Science of the Total Environment 601–602 (2017) 691–702

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sources of groundwater salinity and potential impact on arsenic mobility in the western Hetao Basin, Inner Mongolia

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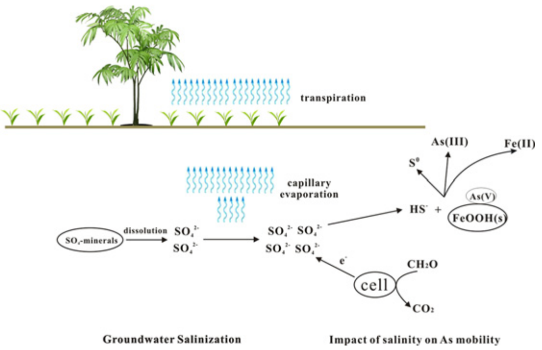
HIGHLIGHTS

- The build-up of groundwater salinity was related to natural processes.
- Non-direct evaporation and mineral/evaporite dissolution contribute to groundwater salinity.
- Co-occurrence of high As and high salinity groundwater were found.
- High salinity groundwater (high SO_4) may enhance As hazard in reducing environment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 February 2017
Received in revised form 5 May 2017
Accepted 21 May 2017
Available online 31 May 2017

Editor: F.M. Tack

Keywords:
Groundwater arsenic
Salinization
Evaporation
Cl/Br ratio
Sulfate reduction
Hetao Basin

ABSTRACT

The quality of groundwater used for human consumption and irrigation in the Hetao Basin of Inner Mongolia, China is affected by elevated salinity as well as high arsenic (As) concentrations. However, the origin of high salinity and its potential impact on As mobility in the Basin remain unclear. This study explores both issues using stable isotopic compositions and Cl/Br ratios of groundwater as well as the major ions of both groundwater and leachable salts in aquifer sediments. Limited variations in $\delta^{18}O$ and δ^2H (−11.13 to −8.10, −82.23 to −65.67) with the wide range of Total Dissolved Solid (TDS, 351–6734 mg/L) suggest less contribution of direct evaporation to major salinity in groundwater. Deuterium excess shows that non-direct evaporation (capillary evaporation, transpiration) and mineral/evaporite dissolution contribute to >60% salinity in groundwater with TDS > 1000 mg/L. Non-direct evaporation, like capillary evaporation and transpiration, is proposed as important processes contributing to groundwater salinity based on Cl/Br ratio and halite dissolution line. The chemical weathering of Ca, Mg minerals and evaporites (Na_2SO_4 and $CaSO_4$) input salts into groundwater as well. This is evidenced by the fact that lacustrine environment and the arid climate prevails in Pleistocene period. Dissolution of sulfate salts not only promotes groundwater salinity but affects As mobilization. Due to the dissolution of sulfate salts and non-direct evaporation, groundwater SO_4^{2-} prevails and its reduction may enhance As enrichment. The higher As concentrations (300–553 μg/L) are found at the stronger SO_4^{2-} reduction stage, indicating that reduction of Fe oxide minerals possibly results from HS^- produced by SO_4^{2-} reduction. This would have a profound impact on As mobilization since sulfate is abundant in groundwater and sediments. The evolution of

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http://dx.doi.org/10.1016/j.scitotenv.2017.05.196

groundwater As and salinity in the future should be further studied in order to ensure sustainable utilization of water resource in this water scarce area.

1. Introduction

Salinization of soil and groundwater affects a number of sizeable regions around the world, including in Argentina (Nicolli et al., 2012; Zabala et al., 2015), the western America (Fram and Belitz, 2012), Mexico (Mahlknecht et al., 2017), the Murray-Darling Basin in Australia (Cartwright et al., 2010), France (Montety et al., 2008), Syria (Kattan, 2008), Israel (Vengosh et al., 1999), South Africa (Sami, 1992) and the Indus River Basin of Pakistan (Qureshi et al., 2010). Groundwater with Total Dissolved Solid (TDS) levels >1000 mg/L is typically not tolerated for human consumption (WHO, 2011) and with TDS >2000 mg/L is harmful to many plants and crops (Bauder et al., 2005). Previous studies have shown that both natural processes and human activity can cause salinization of groundwater (Greenman et al., 1967; Cartwright et al., 2010; Yu et al., 2010; Mahlknecht et al., 2017). Natural processes include strong evaporation, mixing with deposited brine, and dissolution of salt deposits (Banner et al., 1989; Herczeg et al., 2001). Human activities, such as large-scale irrigation, discharge of brine, and over-exploitation of groundwater in coastal areas, are shown to trigger or enhance groundwater salinization (Greenman et al., 1967; Vengosh et al., 1999; Werner et al., 2013; Mahlknecht et al., 2017).

The build-up of salt in groundwater is a concern in the heavily irrigated and arid or semi-arid Hetao Basin of northern China (Zhu et al., 2014). Flood irrigation is widely applied in this area and has raised the groundwater table by 0.5–3 m compared with no-irrigation season (Guo et al., 2013a). This has resulted in widespread water-logging and evaporation. Gao et al. (2014) reported that TDS in shallow (10–40 m) groundwater of Hetao Basin averages 2500 mg/L ($n = 634$) up to 54,000 mg/L, and showed that proportions of the area with groundwater TDS <1000 mg/L, between 1000 and 3000 mg/L, and >3000 mg/L of approximately 9, 72, and 19%, respectively. To mitigate water-logging and salinization, a network of drainage channels was constructed in Hetao Basin in the 1960s, and updated in 1988. Over this period, the salinity of water in the main drainage channel increased from 1200 mg/L in 1980s to an average of 2000 mg/L from 2000 to 2006 (Zhu et al., 2014). Remote-sensing showed that the areal extent of soil salinization may have declined in the western Hetao Basin between 1991 and 2005 (Yu et al., 2010).

In addition to evaporation, the dissolution of salt deposits has been invoked to explain high groundwater salinity in different parts of the world (Vengosh et al., 1999; Herczeg et al., 2001). Sediments of Hetao Basin contain halite, gypsum, and mirabilite (Inner Mongolia Institute of Hydrogeology, 1982; Zhu et al., 2014). Sulfate concentrations of 4000 mg/kg were observed in sediments at depths of 80 m in both Hetao and the nearby Hubao Basin (Chen, 2013). These salt deposits probably formed as a vast paleolake dried out in response to climatic conditions as well as tectonic forcing (Inner Mongolia Institute of Hydrogeology, 1982; Gao et al., 2014).

To distinguish the build-up of salt in Hetao Basin groundwater due to evaporative processes and the dissolution of salt deposits could have significant implications for continued efforts to reduce salinization through hydrologic management of the basin (Ghassemi et al., 1995). One of the widely-used indicators of evaporation applied here are deviations in the stable isotopic composition of groundwater relative to that of local precipitation (Craig, 1961; Clark and Fritz, 1997). Another potential indicator of the source of groundwater salinity used in the present study is the ratio of the conservative anions Br and Cl. Whereas the Cl/Br ratio of groundwater is not affected by evaporation, halite (NaCl) dissolution reduces this ratio (Davis et al., 1998; Herczeg et al., 2001; Cartwright et al., 2006; Alcalá and Custodio, 2008; Xie et al., 2012; Li et al., 2016), although Cl and Br can be input from human waste (McArthur et al., 2012) and from the decomposition of organic matter or pesticides (Katz et al., 2011; Desbarats et al., 2014), respectively.

Another serious problem related to groundwater quality in the study area is the elevated levels of groundwater arsenic (As) which have affected the population of about 300,000 for decades (Asia Arsenic Network, 1997; Smedley et al., 2003; Guo et al., 2008; Deng et al., 2009). Geochemical data suggests that the release of As to groundwater is primarily the result of microbial reduction of Fe oxide minerals (Smedley et al., 2003; Guo et al., 2011; Deng et al., 2009; Jia et al., 2014). This does not exclude the possibility that high levels of salinity affect the microbial processes regulating As mobilization (Welles et al., 2015). High levels of sulfate, in particular, could affect the partitioning of As between sediment and groundwater through the formation of sulfide species under reducing conditions (Kirk et al., 2004; Buschmann and Berg, 2009; Planer-Friedrich and Wallschläger, 2009; Burton et al., 2013). Elevated levels of salinity and bicarbonate in groundwater could potentially lead to the release of As to groundwater via competing adsorption, as documented in Argentina and the Southwest American (Welch and Lico, 1998; Smedley et al., 2002, 2005; Bhattacharya et al., 2006; Bundschuh et al., 2012). However, the origin of groundwater salts and the connection between salinity and As enrichment are still unknown in the basin. In order to assess the evolution of As and make sure of sustainable utilization of groundwater resources in the future, full consideration should be given to the origin of salts especially SO_4^{2-} and their impact on As mobilization.

Therefore, the main objectives of this study are to (1) reveal the origin of groundwater salinity, (2) determine to what extent the distribution of As in groundwater of Hetao Basin is influenced by salinity.

2. Materials and Methods

2.1. Study area

The Hetao Basin of Inner Mongolia lies to the Northwest of China with 250 km from east to west and 60 km from north to south (Fig. 1). The northern and southern borders of the basin are Langshan Mountain and Yellow River, respectively. The western part is close to Ulanbuh Desert and eastern part borders to Wuliangsu Lake. The Hetao Basin is located in arid to semi-arid area with average annual precipitation from 130 to 220 mm and evaporation from 2000 to 2500 mm. It is famous to be known as the biggest Yellow River irrigation basin in Northern China. More than 3/4 part of the basin is irrigated by Yellow River water, while the rest part near the mountain with high elevation relies on groundwater irrigation. 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 Mountain and partly from fluvial deposits of the Yellow river (Guo et al., 2008; Deng et al., 2009). According to hydrogeologic report (Inner Mongolia Institute of Hydrogeology, 1982), Hetao Basin subsides to inland lake during Jurassic and Cretaceous period when hot and humid climate prevails. It turns to hot and arid climate during Paleogene and Neogene Period, so the lake is highly evaporated and its area is decreased. A large amount of salts like gypsum, calcite and halite are accumulated in the sediment during this period. During Quaternary period the Hetao Basin continues to subside and is occupied by lake in whole Pleistocene period. After Mid-Pleistocene the climate mainly turns to arid with two cycles from cold to warm. The arid trend leads to salts accumulation in sediment in late Mid-Pleistocene. Several large or middle scale polymetallic (Fe, Cu and