



Diverse mechanisms drive fluoride enrichment in groundwater in two neighboring sites in northern China[☆]

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ABSTRACT

Excessive amounts of fluoride in drinking groundwater are harmful to human health, but the mechanisms responsible for fluoride enrichment in groundwater are not fully understood. Samples from two neighboring areas with endemic fluorosis were collected to test the hypothesis that there are distinctly different mechanisms responsible for the enrichment of fluoride in these groundwater. Hydrochemistry, stable isotopes and geochemical simulation were conducted together to investigate the fluoride spatial distribution and the diversity of responsible mechanisms. Our results showed that the spatial distributions of fluoride are different: I) high [F] in fresh shallow groundwater (SG_{QJ}) and II) medium [F] in fresh to brackish deep groundwater (DG_{QJ}) in the Qiji area; and III) medium [F] in brackish shallow groundwater (SG_{YH}) and IV) low [F] in fresh deep groundwater (DG_{YH}) in the Yanhu area. We also found that the fluoride concentration in groundwater is primarily controlled by the dissolution equilibrium of fluorite, as suggested by the correlation between [F] and [Ca]. However, there are other significant mechanisms: 1) for SG_{QJ}, fluoride-bearing minerals (such as fluorite) dissolution, along with moderate evaporation, cation exchange and the more alkaline conditions are the driving factors; 2) for SG_{YH}, the contributing factors are strong evaporation, the salt effect, dissolution of evaporites, gypsum and dolomite, bicarbonate-fluoride competition and anthropogenic activity; 3) for DG_{QJ}, cation exchange, alkaline conditions and competitive adsorption are major factors; and 4) dolomite dissolution promotes the [F] increase in DG_{YH}. Our findings suggest that the hydrogeochemical conditions play key roles in the enrichment of fluoride and that caution should be taken in the future when evaluating fluoride occurrence in groundwater, even in nearby areas.

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1. Introduction

High fluoride (F) concentrations (>1.5 mg/L) in groundwater used for drinking can adversely impact the health of people, and this has been occurring in China (Bacquart et al., 2015; Farooqi et al., 2007; Amini et al., 2008; Mondal et al., 2017; Ding et al., 2011). Skeletal fluorosis such as bone deformities, dental fluorosis, and kidney and liver malfunction are some of the consequences of exposure to drinking water with excessive fluoride concentrations (Cherukumilli et al., 2017). Children are especially at risk of being exposed to non-carcinogenic fluorosis in China (Zhang et al., 2017).

The fluoride in groundwater may originate from natural sources and from anthropogenic activities such as industry and agriculture (Edmunds and Smedley, 2013; Su et al., 2011; Ando et al., 2001). The natural sources of fluoride are volcanic gases, marine aerosols and soluble fluoride-bearing minerals such as fluorite, biotite and apatite (Kumar et al., 2016; Brahman et al., 2013).

Lots of studies have described the mechanisms and geochemical processes involved in the genesis of fluoride-rich groundwater (Chae et al., 2007; Li et al., 2017; Zabala et al., 2016; Jacks et al., 2005). The factors causing the enrichment of fluoride in groundwater include dissolution-precipitation reactions, adsorption-desorption processes, ion exchange, complex formation, mixing, evapotranspiration and even human activities (Padhi and Tokunaga, 2015; Ma et al., 2017; Bagastyo et al., 2017). Fluoride in groundwater mainly comes from the dissolution of F-bearing minerals in aquifer sediments (Chae et al., 2007; Edmunds and Smedley, 2013). Weathered minerals dissolve fluoride into groundwater during percolation (Jha et al., 2013). Where high fluoride concentrations occur, [Ca²⁺] is typically low due to the

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fluorite dissolution balance. Thermodynamic modeling has been employed to show that the precipitated of calcite could cause the removal of Ca^{2+} and enhance fluorite dissolution and F enrichment significantly (Raju et al., 2012; Brahman et al., 2013). Moreover, cation exchange between Na^+ and Ca^{2+} and the replacement of F^- by OH^- have been identified as the major ion-exchange processes involved in the formation of fluoride-rich groundwater (Kour and Kour, 2016; Padhi and Muralidharan, 2012). For instance, the hydrolysis of fluorapatite was regarded as the primary factor of fluoride enrichment in groundwater, illustrated by factor analysis in an area southwest of Riyadh (El Alfy et al., 2017). Several studies have shown that the mixing of different water sources, such as brackish water and fresh water, can cause fluoride enrichment in groundwater (Gao et al., 2007; Wu et al., 2015). Furthermore, an arid climate with high evaporation rates also facilitates the occurrence of F^- in groundwater (Rezaei et al., 2017). A statistical analysis demonstrated that evaporation was the primary cause of high [F] in shallow groundwater in northeastern India (Rao et al., 2017). Anthropogenic inputs can also leach fluoride into groundwater via precipitation leaching and agricultural irrigation, as well as surface water leakage (Currell and Cartwright, 2011; Gao et al., 2007). Consumption and/or application of phosphate fertilizers, insecticides and herbicides create a non-point source of fluoride in groundwater (Ayoobo and Gupta, 2006; Datta et al., 1996).

Numerous factors may affect the occurrence of fluoride in groundwater, and the situations may be complex in the underground environments where groundwater is stored. To gain some universal rules for the genesis of F-rich groundwater, comparisons of works done in different sites or areas have received extensive attention (Jacks et al., 2005; Edmunds and Smedley, 2013; Li et al., 2017; Zabala et al., 2016; Kierdorf and Kierdorf, 2003). However, the significance of these comparisons is limited due to the differences in climatic, topographic and geological conditions of different places, and they cannot provide extensive reference value in a broad sense. Therefore, to further understand the key factors responsible for fluoride enrichment, it is meaningful to find ideal places with fewer limitations.

Here, two neighboring sites (Qiji and Yanhu) with similar climate and topography were chosen to test the hypothesis that the mechanisms responsible for the enrichment of fluoride in groundwater may be different across the same basin. By comparing two areas in the same basin, more attention was paid to the hydrogeochemical conditions and human activities while keeping climatic and topographic factors constant. Hydrogeochemistry, stable isotopes and geochemical simulation were employed together 1) to identify the major geochemical processes controlling groundwater chemistry, 2) to investigate the spatial distribution of fluoride in shallow and deep aquifers, and 3) to interpret the mechanisms involved in the genesis of F-rich groundwater in the two neighboring sites.

2. Study areas

The Yuncheng Basin, situated between $34^{\circ}40'$ and $35^{\circ}30'$ N and $110^{\circ}150'$ and $111^{\circ}25'$ E with a total area of 6211 km^2 , is an area in China with severe fluorosis (Cao, 2005) (Fig. 1). In the basin area, approximately 60% of the shallow groundwater and 40% of the deep groundwater have fluoride concentrations higher than 1.0 mg/L (the maximum allowable concentration in China) (Li et al., 2015; Gorchev and Ozolins, 2011). The widespread occurrence of fluoride in groundwater has limited the available water resources in the area.

The study area has an average rainfall of 550 mm/year , with most of it occurring in the east-Asian summer monsoon season between June and October (China Geological Survey, 2006). The

total annual evapotranspiration is approximately 2000 mm , which is greater than the average rainfall. The surface water in the study area is mainly the Sushui River and its tributaries. The total consumptive use of water of the City is $14.48 \times 10^8 \text{ m}^3$, of which groundwater accounts for over 57% of the total. Due to the shortage of water resources, overexploitation of groundwater has caused a series of environmental and geological problems such as water table decline. As one of the important food producing regions in Shanxi Province, agricultural land is the major land-use type in the basin. There is not much industry in the basin, as it is typically located major cities which are far from our study area.

The two neighboring sites (Qiji and Yanhu) chosen for this case study are both typical endemic fluorosis areas (Li and Dong, 2014). Over 90% of the inhabitants in the rural villages are suffering from dental fluorosis in these two areas. The two study sites are 15 kilometers apart, and both are located in the central part of the basin. The groundwater in these two areas is stored in the Quaternary sediments (Q1-Q4), which are primarily aeolian loess along with lacustrine clays, fluvial sands and little gravels (Supplementary Fig. S1). The majority of the shallow aquifer sediments in the Qiji area consist of gravel, medium-coarse sand, medium sand, and fine sand; the shallow aquifers of the Yanhu area consist of fine sand, clay and sandy clay, while the deep aquifers mainly consist of fine to medium sand, clay and sandy clay. The mineral constitutions in each site are mainly aeolian loess composed of quartz, feldspar, calcite and clay minerals (Han et al., 2006; Oyelola and Tang, 2008). In this case study, groundwater in the study areas is divided into a shallow unit ($<70 \text{ m}$) and a deep unit ($>70 \text{ m}$), although they are probably hydraulically connected with each other in some sites. Horizontal groundwater flow is from the basin margins toward its center (China Geological Survey, 2006). The groundwater in this area is recharged mainly by vertical seepage of meteoric water in the basin and by lateral penetration of fissure water along the basin margin. The major discharge pathways of groundwater include evapotranspiration and artificial extraction.

3. Materials and methods

A total of 53 samples were collected from the two areas (Qiji and Yanhu) during August 2014 (Fig. 1). The collected samples include 1) ten shallow groundwater samples and eleven deep groundwater samples from the Qiji area, and 2) eighteen shallow groundwater samples and sixteen deep groundwater samples from the Yanhu area. All of the samples were filtered through a $0.45\text{-}\mu\text{m}$ Millipore membrane, and the total alkalinity was analyzed by the Gran titration method in triplicate with analytical error $<\pm 2\%$. For the determination of cations and trace elements, reagent-quality HNO_3 was added until the pH of the samples was less than 2.0. The concentrations of F^- , Cl^- , SO_4^{2-} and NO_3^- were measured using ion chromatography (IC) (Dionex 120, Dionex, Sunnyvale, CA, USA). Analytical charge imbalances were within the standard limit of $\pm 5\%$. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the groundwater samples were determined using a Finnigan MAT 253 isotope ratio mass spectrometer at the Institute of Karst Geology, Chinese Academy of Geological Science. Isotope values ($\delta^{18}\text{O}$, $\delta^2\text{H}$) were reported in permillage relative to Vienna Standard Mean Ocean Water (VSMOW). The analytical accuracy for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was within $\pm 0.2\%$ and $\pm 1.0\%$, respectively.

4. Results

4.1. Fluoride and major ions in groundwater

The characteristics of groundwater samples from the two neighboring sites are listed in Supplementary Table 1. Groundwater

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