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Geochemical controls on fluoride concentrations in natural waters from the middle Loess Plateau, China

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ABSTRACT

Water resources play a key role in the development of regional economy and stability of ecosystem in the middle Loess Plateau, China. Spatial variability of fluoride (F^-) and its geochemical control with other dissolved ions in the middle Loess Plateau were discussed. Samples were neutral to weak alkaline (pH = 7.4–9.6) with little variation of ion concentrations between river water and groundwater. The F^- concentrations ranged from 0.2 to 3.1 mg/L, with an mean value of 0.9 mg/L. Approximately 31% of samples in northern and southern part of the study area were HCO_3^-–Na^+ water type with F^- levels higher than the Chinese Drinking Water Standard of 1.0 mg/L. About 12% samples in the central part were HCO_3^-–Ca^{2+} water type with F^- content lesser than recommended value for caries control of 0.5 mg/L. The Quaternary deposits in the study area were the mainly F^- sources of natural waters, and rainwater also contributed some F^-. The alkaline characteristic of natural waters favored desorption of F^- from hydrous metal oxides in loess, the climate of the study area, cation exchange, and $CaCO_3$ precipitation further increased F^- concentrations in natural waters in the middle Loess Plateau. Moreover, the chemical data analyzed in the principal component analysis (PCA) also indicated that climate coupled with geochemical processes was the main controlling factor for high F^- in natural waters in the area. For the supply of high quality drinking water with safe F^-, short-term and long-term action plans as well as awareness/education programs for the public were advocated.

1. Introduction

Fluorine is the 13th most abundant element on the planet and is found in significant quantities in the oceans, atmosphere and the Earth's crust (Singh et al., 2011). Fluorine is usually found as fluoride mineral complexes, such as fluorite (CaF_2), sellaite (MgF_2), cryolite (Na_3AlF_6), topaz [$Al_2F_2(SiO_4)$], fluorapatite [$Ca_5(PO_4)_3(Cl,F,OH)$], tourmaline, muscovite, biotite, hornblende, and villianmite (Subba Rao et al., 2013; Singh et al., 2011, 2013; Singh and Mukherjee, 2015). During weathering and circulation of water in rocks and soils, fluoride (F^-) leaches out and dissolves in water. Therefore, high F^- are expected in the areas, where such F-bearing minerals are abundant in the rocks. The solubility of CaF_2 has been recognized as the most important control for F^- concentration. The F^- in natural water is governed principally by climate, composition of host rock, hydrogeology, and anthropogenic activities (Ayoob and Gupta, 2006; Rafique et al., 2008; Singh and Mukherjee, 2015). Groundwater is a major source of human intake of F^- and high F^- groundwater commonly has low Ca^{2+}, alkaline pH, and HCO_3^--Na^+ water type (Guo et al., 2007; Rafique et al., 2008, 2009). Small concentrations of F^- have beneficial effects on the teeth by hardening the enamel and reducing the incident of tooth decay. Chronic exposure to elevated concentrations of F^- in drinking water above the World Health Organization guideline value of 1.5 mg/L often results in endemic diseases such as dental and skeletal fluorosis (WHO, 2011). The threshold value of F^- in Chinese drinking water standard is 1.0 mg/L (Ministry of Health, 2006). F^- is considered as a major pollutant of drinking water on global scale. Around 200 million people from 25 nations suffer from ill-health because of high F^- concentration in drinking water (Ayoob and Gupta, 2006; Vikas et al., 2013). India and China, the two most populous countries of the world, are the worst affected (Wang et al., 2004; Subba Rao, 2009; Subba Rao et al., 2012, 2013; Singh and Mukherjee, 2015). In China, high F^- waters are mainly in semiarid and arid area of northern China (He et al., 2010; He et al., 2013a; Su et al., 2013; Wen et al., 2013). Approximately 50 million people are exposed to high F^- groundwater and about 60% of the exposed population suffer from dental fluorosis, and about 10% suffer from skeletal fluorosis in northern China (Wang and Cheng, 2001; He et al., 2013b). To utilize and protect valuable groundwater resources effectively and to safeguard the health of people, it is important to understand the occurrence and the hydrochemical characteristics of high F^- groundwater.

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Covered by Quaternary deposit, the middle Loess Plateau (is also known as the Huangtu Plateau) is a cradle of human civilization, and is water-deficient. Water resources and water quality play a key role in the development of the regional economy and stability of ecosystem. Meanwhile, the F^- concentration of groundwater is high, which harms residents' drinking water safety, and impediments the development of economic construction (He et al., 2010). Understanding the factors governing spatial distribution of F^- in natural water and the characterization of high F^- environments is very important to ensure human and animal health through an effective control of F^- poisoning. However, only very few works focused on the genesis and controlling factors of F^- in Quaternary aquifers, especially in the Loess Plateau (Guo et al., 2007; Currella et al., 2011; He et al., 2013b). Guo et al. (2007) and Currella et al. (2011) delineated geochemical processes controlling the elevated F^- concentrations in groundwater of Taiyuan Basin and Yuncheng Basin in the eastern part of the Loess Plateau, respectively. He et al. (2013b) studied geochemical characteristics and F^- distribution in groundwater of Zhangye Basin in the western part of the Loess Plateau.

In the present study, major ions and F^- in river water and groundwater in the middle Loess Plateau have been measured. The main objectives are as follows: 1) to delineate the spatial distribution of F^- enrichments, 2) to illustrate sources of high F^-, 3) to evaluate hydrogeochemical factors and processes controlling high F^- in natural waters in the middle Loess Plateau. This will fill the research gap of F^- geochemistry in the middle Loess Plateau and add new data to the world water F^- geochemistry.

2. Materials and methods

2.1. Study area

The study area is in the middle Loess Plateau (34°9′–39°4′N, 105°2′–110°3′E), which covers about 27×10^4 km^2 and mainly includes the northern and central of Shaanxi Province (Fig. 1). One of the most notable geological features of the study area is the dominance of Quaternary loess and loess-like deposits, which are mainly from the Gobi Desert in northern China (Liu, 1985). In addition to loess, outcrops of granites and metamorphic rocks can be found in areas near the Qinling Mountains (Fig. 1). The pivotal natural vegetation in the study area includes broadleaved deciduous forest, forest-steppe, steppe, and desert-steppe (Su and Fu, 2013). Presently, forest cover is 6.5%, and grass cover varies from 25 to 65%. The region belongs to a temperate continental climate with mean annual temperatures ranging from 4 °C to 14 °C and annual precipitation ranging from 200 to 750 mm. Around 60–70% of the rainfall occurs in highly erosive heavy storm-lit that fall from June to September (Su and Fu, 2013).

According to administrative zoning, the Shaanxi Province is divided into three districts: northern, central, and southern (Liu et al., 2013). The geography of the Shaanxi Province is described as being part of the Ordos Desert in the north along the border with Inner Mongolia, the Loess Plateau in the central part of the province, the Qinling Mountains running east to west in the south central part, and subtropical climate south of the Qinling (Fig. 1). In between the Loess Plateau and the Qinling lies the Wei River Valley, or Guanzhong Plain. Due to its large span in latitude, Shaanxi has a variety of climates. The northern parts have either a cold arid or cold semi-arid, with cold and very dry winters, dry springs and autumns, and hot summers. The Guanzhong is mostly semi-arid, though there are a few areas with a humid subtropical climate, with cool to cold winters, and hot, humid summers that often see early-season heatwaves. The southern portion is much more humid and lies in the humid subtropical zone, with more temperate winters and long, hot, humid summers.

2.2. Sampling and analytical procedure

Ninety river waters and forty-three dug well waters were collected from April 1 to 26, 2013, which was the dry season of the study area. These natural waters are the only available sources for drinking and other domestic use in the study area. The Total Dissolved Solids (TDS), electrical conductivity (EC), temperature (T), and pH were measured onsite using portable Orion EC/pH meter that was calibrated before use. Samples were *in situ* filtered on collection through 0.22 μm Whatman® nylon filters to remove the insoluble particles. A 60 mL aliquot was stored in a pre-cleaned high density polyethylene (HDPE) bottle and acidified to pH < 2 with 6 M ultrapure HNO_3 for cation analysis. A 30 mL aliquot of the un-acidified sample was collected for anion analysis. Then, the bottle was slightly stretched and wrapped a parafilm strip around the closure to ensure no leakage after the outside of the bottle was dried. All of the samples were stored at 4 °C until analysis. Water samples were analyzed for Ca^{2+}, K^+, Mg^{2+}, Na^+, and SiO_2 by a Leeman Labs Profile ICP-OES at Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. Repeated analyses demonstrated reproducibility within 2%. A Dionex-600 ion chromatograph was used for F^-, Cl^-, NO_3^-, and SO_4^{2-} analysis at the Institute of Earth Environment, Chinese Academy of Sciences. The average replicated sample reproducibility was 0.5–1% (2σ). Alkalinity was titrated by hydrochloric acid within 12 h, by Gran titration using 0.1 N HCl. Saturation index (SI) values of the samples were calculated using the Geochemist's Workbench 8.0 software (Bethke and Yeakel, 2009). The existence forms of fluorine in samples were simulated using Visual MINTEQ 3.0 software (http://hem.bredband.net/b108693/). The analytical precision of the ions was determined by calculating the normalized ionic charge balance error, which varied within ±6%.

3. Results and discussion

3.1. Hydrochemistry

The statistics for the samples are listed in Table 1. Samples were neutral to slightly alkaline, with pH values ranging from 7.55 to 9.60 (average 8.67) in river water and from 7.36 to 8.86 (average 8.06) in groundwater. The TDS values varied from 203 to 6318 mg/L (average 1076 mg/L) in river water and from 306 to 6358 mg/L (average 1125 mg/L) in groundwater. Approximately 36% and 64% of the samples belonged to brackish water and fresh water, respectively. The brackish water samples were mainly distributed in the northern part of the study area. The average concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, F^-, Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- were 182, 64, 62, 5.0, 0.92, 161, 235, 3.24, and 358 mg/L in river water, and 166, 79, 62, 2.8, 0.84, 121, 215, 2.75, 467 mg/L in groundwater. The relative abundance of major cations and anions in river water and groundwater were ranked in the following order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$, respectively (Table 1). Na^+ and HCO_3^- were the dominant cation and anion in both river water and groundwater. Generally, variation and difference of ion concentrations between river water and groundwater were little (Table 1). This may be related with the recharge situation between river water and groundwater in this area.

3.2. Spatial variation of F^- concentration

In the present study, F^- concentrations varied from 0.20 to 3.10 mg/L (average 0.92 mg/L) in river water and from 0.20 to 2.70 mg/L (average 0.84 mg/L) in groundwater. These values were basically similar to Zhangye Basin (He et al., 2013b), Taiyuan Basin (Guo et al., 2007), and Hetao Basin (Guo et al., 2012; He et al., 2013a), but lower than that in Datong Basin (Su et al., 2013), basins located near the study area. The coefficient of variation is 52%, which indicates that the variation degree of F^- contents of the samples is relatively high. Because high TDS values can enhance the ionic strength and lead to the increase of F^- solubility in water (Rafique et al., 2009), F^- and TDS has a positive relationship in river water and groundwater (Table 2). Thus, in addition to its direct effects on human health,