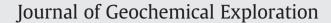
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Dynamic behaviors of water levels and arsenic concentration in shallow groundwater from the Hetao Basin, Inner Mongolia



Huaming Guo ^{a,b,*}, Yang Zhang ^a, Yongfeng Jia ^{a,b}, Kai Zhao ^{a,b}, Yuan Li ^{a,b}, Xiaohui Tang ^c

^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

^c Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology (KIT), Adenauerring 20 b, 76131 Karlsruhe, Germany

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ABSTRACT

Temporal variations in groundwater As concentration are crucial for understanding the mechanisms of As cycling and developing effective strategies for sustainable usage of low As groundwater in As-affected areas. Little is known about temporal variations in As concentration of shallow groundwater from the Hetao basin. Groundwater samples were taken once each year in July/August from 2006 to 2010. Another sampling campaign was carried out in November 2006. Groundwater tables were monitored as well. Results showed that water levels were higher during December-April than during May-September in the front of the alluvial fans where irrigation relied mainly on groundwater. In contrast, the highest water levels were observed in May-June and in November in the flat plain region where the diverted Yellow River water was utilized for irrigation. Concentrations of Na⁺, Cl⁻, and HCO₃⁻ were relatively constant over 4 years, although most wells showed slight decreasing trends in concentrations of Ca^{2+} and Mg^{2+} . Although concentrations of As in most wells were lower in 2006 than in 2007, there were no significant changes in As concentration between 2006 and 2010 at p = 0.05. Shallow groundwaters sampled in November from the flat plain region with surface water irrigation showed generally higher As concentrations than in July. This was caused by more reducing conditions due to less oxygen dispersing into the aquifers when irrigation water flooded the soil and perhaps the un-saturated zone, as evidenced by the lower redox potential of shallow groundwater in November. Results of µ-XRF showed that As contents were well correlated with Fe contents in the sediment samples from the shallow aquifers. The most plausible explanation for the decoupling between temporal variation in As concentration and in Fe concentration was expected to be the reductive desorption of $A_{S}(V)$, due to the analogical variation trends between As(III) and total As.

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1. Introduction

High As groundwater is a world-wide environmental issue, which has been found in both reducing and oxidizing aquifers (Smedley and Kinniburgh, 2002). In comparison with oxidizing conditions, more groundwater with high As concentrations is related to reducing conditions, which have been observed in Bangladesh, India, China, Pakistan, Nepal, Cambodia, Vietnam, Hungary, Romania, and some regions in USA (such as California, Arkansas, Maryland, and Nevada) (Chauhan et al., 2009; Gurung et al., 2005; Haque et al., 2008; Nickson et al., 2005; Polya et al., 2005; Ryu et al., 2010; Sharif et al., 2008; Smedley and Kinniburgh, 2002). Many studies have been made for high As groundwater in the Ganges delta. Although reducing aquifers were believed to be associated with groundwater As enrichment in some areas of Northwest China, especially in Xinjiang, Inner Mongolia (Guo et al., 2008a; Smedley et al., 2003), and Shanxi (Guo and Wang, 2004; Xie et al., 2012), geologic condition, groundwater chemistry and climate were different between inland basins of Northwest China and Ganges delta (Guo et al., 2011a).

The Hetao basin is a sedimentary basin hosting high As groundwater, where the prevalence of endemic arsenicosis was up to 25% (Jin et al., 2003). The spatial distribution of groundwater As has been investigated, showing that high As groundwaters generally occurred in shallow alluvial-lacustrine aquifers (Guo et al., 2008a). Groundwater As was believed to originate from exchangeable As and Fe–Mn oxide-binding As in the aquifer sediments (Guo et al., 2008a), which was confirmed by microcosm study of intact aquifer sediments in the lab (Guo et al., 2008b). In the high As groundwater of the Hetao basin, As would be more likely associated with small-size organic colloids than Fe colloids (Guo et al., 2011b), which indicated controls of organic colloids on As distribution. Furthermore, hydrogeologic and biogeochemical constrains on As mobilization in shallow groundwater were illustrated, showing that low As groundwater occurred near the irrigation channels and the drainage channels (Guo et al., 2011a). Distribution of As in shallow groundwaters was highly patchy on a local or regional scale both vertically and horizontally

^{*} Corresponding author at: School of Water Resources and Environment, China University of Geosciences, 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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(Guo et al., 2012). Such spatial variability results in the concern that shallow groundwater As concentrations may change over time, especially because flood irrigation both in summer and in winter likely affects subsurface groundwater flow in the area of farmlands. It was observed that groundwater levels were much higher in winter than in summer in groundwater-irrigated areas, where a large amount of groundwater was withdrawn for irrigation in summer. Fluctuation in the water levels has been documented in Bangladesh (Dhar et al., 2008), where the lowest As and P concentrations, and the highest major cation, S, and Mn concentrations, were observed during the dry season in some wells (Cheng et al., 2005), or a decrease in As concentration was found during high groundwater level season (Farooq et al., 2011; Kumar et al., 2010). However, there is no information on the change of As concentration related to water table fluctuation in the Hetao basin.

Temporal change of As concentrations has been reported in Bangladesh, West Bengal of India, and Vietnam (Berg et al., 2001; CGWB, 1999). A long term rise in groundwater As concentration was observed in a number of private wells in 23 villages out of 100 villages of West Bengal (Chakraborti et al., 2002). However, there is no highquality time series data of groundwater As concentrations from the Hetao basin, although high As concentrations were first reported in drinking groundwater in 1994 (Sun, 1994). Limited information showed an increasing trend in As concentration in some wells (around 60 m depth). This increase would increase the exposure of well users to excessive As without their knowledge. It is crucial to characterize temporal variations in groundwater As concentration to understand the mechanisms of As cycling and to help to develop effective strategies for sustainable usage of low As groundwater in As-affected areas.

The objectives of this study are to (1) characterize temporal change of groundwater tables in shallow aquifers; (2) document temporal trends in As concentrations on seasonal and inter-annual time scales; (3) provide new insights into the mechanisms of As mobilization.

2. Materials and methods

2.1. Study area

The Hetao basin, one of the Cenozoic rift basins, is located to the north of the Yellow River, to the east of the Wuranbuh Desert, and to the south border of Langshan Mountains (Fig. 1). The Langshan Mountains are consisted of a metamorphic complex (slate, gneiss and marble), generally of Jurassic to Cretaceous age. As one of the Cenozoic rift basins, the basin is fault-bounded. Aquifer sediments were composed of alluvial–pluvial sand, sandy silt, lacustrine and fluvial–lacustrine sandy silt, silty clay and clay rich in organic matter in the central part of the basin, fluvial sandfine sand on river banks, and alluvial sand in fan areas. High As groundwaters were mainly present at the transition zone between alluvial–pluvial aquifers and alluvial–lacustrine aquifers, and in alluvial–lacustrine aquifers in reducing conditions, where dark gray fine sand layers were universally found (Guo et al., 2008a). The radiocarbon age of the shallow aquifer sediments hosting high As groundwaters indicated that the aquifers were deposited in late Pleistocene.

Arsenic concentrations were patchy over local (~100 m) and regional (~10 km) scales, with inorganic As(III) as the dominant species (Guo et al., 2008a). High As groundwaters clustered in five hotspot zones, including Shuangmiao-Sandaoqiao, Shahai-Manhui, Bainaobao-Langshan, Taerhu and Shengfeng. Groundwater was anaerobic with high concentrations of total Fe and Mn (Guo et al., 2008a).

In the basin, the average annual precipitation was around 188 mm, which was much less than potential evaporation of 2000 to 2500 mm (Guo et al., 2008a). Groundwater in the basin-fill sediments was mainly recharged by vertically infiltrating precipitation, ditch water (irrigation channels) and irrigation water, and discharged mainly via evapotranspiration and drainage (near drainage channels) in the flat plain. Due to the gentle land surface, groundwater flow conditions were generally sluggish, with a relatively slower horizontal flow rate in comparison with the amount of vertical movement. However, the shallow groundwater flow system was affected by irrigation channels and drainage channels in most of the study area (Guo et al., 2011a), as well as irrigation practices on the farmlands.

2.2. Sample collection

Thirty groundwater wells with depth from 9 m to 33 m were sampled once each year in July/August between 2006 and 2010 (Fig. 1). In addition, 23 wells were sampled in both July and November 2006 (Fig. 1). Parameters, including water temperature, electrical conductivity, pH, and ORP, were measured using a multiparameter portable meter (HANNA, HI 9828), and H₂S using a portable spectrophotometer (HACH, DR2800) at the time of groundwater sampling in the field. Prior to groundwater sampling, wells were pumped for more than 20 min until these parameters were stable. Alkalinity was determined by the Gran titration method on the day of sampling. The redox potential values reported in this study have not been corrected to the standard hydrogen electrode (SHE) but instead can be used as relative values. The samples for major and trace element analysis were filtered through 0.45 µm Millipore filters on site into 100 mL HNO₃washed polyethylene bottles. Those for analysis of trace elements were acidified to pH 1 using 6 M HNO₃. Those for analysis of As species were preserved with 0.25 M EDTA in amber bottles, which is

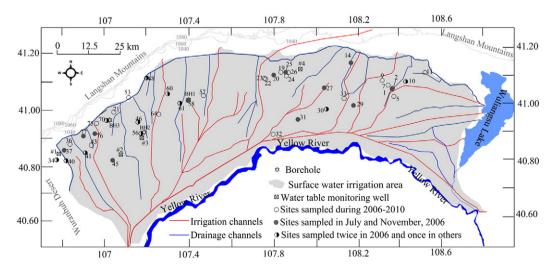


Fig. 1. Location of sampling sites and drilling boreholes in the study area.

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