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High arsenic groundwater in the Guide basin, northwestern China: Distribution and genesis mechanisms

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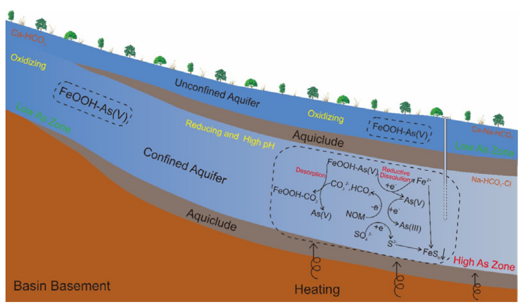
HIGHLIGHTS

- Natural high As groundwater widely occurs in the Guide basin of northwestern China
- Along the flow path, As was enriched rapidly in groundwater in confined aquifer
- Arsenic release was mainly caused by reduction of Fe oxides, followed by desorption
- The unconfined aquifer is vulnerable to As contamination from confined aquifer

GRAPHICAL ABSTRACT



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ABSTRACT

High arsenic (As) groundwater has been found in Pliocene confined aquifers at depths from 100 to 300 m of the Guide basin, but little is known on the main hydrogeochemical processes leading to its elevated concentrations. Ninety-seven water samples and fifty-three sediment samples were collected for chemical and/or isotopic analysis. Concentrations of As in groundwater of confined aquifer range from 9.9 to 377 μg/L (average 109 μg/L), which generally show a sharply increasing trend along with NH_4^+, HCO_3^-, CO_3^{2-} and TOC along the inferred flow path, while NO_3^-, SO_4^{2-}/Cl^- and redox potential (Eh) have decreasing trends. Results of sequential extraction show that As bound to amorphous and crystalline Fe oxide minerals are the main As forms, accounting for around 50% of total As in sediments. Reductive dissolution of As-bearing Fe(III) oxide minerals under reducing conditions in confined aquifers lead to the mobilization of As in groundwater. In addition, alkaline environment and high concentrations of HCO_3^- and CO_3^{2-} may make contributions to As enrichment in groundwater. High As groundwater in confined aquifer continuously flows out on the ground surface through tens of artesian wells, which may potentially contaminate low As groundwater in unconfined aquifer. Thus, further investigation is needed to evaluate long-term variations of water chemistry of low As groundwater and assess vulnerability of unconfined aquifer to As contamination.

1. Introduction

Naturally-occurring high arsenic (As) groundwater is widely distributed in the world, including the USA (Chappells et al., 2014), Mexico (Wurl et al., 2014), Argentina (Zabala et al., 2016), China (Guo et al., 2014b), Chile (Sancha and O'Ryan, 2008), Vietnam (Erban et al., 2014), India (Chakraborti et al., 2016) and Bangladesh (Fendorf et al.,

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2010). Long-term intake of high As groundwater has negative effects on human health (Cheng et al., 2010; Yunus et al., 2011; Liu et al., 2013), including hematological, cardiovascular, neurological, respiratory and renal diseases (Smith et al., 2000; Celik et al., 2008; Mink et al., 2008).

Numerous studies have focused on investigating the source and distribution of As in affected regions and on the processes controlling As mobility in groundwater. Generally, there are many mechanisms for mobilization of geogenic As from aquifer solids. Firstly, As is mobilized under oxidizing conditions that lead to dissolution of sulfidic minerals or arsenopyrite (Welch et al., 2000; Smedley and Kinniburgh, 2002). Secondly, As(V) is desorbed from As-bearing Fe oxides, hydroxides and oxyhydroxides (hereafter referred to collectively as Fe(III) oxides) at high pH (Sø et al., 2008; Ravenscroft et al., 2009; Thi et al., 2014; Guo et al., 2014a). Thirdly, microbially mediated reductive dissolution of As-bearing Fe(III) oxides by oxidation of organic matter is the most widely accepted mechanism under reducing conditions (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Zheng et al., 2004; Islam et al., 2004; McArthur et al., 2004; Mukherjee et al., 2008; Nath et al., 2008; Guo et al., 2013). Microbial reduction of oxidized humic quinones, which are able to shuttle electrons and accelerate microbial reduction of Fe oxides (Lovley et al., 1996; Kappler et al., 2004; Jiang and Kappler, 2008; Roden et al., 2010), has been shown to be an important step in the cascade that results in Fe oxide reduction and may consequently contribute to As mobilization (Lovley et al., 1996). After reductive dissolution of Fe-oxides, a part of the released As is adsorbed on the surface of the remaining Fe-oxides and in this way may be retarded (Postma et al., 2007; Rotiroti et al., 2015). However, others argued that As once liberated from adsorbed solid phase would tend to remain in solution and would not be sequestered even in highly reducing conditions (Mukherjee et al., 2008).

The occurrence of high As groundwater is usually associated with specific geological and hydrogeochemical environments. The high-As groundwater in eastern Asia typically occur in young Quaternary aquifers of Holocene age in alluvial and deltaic sediments without containing extraordinary As-rich sources (BGS and DPHE, 2001; Smedley, 2003; Smedley and Kinniburgh, 2002).

Geothermal fluids frequently contain high concentrations of As (Stauffer and Thompson, 1984; Lord et al., 2012; Mitsunobu et al., 2013), which may contaminate surface waters or groundwater in adjacent areas. In addition, human activity, such as mining activity, may contribute to high levels of groundwater As due to the enhanced oxic weathering of sulfide minerals (Komnitsas et al., 1995).

China is one of the most heavily affected countries by high As groundwater, which has been frequently observed in inland basins and river deltas (Guo et al., 2014a; Zhang et al., 2018). The inland basins mainly include the Datong Basin (Xie et al., 2013), the Hetao Basin (Guo et al., 2016a,b), the Yinchuan Basin (Q. Guo et al., 2014; Han et al., 2010), the Songnen Basin (Guo et al., 2014b) and the Dzungaria Basin (Liu et al., 2013), which contain thick Quaternary unconsolidated sediments.

The Guide basin is an inland basin with high As groundwater. Being different from high As groundwater in other inland basins, high As groundwater in the Guide basin usually has higher pH values (Guo et al., 2014a). Previous studies indicated that geothermal activity in deep aquifers result in As enrichment in groundwater in the deep confined aquifer (Shi et al., 2010; Liao et al., 2013). However, the hot springs around the basin mostly have low As concentrations suggesting that geothermal waters are not an important source of As (Liao et al., 2013). Therefore, some other factors are expected to control distribution of groundwater As. However, little is known about which hydrogeochemical processes result in enrichment of As in groundwater in the Guide basin. Understanding the processes leading to As mobilization and accumulation in groundwater is important for remediating As-contaminated groundwater and/or locating low As groundwater for drinking water production.

The objectives of this study are to (1) characterize the hydrogeochemical processes taking place in confined aquifers and unconfined aquifers, (2) evaluate the sources of groundwater As in the Guide basin, and (3) identify hydrogeochemical processes controlling As release and enrichment in groundwater in the confined aquifer.

2. Study area

The Guide basin is located between the Laxiwa Gorge and Songba Gorge on the upper reaches of the Yellow River in Qinghai Province (northwestern China) (Fig. 1a), which has a semi-arid continental climate (Song et al., 2008). The annual average temperature, precipitation, evaporation and relative humidity are 7–8 °C, 252 mm, >2000 mm and 49%, respectively. Rainfall occurs predominantly from June to September, which accounts for 72% of annual precipitation. The elevation approximately ranges from 2400 to 3000 m above mean sea level (ASL). It is bordered by the foothills of Qinghainan mountains and Laji mountains to the north and Waligong mountains ranges to the south. The Guide basin is a typical Cenozoic fault basin and filled by Neozoic clasts with a thickness of >1000 m (Yan et al., 2005).

The basin is drained by the Yellow River and its tributaries, which is incised >900 m into the Cenozoic strata (Yan et al., 2005). The strata include the Paleocene-Oligocene Xining group, the Miocene-Pliocene Guide group and the Quaternary deposits from the bottom to the top of the basin. The Guide group forms a wide and syncline gently tilting from the southern and northern sides towards the Yellow River and from the west to the east, forming a south-north symmetrical confined aquifer with a dip towards east (Zhang et al., 2016). As shown in Fig. 1b, the Pliocene group can be further divided into three subgroups: the early N_2^1, the middle N_2^2 and the later N_2^3. The N_2^1 mainly consists of red thick laminated shale with grey lenticular sandstone at depths >310 m below land surface (bls) in the central basin, which is generally believed to be an aquitard. The N_2^2 is mainly composed of grey, brown grey or maroon mudstone and grey sandy mudstone, sandstone and pebbly sandstone at depths between 100 and 310 m bls in the central basin. The sandstone with fractures and pores host groundwater in the confined aquifer with water head declining from southeast to northwest (Fig. 1b). High As groundwater mainly occurs in this confined aquifer. The N_2^3 mainly distributes in the north of the reverse fault (Fig. 1b), which is composed of mudstone with thick sandstone or conglomeratic sandstone lenses. The Quaternary unconfined aquifers are located at depths <100 m bls, and are composed of well-rounded and well-sorted gravel and sand with a thickness of around 12–32 m (Xu et al., 1976).

Unconfined aquifers are recharged from precipitation, surrounding mountains and riverbed of the tributary of the Yellow River along widely distributed Quaternary sandy gravel layers (Fig. 1b). Confined aquifers are mainly recharged from surrounding mountains and overlying unconfined aquifer. The Yellow River is the final discharge area of groundwater in the Guide basin. The speculated compressional reverse fault with east-west direction may be the channel for discharge of groundwater in the confined aquifer into rivers due to high fluid pressure of groundwater in confined aquifer and formational upward leakage (Fig. 1a and b) (Xu et al., 1976). This hydrogeochemical condition of aquifer in the Guide basin is similar to some other famous aquifers, such as Madison, Middendorf, Aquia and Sherwood (Thompson, 1979; Park et al., 2009; Zhang, 2010; Christine et al., 2011).

3. Materials and methods

3.1. Groundwater sampling and analysis

Seventy groundwater samples from unconfined aquifers, twenty groundwater samples from confined aquifers, two hot spring water samples and five surface water samples were collected from the basin (Fig. 1a). The groundwater in unconfined aquifer (UG) samples were collected at depths from 3 to 106 m and groundwater in confined aquifer (CG) samples were taken at depths between 119 and 322 m.