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Geochemical sources, hydrogeochemical behavior, and health risk assessment of fluoride in an endemic fluorosis area, central Iran

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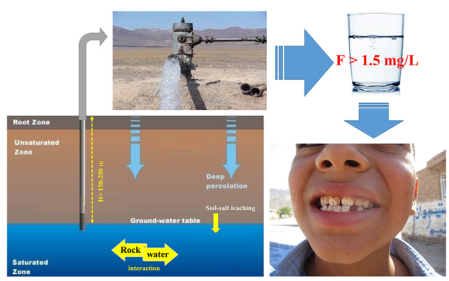
HIGHLIGHTS

- Geochemical cycle of fluoride is assessed in the study area.
- Na-Cl- and Na-SO4-type waters are contaminated with F.
- Soil and shale rocks are the main sources of fluoride.
- People are exposed to high levels of fluoride intake through drinking water.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study is the first attempt to put forward the possible source(s) and health risk assessment of fluoride in Bahabad, central Iran. Fluoride concentrations ranged from 0.22 to 2.35 mg/L and 292–355 mg/kg in the groundwater and soil samples, respectively. Geochemical provenance techniques using major and rare earth elements in soils revealed that local shale is the most probable source rock of fluoride in the area. A two-step chemical fractionation method applied on soil samples demonstrated that residual and water-soluble fractions were the most probable modes of fluoride in soil, whereas exchangeable fraction had a minor role. The coefficient of aqueous migration showed that fluoride in the studied soils behaved as a mobile element. Moreover, the relative mobility indicated that soils played a more important role than rocks in releasing fluoride into groundwater. In groundwater medium, chemical weathering, evaporation, and ion exchange acted as the main geochemical controlling factors of fluoride enrichment. Findings of this study signify that the role of Na–Cl– and Na–SO_4-type waters should be considered more to recognize susceptible areas to fluoride contamination in groundwater. People in the study area are exposed to high levels of fluoride intake through drinking water, thus making dental fluorosis a major public health concern in the area. Scanning electron microscopy of the dentin's enamel showed morphological modifications (e.g., cracks and fissures) in residents' enamel structures. The results of this study may lead to suitable management strategies to mitigate the endemic fluorosis problem.

1. Introduction

Fluorine is an abundant trace element in the Earth's crust (Tavener and Clark, 2006). The mineralogy of bedrocks is the primary source of fluoride in groundwater; however, fluoride

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occurrence varies greatly in different rock types (Keshavarzi et al., 2010). Elevated F^- concentrations are found in groundwater of regions with dominance of igneous rocks (Moghaddam and Fijani, 2008; Berger et al., 2016). Volcanoes represent the main natural persistent source of fluoride into the groundwater and atmosphere (Halmer et al., 2002; D'Alessandro et al., 2012; Bosshard-Stadlin et al., 2017). Fluoride enrichment in groundwater is mainly affected by the solubility of F-bearing minerals, temperature, pH, vegetation, anion exchange, groundwater residence time, salinity, evapotranspiration, and presence of precipitating or complexing ions (Ozsvath, 2006a,b; Jacks et al., 2005; Battaleb-Looie et al., 2012a). Fluoride in groundwater is mostly geogenic and originated from natural minerals such as fluorite, apatite, topaz, micas, and amphiboles (Kumar et al., 2015; Grützmacher et al., 2013). Groundwater circulates through F^--rich rocks, and sediments result in the dissolution and subsequent enrichment of fluoride in groundwater (Chae et al., 2007). Typically, high-F groundwaters are associated with low Ca^{2+}, alkaline pH, and Na-HCO_3-type waters (Amini et al., 2008; Gomez et al., 2009), or hydrothermal waters (Deng et al., 2011), especially in arid and semiarid environments (Nordstrom and Jenne, 1977).

The occurrence of high-fluoride groundwater has been reported worldwide because it has a considerable impact on human health (Ayenew, 2008; Mondal et al., 2014). Depending on the concentration and daily ingested dose, fluoride in drinking water can be either beneficial or harmful to human health (Apambire et al., 1997; Gómez-Hortigüela et al., 2013). In arid regions, high fluoride concentrations occur in groundwater because of low groundwater infiltration and flow rates leading to prolonged water–rock interaction (Fuhong and Shuqin, 1988; Handa, 1975).

Low fluoride intake leads to the development of dental caries. However, the chronic ingestion of high doses has been linked to the development of dental fluorosis, and in extreme cases, skeletal fluorosis (Edmunds and Smedley, 2013). Although dental fluorosis is not a life-threatening illness, it can result in considerable added dental care costs, significant psychological stress (e.g., aesthetic disfiguration) (Apambire et al., 1997), and a global eco-toxicological problem for affected populations worldwide (Luo et al., 2011). Many high-fluoride water sources are used without treatment, and hence, large populations in developing countries suffer from the effects of chronic endemic fluorosis (Amini et al., 2008; Edmunds and Smedley, 2013). More than 200 million people worldwide use drinking water with F^- concentrations above the WHO guideline value of 1.5 mg/L and suffer from various forms of fluorosis (Susheela et al., 1999; Ayoob and Gupta, 2006; Taghipour et al., 2016). Excessive fluoride ingestion mainly occurs through drinking water (Jacks et al., 2005), foodstuff (Battaleb-Looie et al., 2013), toothpaste, and products used for dental health (Ozsvath, 2009). However, fluoride intake through drinking water is responsible for about 75% of daily fluoride intake (Amini et al., 2016). Groundwater is the major source of drinking water and daily fluoride exposure in Iran (Esmaeili and Moore, 2012; Keshavarzi et al., 2010; Battaleb-Looie et al., 2013). Fluoride concentration is low in drinking water of most areas in Iran (Taghipour et al., 2016). However, there are some regions with an anomalous content of fluoride in drinking waters, mainly located in the northwest and south of Iran (Battaleb-Looie et al., 2012a; Moghaddam and Fijani, 2008). In the south of Yazd province in central Iran, excessive fluoride concentrations are frequently encountered in groundwater resources resulting in a serious problem in the exploitation and use of groundwater (Mesdaghinia et al., 2010). The objectives of this study were to characterize the geological sources and behavior of fluoride in soils, signify the controlling factors of fluoride enrichment in water, and health risk assessment of fluoride in water samples. The methodology involves analyses of rocks and water samples along with water–rock interaction to seek fluoride sources and mechanisms of fluoride enrichment in groundwater.

2. Location and geological settings

The study area covers approximately 3000 km^2 in the southeast of Yazd province in southcentral Iran (Fig. 1a). Geologically, the study area is located in central Iranian microcontinent and in the south of Tabas-Posht-e-Badam metallogenic belt (Stocklin, 1968) (Fig. 1a), which hosts iron oxide–apatite deposits, Zn–Pb deposits, and coal beds (Seyed-Emami, 2003; Moore and Modabberi, 2003; Rajabi et al., 2015). Bedrocks in the area are mainly composed of Cambrian carbonates and clastic rocks, Permo-Triassic volcano-sedimentary rocks, Triassic–Jurassic dolomites, marls, limestones, coal-bearing micaceous sandstones and shales, Cretaceous limestones, Neogene conglomerates, and quaternary deposits (Mahdavi, 1996). Granitoid is the main intrusive rock in the area, which is situated in the west of Bahabad city (Balaghi et al., 2010) (Fig. 1b).

3. Hydrogeology

The climate of the study area is classified as arid to semiarid with an annual average temperature of 17.8 °C, annual rainfall of 57.2 mm, and total annual evaporation of 3113 mm (Yazd Meteorological Organization, 2015). Groundwater is the only available water resource for drinking, agricultural, and industrial use. An alluvial unconfined aquifer with a relative thickness of 101.6 m composes the main aquifer system in the area. The aquifer covers an area of 529 km^2 and extends from the south to the north of the plain (Dehbandi, 2017) (Fig. S1). The annual volume of abstracted groundwater is 34.04 mm^3. Precipitation is the main recharge source, which infiltrates into the aquifer (IWRMO, 2011). Secondary recharge appears on the slopes of the highlands bordering the systems. Isopotential map indicates that groundwater mainly flows from south towards north following the direction of discharge and the topography of the basin (Fig. S1). Over time, because of the continuous drought and the overexploitation of aquifers, a local drawdown occurred in the water table.

4. Materials and methods

4.1. Sample collection and preparation

Groundwater samples ($N = 23$) were collected from wells, qanats, and springs in the study area using 1 L polyethylene bottles. For a reliable evaluation of the hydrogeochemical behavior and health risk assessment of fluoride, water sample stations were distributed over the entire basin and chosen from water resources of population centers (e.g., urban and rural areas).

The samples were collected, preserved, and transported to the laboratory according to standard procedures (APHA, 1995; WHO, 2008). Eight representative fresh rock samples and seven ore samples were collected from major lithological units and mineral deposits, respectively. Furthermore, 12 (6 non-residual and 6 residual) composite surface soil samples (0–15 cm) were collected using a stainless steel spade and mixed thoroughly to obtain approximately 1.0 kg of fresh samples, which were kept in plastic bags. It is worth mentioning that rock and their overlying residual soil samples were selected from the marginal parts of Bahabad plain to represent the geochemical characteristics of predominant lithological units and their probable roles in groundwater chemistry. All the soil samples were air-dried at room temperature and then passed through a 2-mm sieve. A fraction of the sieved samples was finely powdered to less than 200 mesh size to determine the elemental contents (D'Alessandro et al., 2012; Chen et al., 2014).