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Research Article

# Evaluation of aqueous geochemistry of fluoride enriched groundwater: A case study of the Patan district, Gujarat, Western India

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**Abstract**

High fluoride ($F^-$) groundwater causes fluorosis which might at severe stages lead to deformation of bones, bilateral lameness. The concentration of $F^-$ ranged from 0.4 to 4.8 mg/L. This study suggests that high $HCO_3^-$ and $Na^+$ in alkaline medium along with water–rock interaction plays important role in enrichment of $F^-$ in groundwater. Na-$HCO_3$ is the dominant water type followed by Ca-$HCO_3$ suggesting dominance of $Na^+$, $Ca^{2+}$ and $HCO_3^-$ ions in groundwater. Factor analysis of water quality parameters suggests that four principal components account for 74.66% of total variance in the dataset. Factor 1 shows higher positive loading for pH, $HCO_3^-$ negative loading for $F^-$, $Ca^{2+}$, $SO_4^{2-}$ depicting ion-exchange and $HCO_3$ dominant water type responsible for F enrichment in groundwater.

Saturation index for selected minerals suggests that most of the samples are oversaturated with calcite and undersaturated with fluorite. Calcite precipitation leads to the removal of $Ca^{2+}$ from solution thus allowing more fluorite to dissolve. These released $Ca^{2+}$ ions combine with $CO_3^{2-}$ ions to further enhance the precipitation of $CaCO_3$.


*Keywords:* Fluoride; Rock–water interaction; Saturation index; Groundwater

## 1. Introduction

Fluoride is a normal constituent of natural water. Globally the health of millions of people is threatened by endemic fluorosis because of consumption of groundwater polluted with $F^-$ (UNICEF, 2008). At the global scale, high concentrations of $F^-$ (i.e. >1.5 mg/L) are found in groundwater in China, Syria, Jordan, Ethiopia, Sudan, Tanzania, Kenya

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and Uganda (Ando et al., 2001). In the case of India, groundwater contamination with $F^-$ is well reported at numerous places in the States of Andhra Pradesh, Gujarat, Karnataka, Madhya Pradesh, Rajasthan, Chhattisgarh, Haryana, Orissa, Punjab, Haryana, Uttar Pradesh West Bengal, Bihar, Delhi, Jharkhand, Maharashtra, and Assam (Keshari and Dhiman, 2001; Jacks et al., 2005; CGWB, 2010). Occurrence of $F^-$ in groundwater at different parts of Rajasthan is extensively documented by the scientific community (Madhavan and Subramanian, 2002; Singh et al., 2012; Hussain et al., 2012). In case of Gujarat, Mehsana district is well reported for factors responsible for $F^-$ pollution in groundwater by Dhiman and Keshari (2006), however it is still poorly reported for many administrative units of Gujarat where people are suffering from fluorosis.

Because of its high reactivity, fluorine normally, exists in the form of $F^-$ in natural waters (Leung and Hrudey, 1985). Although geological sources contribute to the occurrence of $F^-$ in water, the major contribution comes from geological sources and conditions in hydro-geoenvironment such as the porosity and acidity of the soil and rocks, temperature i.e. semi-arid climate, the action of other chemicals, advanced stage of groundwater development and the depth of wells (Johnson et al., 2008; Ranjan et al., 2013). $F^-$ in groundwater is mainly derived from the weathering and leaching of rocks commonly containing minerals such as fluorite, fluorapatite, cryolite, amphibole, muscovite, biotite, (Carrillo-Rivera et al., 2002; Avtar et al., 2013). Due to a presumed lack of geochemical controls $F^-$ concentrations vary by more than an order of magnitude, the $F^-$ concentrations in groundwater range from well under 1.0 mg/L to more than 35.0 mg/L (IPCS, 1984).

$F^-$ helps in the normal mineralization of bones and formation of dental enamel (Cao et al., 2000). The total daily intake of $F^-$ from food is about 0.2–0.5 mg which is about only 10–15% of the required dose and hence humans are dependent on groundwater to fulfill this deficit (Boyle and Chagnon, 1995). The desirable safe limit of $F^-$ in drinking water is 1.5 mg/L (WHO, 1993). In case of daily intake of $F^-$ is low (i.e. $<0.5$ mg/L), various health issues may occur viz. dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially affecting the children (Mondal et al., 2009). When $F^-$ is consumed in the range of 1.5–2.0 mg/L, dental fluorosis or dental mottling may occur which is characterized by brown or black opaque patches on the enamel/tooth surface (Kharb and Susheela, 1994). When long term intake of $F^-$ exceeds 3.0 mg/L, skeletal fluorosis may occur characterized by deformation of bones (Goldman et al., 1991). Other than the above mentioned health issues, excessive intake of $F^-$ may lead to too much thirst, skin rashes, muscle fibre degeneration, blood cells deformation, gastrointestinal problems, urinary tract malfunctioning, and overall reduced immunity (Meenakshi and Maheshwari, 2006; Singh et al., 2011a).

With the above background, this work strives to evaluate the geochemistry of groundwater with special focus on geochemical processes controlling $F^-$ mobilization in Patan district, Gujarat, India.

## 2. Study area

The study area (Patan district) showing groundwater sampling location and $F^-$ safe and unsafe water is given in Fig. 1. The study area is located between 23° 55′ and 24° 41′ N and 71° 31′ and 72° 20′ E. Patan is situated in the northern part of Gujarat on the bank of the Saraswati River. The study area is bound on the North West by Rann of Kutch, on the North by Banaskantha district and in South East sharing a common border with Patan district. The total geographical area of the district is about 5740 $km^2$. The climate of the area is warm, sub-humid and sub-tropical. May is generally the hottest month and January, the coldest. The region has a minimum temperature as low as 5 °C–10 °C and a maximum temperature as high as 40 °C–48 °C. The mean annual rainfall is 765 mm, 95% of which is received due to Southwest monsoon, from June to mid-September. The topography varies from plains to low hilly ranges, with elevation gradients of 10 m–190 m above mean sea level. Patan district is a part of Gujarat plain and is sub-divided into three sub-micro regions, namely Western Sandy Waste, Central Alluvial Plain and Mahesana Low Land. Western Sandy Waste region has low relief in comparison to other regions of the district. Saraswati is the main river of the region, flows from north-east to south-west direction and ultimately submerges into the Little Rann of Kachchh. Geologically all the three divisions are part of wind-blown sand and almost the entire region has alluvium deposition and the clay layer thickness is 4 m. The region has Orthids-Aquepts, Orthids-Psamments and Ochrepts-Psamments types of soils. Central Alluvial Plain region slopes towards west. Thus, all the rivers Banas, Saraswati, Rupen and their tributaries which form the drainage pattern of this region, flow towards westerly direction. The Mahesana Low Land is flat and of sandy plain. Geological origin of the entire Patan landscape implies that it is generated due to prolonged alluvial action in Quaternary period. Since the area is geotectonically a graben of early Tertiary period, it provides a room

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