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Fluoride prevalence in groundwater around a fluorite mining area in the flood plain of the River Swat, Pakistan

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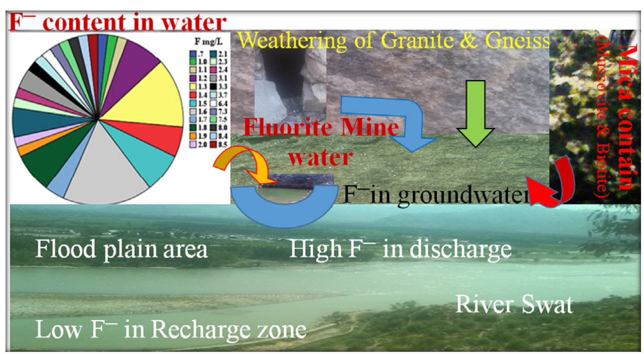
HIGHLIGHTS

- Groundwater of flood plain area of river Swat, Pakistan was analysed for F^-.
- Groundwater samples (62.2%) exceeded the WHO safe limit of F^- (1.5 mg/L).
- Fluoride enrichment was due to weathering of rocks and ion exchange processes.
- Minerals phases suggested both saturated (55%) and unsaturated (38%) groundwater.
- Health risk via (CFI) identified that groundwater is unfit for drinking purposes.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the fluoride (F^-) concentrations and physicochemical parameters of the groundwater in a fluorite mining area of the flood plain region of the River Swat, with particular emphasis on the fate and distribution of F^- and the hydrogeochemistry. To better understand the groundwater hydrochemical profile and F^- enrichment, groundwater samples ($n = 53$) were collected from shallow (24–40 m), mid-depth (48–65 m) and deep (85–120 m) aquifers, and then analysed using an ion-selective electrode. The lowest F^- concentration (0.7 mg/L) was recorded in the deep-aquifer groundwater, while the highest (6.4 mg/L) was recorded in shallow groundwater. Most groundwater samples (62.2%) exceeded the guideline (1.5 mg/L) set by the World Health Organization (WHO); while for individual sources, 73% of shallow-groundwater samples (F^- concentration up to 6.4 mg/L), 42% of mid-depth-groundwater samples, and 17% of deep-groundwater samples had F^- concentrations that exceeded this permissible limit. Assessment of the overall quality of the groundwater revealed influences of the weathering of granite and gneisses rocks, along with silicate minerals and ion exchange processes. Hydrogeochemical analysis of the groundwater showed that Na^+ is the dominant cation and HCO_3^- the major anion. The anionic and cationic concentrations across the entire study area increased in the following order: $HCO_3 > SO_4 > Cl > NO_3 > F > PO_4$ and $Na > Ca > Mg > K$, respectively. Relatively higher F^- toxicity levels were associated with the $NaHCO_3$ water type, and the chemical facies were found to change from the $CaHCO_3$ to

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($Na—HCO_3$) type in calcium-poor aquifers. Thermodynamic considerations of saturation indices indicated that fluorite minerals play a vital role in the prevalence of fluorosis, while under-saturation revealed that – besides fluorite minerals – other F^- minerals that are also present in the region further increase the F^- concentrations in the groundwater. Finally, a health risk assessment via Dean's classification method identified that the groundwater with relatively higher F^- concentrations is unfit for drinking purposes.

1. Introduction

Fluoride (F^-) is an essential micronutrient for human beings, strengthening both teeth and skeletal tissue (Nielsen, 2009; Rafique et al., 2009). It is the main inorganic toxicant of fluorine, predominantly promoted by alkaline pH, high concentrations of sodium cations (Na^+) and bicarbonate (HCO_3^-), and low concentrations of calcium ions (Ca^{++}) (Guo et al., 2007; Rafique et al., 2009). Fluoride enrichment mostly occurs in groundwater, soil, rocks, food, air, flora, fauna, and the human body (Rakshit, 2004; Raju et al., 2012; Varol et al., 2013; Raju et al., 2014; Singh et al., 2015; Xiao et al., 2015a, 2015b; Patel et al., 2016). Groundwater is the principal source of F^- for human ingestion, potentially recognized and controlled by the regional chemistry of the host rock, hydrogeology, anthropogenic activities, and climatic factors (Frengstad et al., 2001; Saxena and Ahmed, 2003; Edmunds and Smedley, 2005; Chae et al., 2007; Khaliq et al., 2007; Rafique et al., 2009; Singh et al., 2015). Soil contributes 0.3 g/kg of the total F^- content of the Earth's crust (Rakshit, 2004; Meenakshi and Maheshwari, 2006; Ghosh et al., 2013), making it the 13th most important source in terms of its natural abundance (Meenakshi and Maheshwari, 2006; Ghosh et al., 2013). Regions with relatively higher groundwater F^- concentrations are mainly situated in discharge zones, particularly where average or shallower depths of groundwater occur.

Several minerals contain F^-, such as fluorite, fluorspar, fluorapatite, topaz, hornblende, tourmaline, villianmite, amphiboles, mica, biotite, and muscovite. Besides these minerals, some weathering silicates, igneous and sedimentary rocks also contribute a significant amount of F^- to groundwater (Frengstad et al., 2001; Kim and Jeong, 2005; Antipin et al., 2006; Sreedevi et al., 2006; Msonda et al., 2007; Rafique et al., 2008; Feng et al., 2012; Doherty et al., 2014). Normally, F^- enters into environment and human beings through food, water, industrial exposure, drugs, cosmetics, or mining activities (Hiyama, 2000). Elevated concentrations of F^- in groundwater are regarded as a major health concern (Eby, 2004; WHO, 2004; Hudak, 2009). The prevalence of fluorosis is a widespread endemic disease of geological origin. Indeed, the link between the severity of fluorosis and concentrations of F^- in groundwater is well recognized (Nayak et al., 2009). The recommendation from the World Health Organization (WHO) in terms of an acceptable concentration of F^- in groundwater is 1.5 mg/L (WHO, 2004, 2006).

Endemic fluorosis afflicts >260 million individuals worldwide in 25 different nations, and >100 million people in southeast Asia, including India, Pakistan and Sri Lanka (Farooqi et al., 2007a, 2007b; Amini et al., 2008; Ravenscroft et al., 2009; Rafique et al., 2009; Kim et al., 2012). Both dental and skeletal fluorosis is a global problem, occurring in various countries, such as Ethiopia, Kenya and Tunisia (Rango et al., 2010, 2013; Olaka et al., 2016; Guissouma et al., 2017), India (Jacks et al., 2005; Vikas et al., 2013), China (Smedley et al., 2003; Guo and Wang, 2005; Guo et al., 2007; Amini et al., 2008; Wang et al., 2009; Currell et al., 2011), Brazil (Souza et al., 2013), and Pakistan (Farooqi et al., 2007a, 2007b; Rafique et al., 2015).

In Pakistan, the overuse and continuous consumption of groundwater for domestic purposes takes place mostly in semiarid and remote areas, potentially causing a deterioration in groundwater quality (Azizullah et al., 2011). Meanwhile, rapid industrialization, mining and urbanization are major environmental issues in developing countries of the world, including Pakistan, India and China. Residents in some local communities even use mine-water for domestic purposes.

In the above context, we studied the contamination of groundwater with F^- in a fluorite mining area in the flood plain of the River Swat, Pakistan. Specifically, we compared the chemistry of fluorite mine–water and surrounding groundwater, with the aim to: (1) identify the hydrogeochemical features responsible for the enrichment of groundwater with F^-, as compared with the depth profile of the aquifer; and (2) evaluate the health risk via Dean's classification (Dean and Elvove, 1935; Dean, 1942) for community fluorosis.

2. Study area

2.1. Profile of the study area

The selected flood plain area (Adenzai, Pakistan) is located at (34°–39°N, 71°–72°E) within a steep plain of the west-flowing River Swat and northwest-flowing River Panjkora. The rivers reach a confluence at Japan Bridge, near Matkhany. The area is located at the northern edge of Khyber Pakhtunkhwa (Fig. 1) and covers 120 km^2. The total population of the study area is 130,000. Topographically, the northeastern and southwestern portion is occupied by the foothills of Hindukush ranges. The study area included five fluorite mining zones and one control area in the flood plain of the River Swat, Adenzai (Fig. 1). The fluorite mines were previously drilled in the premises of Badwan, Chatpat, Ramial, Shamlie, Warsak and Osaky (Khaliq et al., 2007).

2.2. Climate, hydrology and hydrogeological settings

The region of Adenzai is situated in the northern part of Khyber Pakhtunkhwa and is characterised by semiarid climatic conditions of sultry summers and severely cold winters. The average annual maximum and minimum temperature recorded during summer and winter is 35 °C and −8 °C, respectively. Precipitation is bimodal, with peaks during the monsoons. The annual precipitation amount ranges from 254 to 1469 mm, falling mostly during the monsoon season (GOP, 1998). The mean rainfall in 2016 (the year of this study) was 19% lower than usual, although each monsoon still delivered large quantities of precipitation.

The regional hydrology reflects how residents in the various local areas consume groundwater sources differently, all of which are recharged mostly from precipitation. Shallow aquifers of groundwater have mostly low water tables and are used for drinking, domestic activities, agriculture, and industrial purposes. Inhabitants consume groundwater obtained from different sources, such as tube wells, hand pumps, dug wells, bore wells, and springs. Water from the municipal community tube well in the study area is delivered to residents through supply lines. The regional geological setting includes different formations (Fig. 2), such as Chilas complex, Indus suture melange, Khashala nokanai ghar and Saidu formations, Dir meta sediments, Quaternary alluvium, Kamila amphibolite, Kohistan batholith, Peshmal schist, Marghuzar and Duma formations, river beds, Shao formation and Utror volcanics, Swat and Mansehra granite complex. The complex geological setting of the study area includes different fluoride minerals present in the Kamila, Peshmal schist, Dir meta sediment and Swat