation with δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values in groundwaters from moderate flow-reducing zone and low flow-reducing zone, indicating that bacterial reduction of SO\textsubscript{4}\textsuperscript{2-} occurs in the aquifers (Guo et al., 2011a). Although pyrite precipitation may occur in the aquifer, high As concentration in groundwaters being oversaturated with respect to pyrite is possibly due to the greater amount of As released from Fe(III)-oxide reduction than that subsequently eliminated by pyrite precipitation (Guo et al., 2013a). In the Datong basin, Xie et al. (2009a) also found that the high δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values correspond to low SO\textsubscript{4}\textsuperscript{2-} concentration and high As concentrations, and suggested that SO\textsubscript{4}\textsuperscript{2-} reduction accompanies As reduction and mobilization. In the recent study using multiple isotope (O, S and C) approach, they observed that higher As concentrations occur in aquifers with reduction of Fe-oxyhydroxides than with reduction of both Fe-oxyhydroxides and SO\textsubscript{4}\textsuperscript{2-} (Xie et al., 2013). They suggest that, in this reducing condition, more As would be released from reduction of Fe-oxyhydroxides than what would be removed from groundwater during sulfide precipitation.

The above-mentioned redox processes are coupled with the oxidation of a large amount of DOC. Guo et al. (2011b) showed that about 30% of As is associated with organic colloids with molecular weights between 5 and 30 kDa. Decomposition of the low-molecular weight organic matter would also release the colloidal-bound As into groundwater. However, the cycling of colloidal As still needs to be further investigated during redox processes.

5.3. Roles of microbes in As mobilization

Microbes, which are fueled by organic matter in the aquifers and catalyze the formation of favorable reducing conditions, play an important role in As mobilization in both inland basins (Guo et al., 2008b; Xie et al., 2011) and river deltas (Islam et al., 2004; van Geen et al., 2004; Sultana et al., 2011; Dhar et al., 2011). Although no microbe-related data are available in other sites, microbes and their roles in groundwaters and/or sediments have been documented in the literatures in the Hetao basin (Guo et al., 2008b; Li et al., 2013; Jiang et al., 2013) and the Datong basin (Duan et al., 2009; Xie et al., 2011; Wu et al., 2012).

Most probable number (MPN) shows that NO\textsubscript{3}-respiring bacteria (NRB), iron-respiring bacteria (IRB), and SO\textsubscript{4}-respiring bacteria (SRB) are universally present in the As-affected aquifers of the Hetao basin, although the dominant microorganisms are grouped into different microbial groups in different sediments (Guo et al., 2008b). In the microcosm experiments, a larger amount of As has been released in the batches amended with glucose (0.71–3.81 mg/kg) than in the unamended batches (0.03–0.30 mg/kg), which accounts for 60–70% of As bound to Fe/Mn oxides in the sediments (Guo et al., 2008b). The IRB presence would lead to dissipitative reductive dissolution of Fe(III)-oxides/oxyhydroxides. Sediment incubation shows that As is released into aqueous solutions along with the increase in dissolved Fe concentrations in the batches amended with glucose (Guo et al., 2008b). However, Jiang et al. (2013) did not find Fe reducing bacteria strains by means of DGGE and 16S rRNA in the Hetao sediments. Although Li et al. (2013) suggest that Acinetobacter, Brevundimonas, Thermoprotei, Geobacter and Methanosaeta would be associated with high concentrations of As, methane and Fe(II) and low concentrations of SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} in groundwaters, they did not observe Fe reducing bacteria strains in groundwaters. Thiobacillus strain has been found to be the predominated bacterial populations in the Hetao aquifer sediments, which can use As(V) and NO\textsubscript{3} as the terminal electron acceptors (Jiang et al., 2013). In addition, Wu et al. (2012) have isolated an aerobic As(V)-reducing bacterium, Pantoea, which has effective As (V)-reducing capacity under aerobic conditions. Although these As(V)-reducing bacteria do not directly convert the As-hosting minerals (such as Fe/Mn oxides/oxyhydroxides), they may catalytically reduce adsorbed As(V) to As(III), and consequently lead to the reductive desorption of As because the lower adsorption affinity of As(III) to oxide minerals has been known than that of As(V) at near-neutral pH (Dzombak and Morel, 1990; Manning et al., 1998).

Additionally, a SO\textsubscript{4}-respiring archaea, Thermoprotei, has been identified in high As groundwater of the Hetao basin, although bacterial diversity is lower in high-As groundwater than low-As groundwater (Li et al., 2013). Thermoprotei has been known to use SO\textsubscript{4} as the electron acceptor and H\textsubscript{2} the electron donor (Changanti et al., 2012). Reduction of SO\textsubscript{4} may lead to elimination of solution As by means of As sulfide precipitation or coprecipitation of As with sulfides, which play a role in As cycling in the aquifers (Guo et al., 2013a).

In the Datong basin, indigenous bacterium Bacillus cereus has been isolated from high As aquifer sediments, which is capable of mobilizing sediment As, Fe, Mn, and Al (Xie et al., 2011). Although they do not report its 16S rRNA gene clone data, the bacterium may mediate the reduction of Fe oxides, and facilitate the release of As from sediments into groundwater. In the incubation experiments on a sandy loam sample with the addition of Bacillus cereus and labile carbon (glucose and sodium acetate), up to 5.7% of sediment As has been released (bulk As 11.7 mg/kg) (Xie et al., 2011). For a grey fine silt sample taken at depth of 12 m, about 10% of sediment As has been released in the microcosms using As-resistant strains as inoculated strains, and glucose and sodium acetate as carbon sources (Duan et al., 2009). Another bacterium, Bacillus sp., has also been isolated from the high As soil in the Datong basin, which is an aerobic As(V)-respiring bacterium (Wu et al., 2012). The strain effectively reduces aqueous As(V) to As(III) under aerobic conditions, and enhances As mobility in the system.

5.4. Competitive desorption

Groundwater pH values are generally high in both inland basins and the river deltas, with the range between 7.2 and 8.7 (mean 8.0) in the Datong basin, between 7.1 and 8.9 (mean 8.1) in the Hetao basin, between 6.8 and 8.7 (mean 7.6) in the Huhhot basin, between 7.5 and 8.9 (mean 7.9) in the Yinchuan basin, and between 5.7 and 9.5 (mean 7.6) in the Pearl river delta, showing that high As groundwaters are mostly neutral-weak alkaline. As the major As carrier in the aquifer sediments, Fe(III) oxyhydroxides are predominantly positively charged at pH 3.0–7.0 and negatively charged at pH 8.0–10.0 (Dixit and Hering, 2003; Zhang et al., 2004). As pH increases, both As(V) species and the surface of Fe oxyhydroxides become more negatively charged, resulting in the electrostatic repulsion. Therefore, the increase in solution pH > 8.2 drastically decreases As adsorption on Fe-oxyhydroxides (Mamindy-Pajany et al., 2011; Qiao et al., 2012), and consequently leads to As desorption due to the less abundance of positively charged adsorption sites. This can explain the fact that high pH groundwater normally has high As concentration in the same hydrogeological units of the Hetao basin (Guo et al., 2011a) and the Datong basin (Guo et al., 2003).

Additionally, high As groundwaters usually have high HCO\textsubscript{3} concentrations with the range between 198 and 1300 mg/L (mean 484 mg/L) in the Datong basin, between 191 and 1450 mg/L (mean 606 mg/L) in the Hetao basin, between 72 and 1150 mg/L (mean 388 mg/L) in the Huhhot basin, between 198 and 927 mg/L (mean 523 mg/L) in the Yinchuan basin, and between 216 and 3590 mg/L (mean 827 mg/L) in the Pearl river delta. On the one hand, the presence of HCO\textsubscript{3} would alter the surface charge properties of Fe oxides via inner-sphere monodentate mononuclear surface species (Su and Suarez, 1997). On the other hand, HCO\textsubscript{3} readily competes
for adsorption sites on the haematite at concentration >61 mg/L, although low concentrations of $\text{HCO}_3^-$ (<6.1 mg/L) enhance As(V) adsorption (Arai et al., 2004). Experiments show that As adsorption on the activated natural siderite (mostly haematite) decreases by 6.7% when $\text{HCO}_3^-$ concentration increases from 61 to 3050 mg/L (Zhao and Guo, 2013). Although other coexisting anions, such as $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{PO}_4^{3-}$ have also been found in high As groundwaters, they may play a minor role in affecting As concentrations due to their low concentrations in the inland basins and the river delta investigated. Whatever, the relative contribution of competitive desorption and reductive dissolution of Fe oxides to high As concentrations in groundwaters of different areas is still unknown.

6. Conclusive remarks

High As groundwater has been widely found in both arid–semi-arid inland basins and river deltas in China. These arid–semi-arid inland basins are mainly distributed in the northwest of China with thick sedimentary sequences. Groundwater normally occurs in Quaternary sedimentary aquifers, including shallow aquifers, semi-confined aquifers, and confined aquifers. Shallow groundwaters in alluvial lacustrine or lacustrine sediment aquifers usually have high As concentrations. In addition to low permeability of aquifer sediments, low-lying and flat topography attributes to low groundwater flow rates in the aquifers. In the river deltas, high As groundwater mainly occurs in fluvial–marine sedimentary aquifers, which have normally been affected by transgression. The sediments are relatively young. The interbeds of marine and fluvial deposits are mainly composed of silty sand, silt, clayey silt and clay, with high content of natural organic matter. These conditions, together with low groundwater flow rate, readily lead to reducing conditions in aquifers.

Either in the inland basins or in the river deltas, high As groundwater usually occurs in reducing conditions, and is characterized by high Fe and Mn concentrations, high pH and $\text{HCO}_3^-$ concentration, and relatively low $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ concentrations. Arsenic(III) is the major As species, which shows not only high toxicity to human health but also great mobility in the aquifer systems. In the Hetao basin, As would be more likely associated with mill-size organic colloids, instead of large-size Fe colloids. However, distributions of particulate and colloidal As in other inland basins and river deltas are still unknown and remain to be discovered.

Arsenic contents are not abnormally high in the aquifer solids. Groundwater As concentrations do not depend on As contents in the aquifer sediments. High groundwater As concentrations, however, are the result of redox processes, microbe-related reduction, and desorption processes occurring in the aquifer systems. In reducing conditions, both reductive dissolution of Fe oxides and reductive desorption of As are believed to occur in the aquifer systems, and lead to As mobilization. Microbes, which are fueled by organic matter in the aquifers and catalyze the reduction of Fe oxides and As(V), play an important role in As mobilization in both the inland basins and the river deltas. Consumption of organic carbon during microbe metabolization not only releases the low-molecular weight organic colloid-bound As into groundwater, but also increases groundwater $\text{HCO}_3^-$ concentrations. High groundwater pH and $\text{HCO}_3^-$ concentrations are expected to lead to competitive desorption of As from adsorption sites. However, the relative contribution of competitive desorption and reductive dissolution of Fe oxides to high As concentrations in groundwaters of different areas is still unknown.

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