Applied Geochemistry xxx (2016) 1–6

Contents lists available at ScienceDirect

Applied Geochemistry

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

Comparative study on the hydrogeochemical environment at the major drinking water based arsenism areas

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ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form
13 June 2016
Accepted 22 June 2016
Available online xxx

Keywords:
Drinking water
Arsenism
Hydrogeochemistry
As (III)
Organic arsenic
Humic acid

ABSTRACT

In major drinking water based arsenism areas of China, the hydrogeochemical environment is controlled by the geology, structure and depositional environments. The arsenism prevalence and degree are closely linked to local hydro-chemical environments and the form and valence of arsenic in the groundwater. In this paper, field trips, samples monitoring and comprehensive comparison methods, and hydrogeochemical environment are comparatively analyzed at five drinking water based arsenism areas of China comprising Taiwan, Xinjiang Uygur Autonomous Region, Inner Mongolia Autonomous Region, Shanxi and Jilin provinces. The arsenism areas, except Taiwan, are located in arid and semi-arid areas indicating that the climate condition is not the main factor that affects the groundwater arsenic enrichment. All arsenism areas are located in the center of sedimentary basins or relatively lower zones within the plains, and the groundwater for drinking is taken from the Cenozoic layer. The groundwater in Taiwan, Inner Mongolia and Shanxi arsenism areas are located in a complex organic-rich reductive environment, where not only high As (III) contents occur but also detectable levels of organic matter, humic acid and methyl arsine. In the groundwater samples of the Inner Mongolia arsenism area, many gases are detected, such as H_2S, CH_4, and NH_3. Groundwater environments in Xinjiang Uygur Autonomous Region and Jilin province show oxidic conditions with As (V), and organic arsine is rarely or never detected.

1. Introduction

In China, drinking water based arsenism is primarily distributed in the Taiwan province, Xinjiang Uygur Autonomous Region, Inner Mongolia Autonomous Region, Shanxi province and Jilin province. This phenomenon causes great harm to human beings. The drinking water based arsenism primarily includes two types: native type (endemic arsenism) and anthropogenic pollution type. Most arsenism areas are distinguished by high arsenic (As) in the groundwater for drinking.

The hydrogeochemical characters in the endemic arsenism areas of China are controlled by the geological, structural and depositional environment. The arsenism prevalence and degree are closely linked to local hydro-chemical environments and the form and valence of the arsenic in the groundwater. The distribution of endemic arsenism (hereinafter referred to Arsenism) is obviously regional, and the arsenism areas, except in Taiwan, are located in arid and semi-arid areas (Jin et al., 2003). There are several common features in sedimentary environments similar to most of the arsenism areas, which are located in the center of sedimentary basins or at relatively lower zone within the plains, and the groundwater for drinking is taken from the Cenozoic layer. According to the depositional environment of the arsenism areas, Chinese arsenism areas can be divided into three types: including the Mesozoic-Cenozoic rift basin, the Cenozoic coastal plain and the Quaternary alluvial plain (Lin and Tang, 1999). The Mesozoic-Cenozoic rift basin type is mainly distributed in the Hetao Plain of Inner Mongolia, Datong city of Shanxi province (Shanxi Datong hereinafter) and western Jilin province, which is the most distributed and has the largest extensive influence. The Cenozoic coastal plain type is represented by Chiayi County and Nantai County in the Taiwan Province of China; and the Kuitun city in Xinjiang is a representation of the Quaternary alluvial plain type. Research on

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http://dx.doi.org/10.1016/j.apgeochem.2016.06.008
0883-2927/

the relationship between the water environment and arsenism in the high arsenic areas in China is significantly important to the revelation of the hydro-chemical characteristics of the arsenism areas, the targeted implementation of safe drinking water projects, and the prevention of the arsenism prevalence.

In this study, we mainly collected the samples in Inner Mongolia and Jilin province whose geological type is Mesozoic-Cenozoic rift basin. We made field work in Taiwan (the Cenozoic coastal plain type), Shanxi (Mesozoic-Cenozoic rift basin type) and Xinjiang (Quaternary alluvial plain type) and discussed with local researchers. The published papers and relevant data of those researchers were taken reference (Fung, 1990; Wang et al., 2010; Wei, 2010).

2. Sample collection and analysis

One hundred sixty-one water samples were randomly collected in the Hetao Plain arsenism area, and Asaqueous species were analyzed in terms of total arsenic (ΣAs), As (V) and As (III). Ninety-eight of the 161 samples were selected to determine the humic acid. Twelve samples were from arsenism affected villages and were selected to measure methyl arsine (MMA) and dimethyl arsine (DMA), with two control samples from a non-arsenism area. In the Jilin arsenism area, a total of 186 groundwater samples were collected to analyze ΣAs, As (V) and As (III) concentrations, nine of the samples were selected from unconfined and confined groundwater to analyze the methyl arsine (MMA and DMA).

Instantaneous sampling method were used to collect the water samples. The sample bottles were soaked by HNO_3 with a volume fraction of 10% within the 3 days prior to sampling, and then clean it with tap and distilled water. Onsite, 1.5 L bottles and the plugs are washed first with groundwater three to five times. Next, 10 mL HNO_3 with a volume fraction of 10% is added. The samples were stored in 1.5 L polyethylene plastic bottles, and a plug is screwed on and sealed with wax.

Atomic fluorescence spectrometer (AFS) was used to measure the ΣAs and As (III) in the water (Tang et al., 2013): phosphate is used to regulate the pH of sample to 6.5, and AFS is used to measure the AS(III); hydrochloric acid is used to acidize another sample, As(V) is converted to As(III) by using hiourea-ascorbic acid, then, we used potassium borohydride to hydrogenate As(III) into arsine (AsH_3), AsH_3 was pyrolyzed into As^0, and AFS is used to measure the ΣAs. As(V) concentration is estimated by subtracting As (III) from ΣAs. MMA and DMA are analyzed using atomic fluorescence spectrometry after separation and enrichment (Guo et al., 2003). Humic acid in the water is determined by the Folin reagent – spectrophotometry method (Li et al., 1995). The above tests are all realized by the Science Experimental Center of Jilin University (http://cszx.jlu.edu.cn/) under commission.

3. Results

3.1. Hydrogeochemical characteristics in the drinking water based arsenism area

The migration, enrichment and transformation of water arsenic in an arsenism area are controlled by the depositional environment, the hydrogeological conditions and the hydrogeochemical characteristics. The characteristics of the sedimentary environment and hydrogeochemical environment are shown in Table 1.

The Hetao Plain in Inner Mongolia is a fluvial basin between the Yellow River and the Yinshan Mountains, the groundwater is stored in an enclosed structural sedimentary layer with organics, gypsum and rock salt, showing an organic reductive environment. The pH values range from 7.01 to 8.43. Groundwater is weak alkaline with a redox potential of −153 to 98 mV (Tang et al., 1996), suggesting a strong reduction environment. The concentrations of SO_4^{2-} and NO_3^- are low, probably due to reduction, and the arsenic in the water is mostly As(III). The hydro-chemical environment is very complex in the area, especially in the shallow Quaternary stratigraphy layer in the center of the alluvial lake basin. There are not only high concentrations of As and fluorine (F^-) but also large amounts of humus and salt. The concentrations of total iron and total manganese are high. Total iron concentration is up to 5.90 mg/L. The different types of groundwater often intersect and overlap and are distributed among high contents of As, F^-, salt and humic acid, and appear in certain areas with high concentrations of CH_4 gas, self-overflow and can ignite (Lin et al., 1999; Yang, 2008; Guo et al., 2014).

In Shanxi Datong, arsenic content in arsenism area increases from the front edge of the piedmont sloping plain to the center of fluvial plains and forms a concentrated type As enriched zone in the center of the basin between rivers (Wang et al., 2010). The groundwater is mainly HCO_3-type water, and TDS is less than 1 g/L. The arsenism area is consistent with the distribution of high-arsenic groundwater, and the As concentration in the main water supply layer in the areas are generally in the range of 0.1–0.94 mg/L. At some places, As concentrations could be up to 1.0–4.43 mg/L (Wang et al., 1998). The high As groundwater is mainly found in the confined aquifer at the 20–150 m depth, which is formed by the lacustrine silty sand and fine sand layer with salt and humus. It is similar to the Inner Mongolia arsenism area in the cross overlapping distribution of several types of groundwater with high As, high $F^-$and high salt (Wang et al., 1998, 2010).

The groundwater arsenism areas in Jilin are Tongyu County, Taonan city and Qian'an County. We have carried a study about As in groundwater in the area from 2004 to 2011. The results show a certain relationship between the changes of ΣAs content and the hydro-chemical type of groundwater. The hydro-chemical environment changes gradually from a weak to a high mineralized environment from the runoff zone at the northwest piedmont alluvial and colluvial sloping plain, to the transition zone at the leading edge of the alluvial fan, and then to the stagnation zone at the lower plain areas, caused by the weakening leaching and enhancing evaporation effects (Tang et al., 2010, 2014). Due to the prevention of the central uplift in the basin, the groundwater flows slowly from west to east; the groundwater chemistry type transitions from mainly HCO_3–Ca type to HCO_3–Na·Mg and HCO_3–⊜ Ca·Na types; the TDS in the water and the As concentration changes from low to high; and the As concentration increases with an increase in the mass concentration of total iron, total manganese, Cl^-, PO_4^{3-} and HCO_3^- and decreases with a decrease in the mass concentration of SO_4^{2-} and Se. The high As water is mainly distributed at the end of the diffuser area of rivers, such as the southern Taonan city and the middle-eastern Tongyu County. Regarding the vertical variation, As is mainly enriched in the aquifers with a depth less than 150 m, the average As concentration is 0.05 mg/L, occasionally reaching 0.07 mg/L, and the highest As concentration normally appears at the 30–150 m depth (Fig. 1).

The sources of drinking water in the Taiwan endemic area are taken from the sedimentary groundwater at the late Pleistocene middle-deep sea shelf, and the well depth is normally 95–200 m. The lithology of the aquifer is a gray sandy mudstone mixed with organic ooze and results in a typical weak reductive organic environment. There are high levels of CO_3^-, H_2S, CH_4, NH_4^+, etc., and such organic compounds are detected in the organic ooze as Ergot, Chloroform, Trichloroethylene and so on (Fung, 1990).

The phreatic water is HCO_3–Ca and HCO_3–Ca·Na types at high As areas in the Kuitun city of Xinjiang, and the type of confined water is HCO_3·SO_4–Na·Ca. The wells with high As were drilled in

Please cite this article in press as: Tang, J., et al., Comparative study on the hydrogeochemical environment at the major drinking water based arsenism areas, Applied Geochemistry (2016), http://dx.doi.org/10.1016/j.apgeochem.2016.06.008