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Hydrogeochemistry of high-fluoride groundwater at Yuncheng Basin, northern China

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HIGHLIGHTS

- High-F^- groundwater widely occurs in Yuncheng Basin of northern China.
- High-F^- groundwater is Na and HCO_3-rich and Ca-poor, with high pH.
- Major hydrogeochemical processes are mineral dissolution, ion exchange and evaporation.
- Shallow groundwater leakage/evaporite dissolution may cause F enrichment in lower aquifers.

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ABSTRACT

Hydrogeochemical and environmental isotope methods were integrated to delineate the spatial distribution and enrichment of fluoride in groundwater at Yuncheng Basin in northern China. One hundred groundwater samples and 10 Quaternary sediment samples were collected from the Basin. Over 69% of the shallow groundwater (with a F^- concentration of up to 14.1 mg/L), 44% of groundwater samples from the intermediate and 31% from the deep aquifers had F^- concentrations above the WHO provisional drinking water guideline of 1.5 mg/L. Groundwater with high F^- concentrations displayed a distinctive major ion chemistry: Na-rich and Ca-poor with a high pH value and high HCO_3^- content. Hydrochemical diagrams and profiles and hydrogen and oxygen isotope compositions indicate that variations in the major ion chemistry and pH are controlled by mineral dissolution, cation exchange and evaporation in the aquifer systems, which are important for F^- mobilization as well. Leakage of shallow groundwater and/or evaporite (gypsum and mirabilite) dissolution may be the major sources for F^- in groundwater of the intermediate and deep aquifers.

1. Introduction

Waterborne fluorosis is an endemic disease that results from long-term intake of groundwater with elevated F^- concentrations. The WHO provisional drinking water guideline is 1.5 mg/L (WHO, 2004). In China, the maximum contaminant levels (MCL) of F^- in drinking water is 1.0 mg/L. In this case study, the WHO guideline value (1.5 mg/L) was used as the reference value for high F^- groundwater. The sources of F^- in groundwater can be geogenic or anthropogenic. The geogenic sources are diversified and complicated, mostly related to dissolution of fluorine-bearing minerals such as fluorite, biotite, hornblende, fluorapatite and mica (Forsten and Paunio, 1972) in igneous (Chae et al., 2007), metamorphic (Kundu et al., 2001) and sedimentary rocks (Kern et al., 2008). And the anthropogenic sources include leakage from stored pesticides (Kim et al., 2011) and irrigation using high-F^- groundwater (Pettenati et al., 2013). Endemic fluorosis has been widely documented in different countries such as India (Jacks et al., 2005; Vikas et al., 2013), Brazil (Buzalaf et al., 2004; Souza et al., 2013), Mexico (Irigoyen et al., 1995), Africa (Gizaw, 1996; Rango et al., 2010; Tekle-Haimanot et al., 2006) and China (Amini et al., 2008; Ando et al., 2001; Currell et al., 2011; Gao et al., 2007; Guo and Wang, 2005; Smedley et al., 2003; Wang et al., 2009). China has more than 41 million victims in 1325 different counties suffering from dental and skeletal fluorosis (Ministry of Health of China, 2010). Local hydrogeochemical conditions play critical roles in controlling F^- enrichment in groundwater. In this case study, the Yuncheng Basin in northern China is selected for understanding major geochemical processes controlling basin scale F^- enrichment in groundwater.

For many centuries, groundwater has been a major source of water supply in Yuncheng Basin. Endemic fluorosis at Yuncheng Basin was

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first confirmed in 1980s, and severe fluorosis cases have been identified in 22% of the villages in Linyi County (Gao et al., 2007). Liang (2009) has studied hundreds of people in one county of Yuncheng Basin, and the results indicated that up to 95% and 42% of people suffered from dental fluorosis and skeletal fluorosis, respectively. However, little work has been done to delineate the occurrence and origin of F^- in groundwater systems at Yuncheng. Cao (2005) pointed out that rock fluorine should be the source of F^-. Gao et al. (2007) studied the evolution of high F^- groundwater in the basin and the effects of salt-water intrusion on the elevated F^- levels in the shallow groundwater. The recharge history and controls on F^- content in the groundwater in the central part of Yuncheng Basin were studied by Currell et al. (2010) and Currell et al. (2011). In this study lasting for 3 years, the hydrogeochemistry of groundwater and geological formations for enrichment of F^- in groundwater have been evaluated. The main objectives of this paper are as follows: (1) to characterize the hydrogeochemistry of the study area, (2) to evaluate the abundance and spatial distribution of F^- in the groundwater and (3) to identify potential hydrogeochemical processes responsible for the formation of high- F^- groundwater.

2. Regional hydrogeology

The Yuncheng Basin is located in the southwestern region of Shanxi Province and covers an area of approximately 6211 km^2 (between 34°40' and 35°30' N and 110°15' and 111°25' E). The basin has a semi-arid climate with an average rainfall of 550 mm/year, of which approximately 70% is received during the East Asian summer monsoon between June and October (Han et al., 2006). The annual average evapotranspiration in the basin is 1240 mm (Yang and Lu, 2005), which exceeds the average annual rainfall.

The basin is composed of Quaternary sediments (Q_1–Q_4), primarily aeolian loess, lacustrine clays, fluvial sands and gravels. The bedrock in the south of the basin and adjacent to the Zhongtiao Mountains is dominated by Archean metamorphic rocks, including hornblendite, amphibolite and quartzite. The Quaternary sediments are underlain by sedimentary rocks, including Neogene mudstone and Cambrian-Ordivician limestone (Yuncheng Regional Water Bureau and the Shanxi Geological Survey, 1982). Based on the paleosol horizons and fossil assemblages, the Quaternary sediments can be classified into four major stratigraphic units (Liu et al., 1982; Liu et al., 1986; Fig. 1(a) and (b)).

Yuncheng Basin is a closed basin in which the groundwater flows within the Basin area (Han et al., 2006). Generally, the grain sizes of aquifer sediments decrease from the mountain front to the center of the basin. Based on hydrogeological characteristics, the Quaternary groundwater system can be divided into three unconsolidated aquifers: shallow unconfined (<70 m, Q_3 and locally Q_4), intermediate semi-confined (70–120 m, Q_2 and Q_3) and deep confined (>120 m, Q_1 and locally Q_2). The shallow unit is distributed in the Sushui River Basin (Fig. 1b). The thickness of this aquifer is generally 6–20 m, and lithologically, they are gravel and medium-coarse sand in the piedmont plain, medium sand in the alluvial plain and fine sand in the fluvial depression areas. The intermediate and deep units are distributed within the whole basin range. From the basin margins to the central areas, the thickness of these two aquifers increases, and the size changes from the coarse particles to the fine particles gradually. The shallow unconfined, intermediate semi-confined aquifers as well as the uppermost layers of the confined aquifer have been most intensively pumped for water supply. Shallow groundwater is a considerably modern component of the Yuncheng Basin. In addition, the deep groundwater in the basin has residence times between 7000 and 22000 years, while the intermediate groundwater has residence times from modern to 5000 years (Currell et al., 2010). The sample C01 from shallow aquifer, C02 from intermediate and C03 from deep aquifer have residence times of 2400, 3600 and 19000 years, respectively (Fig. 1(a)).

Historically, regional groundwater flows from eastern Yuncheng Basin to the west, toward the Yellow River, while intermediate-scale flow occurs from the sloping southern and northern margins to the central areas of the basin (Fig. 1a; Yuncheng Regional Water Bureau and Shanxi province Geological Survey, 1982). However, due to the over-exploitation of groundwater since 1980s, horizontal groundwater flow now turns toward a cone of depression to the west of the Yuncheng city. The velocity of groundwater in the central basin is slower than the margin areas, which is consistent with the variable permeability of the aquifer sediments (Han et al., 2006). The groundwater is mainly recharged by infiltration of precipitation with respect to E'mei plateau, and artificial abstraction and discharge toward the Sushui River Basin and the Yellow River Terrace in the west are the major ways of groundwater discharge (Fig. 1). In the case of Sushui River Basin, the groundwater is mainly recharged by vertical seepage of meteoric water and by lateral permeation of fissure water along the basin margin. Leakage of non-perennial river water and irrigation return are additional sources of groundwater recharge. Evapotranspiration and artificial abstraction are the major ways of groundwater discharge.

3. Materials and methods

More than 100 groundwater samples were collected across the basin between 2011 and 2012 (Fig. 1(a)). Among them, 26 samples were collected from shallow wells (9–50 m), 58 from deep wells (130–500 m) and 16 from intermediate aquifers (80–120 m). Before sampling, the wells were pumped for more than 1 h. During sampling, all water samples were filtered through 0.45 μm membranes on site. Samples were stored in new 300 mL polyethylene bottles that had been rinsed three times with deionized water. For cation analysis, reagent-quality HNO_3 was added to one of the polyethylene bottles until the pH of the sample was less than 2. Water temperature (T), pH and EC were measured in situ using a portable Hanna EC and pH meter that was calibrated before use. The alkalinity was measured using the Gran titration method on the day of sampling. Within 2 weeks after sampling, the samples were analyzed at State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. SO_4^{2-}, Cl^-, F^- and NO_3^- concentrations were determined using ion chromatography (IC) (Dionex 120, Dionex, Sunnyvale, CA, USA). SiO_2 concentrations were determined using colorimetry, and Ca^{2+}, Mg^{2+}, Na^+ and K^+ were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Intrepid II XSP, Thermo Elemental, Madison, WI, USA). $\delta^{18}O$ and δ^2H compositions of the groundwater samples were measured using a Finnigan MAT 253 isotope ratio mass spectrometer at the Institute of Karst Geology, at the Chinese Academy of Geological Science. The analytical precision for the cation and anion measurements is indicated by the ionic balance error, which was within the standard limit of $\pm 5\%$. The hydrochemical facies were determined using the hydrogeochemical software AQUACHEM. In addition, ten Quaternary sediment samples were collected from 1 to 2 m below the ground. The mineral compositions of these samples were determined using X-ray powder diffractometry (XRD, Bruker AXS D8-Focus X ray diffraction, Germany). These sediment samples were processed by alkali fusion, and a fluoride ion selective electrode was used to determine fluorine content in the sediment (Yao et al., 2009).

4. Results

4.1. Major constituents

The major properties and the hydrochemistry of the water samples are summarized in Table 1. The groundwater chemistry indicated wide variations in concentrations (Figs. 2 and 3). However, all of the groundwater samples were colorless, odorless and mostly alkaline.

Shallow groundwater contained highest concentrations of dissolved constituents (Fig. 2). Na^+ was the dominant cation, with concentrations up to 4967 mg/L, several times higher than other major cations. Sulfate