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# Geochemistry of high arsenic groundwaters in the Yinchuan basin, P.R. China

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#### Abstract

High As groundwaters have been usually found in inland basins of north-west China. However, few data are available on groundwater As in the Yinchuan basin. Ninety-eight groundwater samples were taken from the alluvial fans, basin center, and fluvial plain of the Yellow River in the basin. Results showed that low As groundwater occurred in the alluvial fans and the basin center, while high As groundwater was present near the Yellow River. The redox potential was the key factor controlling the groundwater As concentrations. Arsenic was mobilized in reducing conditions via reductive dissolution of Fe oxides, which was supported by the positive correlation between As and Fe. In comparison to the Hetao basin, the Yinchuan groundwater had lower As concentration, lower pH, and higher redox potential.

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# 1. Introduction

Arsenic contaminations in shallow groundwaters have usually been founded in inland basins in the northwestern China [1]. The Yinchuan basin, being located in the northern parts of the Ningxia Hui Autonomous Region of China, has high arsenic groundwater exceeding guideline concentrations of 10  $\mu$ g/L. High As values were mainly observed in groundwater from wells with depths between 10 and 50 m below land surface.

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Our study area was located in the Shizuishan district of the Yinchuan basin, being bounded by the Jianquan farmland in the north, Shahu in the south, the Helan Mountain in the west and the Yellow River in the east (Fig.1). In this continental arid-semiarid area, the annual average precipitation is 185 mm and mainly occurs during June to September, which accounts for 68.1% of the annual rainfall. The annual potential evaporation with 1825 mm is ten times the precipitation. This paper reports part of our work to understand probable mechanisms of arsenic abnormality in groundwaters, addressing the sources of groundwater As and the condition favoring high concentrations of arsenic in groundwaters.



Fig.1 Location of sampling sites in the study area.

### 2. Regional Geology

The Yinchuan basin is a Cenozoic NNE striking fault basin with quaternary sediments of the thickness of 2000 m, overlying Tertiary deposits with a thickness of more than 1700 m. From the piedmont to the Yellow River, sedimentary sequences evolve from pluvial, alluvial-pluvial, through alluvial-lacustrine, to fluvial deposits. Pluvial sediments mainly occur on the east of the Helan Mountain, which are composed of rock, gravel and sandy gravel, occasionally interblended with thin clay layers. Fluvial deposits are mainly distributed along the Yellow River, with higher thicknesses upstream. In summary, the grain size of sediments decreases from the south to the north and from the basin fringe to the center.

#### 3. Methodology

Ninety-eight groundwater samples were collected in July 2012 (including 40 samples in piedmont pluvial fan, 52 samples along the Yellow River, and 6 samples in the center of the study area). During the sampling, all water samples were filtered through 0.45 µm membranes on site. Unstable hydrochemical parameters including water temperature, pH, ORP, and electrical conductivity (EC) were measured in-situ using portable Hanna EC and pH meter. Alkalinity was measured using a Gran titration. Anions were determined using ion chromatography. Cations and total As were analyzed using ICP-AES within 1 week after sampling.

### 4. Results and Discussion

#### 4.1. Hydrogeochemical characteristics of groundwater

In the piedmont pluvial fans, 39 samples had As concentrations of less than 1.0  $\mu$ g/L. Only one sample showed As values of up to 18.4  $\mu$ g/L. The Arsenic concentration in the central section of study area ranged between 1.4 and 5.1  $\mu$ g/L, with the average of 4.5  $\mu$ g/L. Usually, surface water had low As concentrations (<10  $\mu$ g/L). However, total arsenic concentration ranged from 1.4 to 105 $\mu$ g/L in groundwaters sampled near the Yellow River.

Redox potential is the major factor controlling As mobilization [2]. With the similar pH, groundwaters with lower redox potential had higher As concentrations (Fig.2A). In the piedmont pluvial fans with low As concentration, redox potential was generally high, ranging between 50 and 200 mV, while groundwater near the Yellow River had the redox potential range from -25 to -125 mV. In the As-affected area, low concentrations of  $NO_3$  and  $SO_4^{2-}$  and high concentrations of  $NH_4^+$  and  $Fe^{2+}$  were observed. In moderate reducing conditions, As was preferentially released.

There was positive correction between As concentration and Fe, Mn concentrations in groundwater (Fig.2B). The correlation coefficient ( $\mathbb{R}^2$ ) between As and Fe was 0.59, which demonstrates that the stability of iron and manganese oxyhydroxides would control concentration of As in groundwater. Iron-oxide and oxyhydroxide, being present in groundwater in oxic environment, drastically adsorb As, and therefore decrease As concentration in groundwaters [3]. However, adsorbed As would be released when Fe oxides were reduced in reducing conditions [4].



Fig.2. (A) Correlation between total arsenic concentration and redox potential, pH in groundwater in the Yinchuan north plain (B) Correlation between total arsenic concentration and Fe, Mn content in groundwater in the Yinchuan plain.

#### 4.2. Comparison of the Yinchuan and the Hetao groundwaters

The Hetao basin, Inner Mongolia of China is a sedimentary basin hosting high As groundwater, where the prevalence of endemic arsenicosis was up to 25% [5]. In comparison to the Hetao groundwater, the Yinchuan groundwater showed higher redox potential and lower pH values and As concentrations (Fig.3). In Fig.3, the Yinchuan groundwater samples overlapped the groundwater samples in the Hetao basin at redox values > -125 mV and pH < 8.0. This indicated that groundwater As from the Yinchuan basin and the Hetao basin was controlled by both redox potential and pH. In geochemical conditions with high pH and low redox potential, more As was released from aquifer sediments. The possible reasons included As

desorption from mineral surfaces at high pH [6], and As mobilization via reductive dissolution of Fe oxides at low redox potential [7]. Arsenic mobilization via reductive dissolution in reducing conditions was also supported by the relationship between As and Fe in groundwaters of the Yinchuan basin.



Fig.3 Plots of As vs. ORP (A) and As vs. pH (B) in groundwaters from the Yinchuan basin and the Hetao basin.

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