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Hydrogeochemical zonation and its implication for arsenic mobilization in deep groundwaters near alluvial fans in the Hetao Basin, Inner Mongolia

Yongfeng Jia [a,b], Huaming Guo [a,b,*], Yuxiao Jiang [a,b], Yang Wu [a], Yinzhu Zhou [b]

[a] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, PR China
[b] School of Water Resources and Environment, China University of Geosciences, Beijing 100083, PR China

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SUMMARY

High As groundwater has been found in shallow aquifers of the flat plain of the Hetao basin, but little is known about As concentration in deep groundwaters around piedmont areas, which are the major drinking water resources. One hundred and three groundwater samples from wells with depths >50 m and seven samples from one multi-level monitoring well (89 m in depth) were analyzed for chemical compositions and ^{18}O and D isotopes to examine the geochemical processes controlling As mobilization. According to hydrogeological setting, chemical and isotopic characteristics of deep groundwater, three distinguished hydrogeochemical zones are delineated, including Recharge-Oxic Zone (Zone I), Groundwater Flow-Moderate Reducing Zone (Zone II), and Groundwater Flow-Reducing Zone (Zone III). Zone I is located in proximal fans in the recharge area with oxic conditions, where low As groundwater generally occurs. In Zone II, located in the intermediate between the fans and the flat plain with Fe-reduction predominated, groundwater As is moderate. Zone III lies in the flat plain with the occurrence of SO_4^{2-} reduction, where high As groundwater is mostly found. This indicates that release of As to groundwater is primarily determined by reduction sequences. Arsenic is immobilized in O_2/NO_3^- reduction stage in Zone I and released in Fe-reducing conditions of Zone II, and displays a significant elevated concentration in SO_4-reducing stage in Zone III. Dissolution of carbonate minerals occurs in Zone I, while Ca^{2+} and Mg^{2+} are expected to precipitate in Zone II and Zone III. In the multi-level monitoring well, both chemical and isotopic compositions are dependent of sampling depths, with the similar trend to the hydrogeochemical zonation along the flow path. The apparent increases in δD and $\delta^{18}O$ values in Zone III reveal the possibility of high As shallow groundwater recharge to deep groundwater. It indicates that deep groundwaters in proximal fans have low As concentrations and are considered as safe drinking water resources in the Hetao basin. However, high As concentration is frequently observed in deep groundwater in the flat plain, which should be routinely monitored in order to avoid chronic As poisoning.

1. Introduction

High As groundwater poses an enormous health risk all around the world, which has been found in North and South America, China, Europe, and especially in Southeast Asia like West Bengal (India), Bangladesh (BGS/DPHE, 2001; Smedley and Kinniburgh, 2002). Finding alternative water resources or remediating high As water in a cost effective way in these areas remains a significant challenge. Investigation of the cause of high As groundwater would help us in better understanding spatial and temporal variation in As distribution and efficiently preventing its harm to local people. Three different mechanisms have been used to explain how it occurs, including the oxidation of pyrite (Das et al., 1995; Chowdhury et al., 1999), desorption by competitive anions (Acharyya et al., 2000; Smedley and Kinniburgh, 2002; Appelo et al., 2002), and reductive dissolution of Fe minerals and subsequent As(V) reduction and release (Bhattacharya et al., 1997; Nickson et al., 1998, 2000; McArthur et al., 2001; BGS/DPHE, 2001; Dowling et al., 2002; Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009). The last one has been thought to be the main mechanism to explain groundwater As enrichment in shallow aquifers in both China and other As hotspot areas like Bangladesh.

* Corresponding author at: School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, PR China. Tel.: +86 10 8232 1366; fax: +86 10 8232 1081.
E-mail address: hmguo@cugb.edu.cn (H. Guo).

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In China, about 15 million people have been affected by high As groundwater. It has mostly been reported in northwestern China, especially in Xinjiang, Ningxia, Jilin, Inner Mongolia and Shanxi province (Guo et al., 2008; Mukherjee et al., 2009; Han et al., 2013; Xie et al., 2012; Rodríguez-Lado et al., 2013; Guo et al., 2014). Studies in these areas showed that groundwater As is normally associated with reducing conditions in aquifers. A unique characteristic of high As groundwater in China is the co-occurrence of As and F. Although the same scenario occurs in Latin America with the similar arid and semi-arid climate as northwestern China, desorption and oxidation of sulfide minerals have been considered to be important mechanisms releasing As and F (Alarcón-Herrera et al., 2013; Bundschuh et al., 2012). The enrichment of As in shallow groundwaters of northwestern China is triggered by high concentrations of dissolved organic carbon (DOC), and promoted by the low groundwater flow rate. Dissolved organic carbon (DOC) mostly ranged between 5 and 20 mg/L (Guo et al., 2014). The averages of DOC concentration were 12.0, 8.3, 6.0, and 5.0 mg/L, in the Hetao basin (Guo et al., 2011; Luo et al., 2012), the Huhhot basin (Smedley et al., 2003; Mukherjee et al., 2009), the Yinchuan basin (Han et al., 2013; Guo and Guo, 2013), and the Datong basin (Guo et al., 2003; Xie et al., 2009; Luo et al., 2012), respectively. The flow rate of shallow groundwater was estimated to range between 0.18 and 1.6 cm/d in the Hetao basin, according to the hydraulic conductivity between 2.2 and 20 m/d (Guo et al., 2010) and hydraulic gradient of 0.8‰ (Zhang et al., 2013). In the Yinchuan basin, the groundwater renewal rates ranged from 11% to 15% in the south, while between 0.1% and 6% in the north (Wang et al., 2013). The low flow rate not only led to near equilibrium water–rock interaction, but also the limited flushing of the aquifers, which favors As accumulation in groundwater after being released.

Sulfate reduction plays an important role in As cycling in groundwater systems (Zheng et al., 2004; Stüben et al., 2003). In specific study in eastern and southeastern Bangladesh, arsenic was found to be mobilized under Fe-reducing conditions, and remained mobilized under SO_4-reducing stage (Zheng et al., 2004). However, in statistic studies of Bengal, Mekong and Red River deltas, arsenic levels were found the highest in the methanogenic zones and significantly lower in the SO_4-reducing and Fe-reducing stage (Buschmann and Berg, 2009). In central Illinois, similar phenomenon was observed, where groundwater As usually occurred at low levels under SO_4-reducing conditions and accumulated to high levels in methanogenesis stage (Kirk et al., 2004). The reduction of SO_4^{2-} is considered to be a possible factor inhibiting As mobilization in groundwater since the product of sulfide co-precipitates Fe and As and causes its sequestration from groundwater, which is probably dependent on the amount of SO_4^{2-} (Stüben et al., 2003). In deeper aquifers of the western Bengal basin, Mukherjee and Fryar (2008) observed high As groundwater, which is related to microbially mediated (Fe/Mn)–OOH reduction and less sequestration by authigenic pyrite.

In the Hetao Basin, Inner Mongolia, although previous studies indicate that redox condition is the main factor in controlling groundwater As (Jia and Guo, 2012; Guo et al., 2011), seldom studies on As release in different reduction stage were involved in the Hetao Basin. Especially, effect of SO_4^{2-} reduction on As cycling remains to be discovered. Besides, the relationship between reduction stage and its spatial distribution is rarely reported. Also few studies were involved in As distribution along the deep groundwater flow path, which is very important to combine groundwater dynamics and biochemical process affecting As mobilization. The stable isotopes of oxygen and hydrogen are conservative and widely used to track groundwater recharge and identify groundwater flow path, especially in the arid and semi-arid areas (IAEA, 1980, 1983; Clark and Fritz, 1997; Adams et al., 2001; Zhu et al., 2007). In addition, more than 3000 deep wells at mountain fronts along the margin of the Hetao basin have been used for irrigation and drinking water resources. Arsenic concentration in these groundwaters is unknown, which directly affects people's health and crop quality. Hug et al. (2011) showed that deep groundwater had different water chemistry from shallow groundwater in Munshiganj District, Bangladesh, which may show distinct hydrogeochemical processes. Therefore, it is necessary to reveal As distribution in these deep groundwaters and along the groundwater flow path, which would help in better understanding As behaviors in deep aquifers and identifying target safe aquifers with low As concentration for drinking water resources.

The objectives of this study are to (1) investigate As distribution in deep groundwater near alluvial fans, (2) delineate the different reduction stage related to As geochemical behaviors, and (3) reveal mechanisms of As mobilization in deep aquifers.

2. Materials and methods

2.1. Study area

The Hetao basin of Inner Mongolia lies to the north of the Yellow River with an average annual precipitation from 130 to 220 mm and evaporation from 2000 to 2500 mm. The basin is formed extension of the Neogene faults with fine clastic sediments mainly depositing in inland lakes (Tan et al., 2009). The Tertiary sediments occur in oxic conditions with great amounts of salinity, while the Quaternary sediments have both alluvial and lacustrine sources, which are mainly derived from the Langshan Mountains and partly from fluvial deposits of the Yellow river (Guo et al., 2008; Deng et al., 2009).

The study area is located in the northwest of the Hetao basin and immediately to the southeast of the Langshan mountains, with an area of approximately 25 km^2. The Langshan mountains are mainly composed of Jurassic to Cretaceous metamorphic rocks (slate, gneiss and marble) (Guo et al., 2008). Alluvial fans extend from the front of the mountain range to the flat plain. The depth of water table was around 20 m below land surface (BLS) in alluvial fans, and decreased to about 1 m in the flat plain. Groundwater in the basin-fill sediments is mainly recharged through the alluvial fans by water flowing through fractures along the mountain front, and by vertically infiltrating precipitation, irrigation channels, and irrigation water in the plain. It is discharged mainly via evapotranspiration, drainage, and pumping. The general direction of groundwater flow is from north to south. Hydraulic conductivity decreases from ~2.0 m/d along the mountain front to ~0.2 m/d in the downdip region (Inner Mongolia Institute of Hydrogeology, 1982). In the study area, deep groundwater is mainly used for agricultural irrigation (Guo et al., 2013a). During the irrigation seasons (usually in April–July), deep groundwater level decreases by around 4 m, which would result in the recharge of shallow groundwater to deep groundwater.

According to our borehole loggings and previous hydrogeologic report (Inner Mongolia Institute of Hydrogeology, 1982), there are usually clay layers with several meters at depth around 40 m BLS. Aquifers overlying the clay layers host shallow groundwater, while aquifer underlying the clay layers, being regarded as the first semi-confined aquifer, host deep groundwater (>50 m). A groundwater flow path was selected from the mountain side to the flat plain, where shallow groundwaters are discharged to a pond (Fig. 1). The vertical profile was also used for investigating variations in groundwater chemistry along the depth, which is about 7.9 km south of the end of groundwater flow line and not shown in Fig. 1.