

Geochemical Modeling of High Fluoride Concentration in Groundwater of Pokhran Area of Rajasthan, India

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Abstract The groundwater is the only major source of drinking water in western part of Rajasthan, India. The study was carried out to locate and decipher hydrogeochemical reactions responsible for elevated concentration of fluoride. The concentration of fluoride ranged from 0.6 to 4.74 ppm in groundwater of study area. Since the area is a desertic terrain and no industries are present thus possibility of anthropogenic input of fluoride is all most negligible thus the enrichment of fluoride in groundwater is only possible due to rock-water interaction. The highly alkaline conditions indicated fluorite dissolution as major process responsible for high concentration of fluoride in Pokhran.

Keywords Fluoride · Dissolution · Toxicity · Pokhran

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. The concentration of fluorine in the atmosphere is 2.2 ppbv (Lide 1995) and total mass being 7.5 million tonnes. The concentration of fluorine in hydrosphere and lithosphere (earth crust) is 1.3 and 585 ppm with total mass accounting to 2.16×10^6 and 1.4×10^{10} respectively (Luo et al. 1994). Fluoride is an essential element for human body. It helps in mineralization of bones and formation of enamel of teeth. A daily dose of 0.5 ppm is required for proper formation of enamel and bone mineralization which otherwise may result in formation of dental caries, lack of enamel formation and

bone fragility (Cao et al. 2000; Ayenew 2008). High concentration of fluoride in drinking water is considered as health hazard (Eby 2004; Hudak 2009) and it causes chronic endemic fluorosis. Fluorosis at more severe stage causes bilateral lameness and stiffness of gait (Suttle 1977). The fluoride ion contributes over 95% of the total fluoride present in drinking water (Smedley 2005). Fluoride is present in the form of naturally occurring minerals as fluorite (CaF_2), cryolite (Na_3AlF_6), topaz, tourmaline, muscovite, biotite, hornblende, villianmite (Handa 1975; Pickering 1985; Wenzel and Blum 1992; Msonda et al. 2007). Fluoride is also found in micas where it occurs in combination with silicates, but particularly in association with phosphorus as fluorapatite. The occurrence of fluoride in groundwater where human interference is almost negligible can be attributed to the weathering and leaching of amphiboles, fluorite, apatite and mica. Thus the areas where such rock types are dominant high fluoride concentration can be suspected (Sarma and Rao 1997; Nordstrom et al. 1989; Banks et al. 1995; Gizaw 1996; Frengstad et al. 2001). The fluoride concentrations are found to be higher in water with high alkalinity. In many waters, calcium ions are in excess and under these conditions, the concentration of fluoride is controlled by CaF_2 , which at normal temperatures has a solubility of about 15 ppm and fluoride ion level is limited to about 8 ppm. India has witnessed problems of fluorosis (dental and skeletal) in past as well as in present with 66 billion cases reported be to be affected by it alone. Muralidharan et al. 2002 reported that Rajasthan has maximum number of people affected by high fluoride content in groundwater. There is acute shortage of good quality of drinking water in Jaisalmer district of Rajasthan especially in rural areas.

In the present study the hydro-geochemistry of groundwater and the effect of climate as well as geological

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formations for enrichment of fluoride in groundwater have been evaluated. The study examines the concentration and spatial distribution of fluoride and its possible origin in relation to the geological features of the study area. The inter-relationship of various major ions has also been studied since it can help to decipher the actual cause of fluoride enrichment in the groundwater.

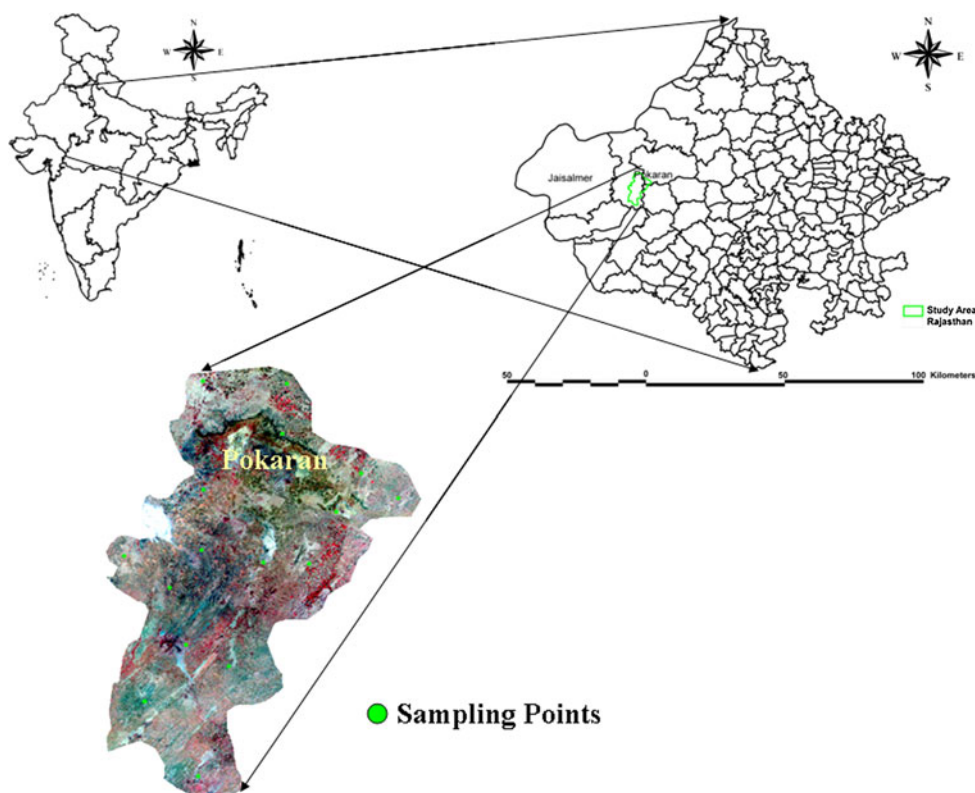
Materials and Methods

The study area is located between 71.76°–72.23°E longitudes and 26.39°–27.04°N latitudes covering an area of approximately 1,781 km² (Fig. 1). The study area is situated amid Thar Desert where monsoon is as good as negligible. Though western disturbance brings around 15 cm of annual rainfall but it remains dry for most parts of the year. Several palaeo-channels are also present throughout the area indicating presence of fluvial system in ancient times in the region. The mean maximum temperature in the region ranges between 40 and 45°C in the summers and the minimum temperature fluctuates between 3 and 10°C in the winters during months of January–February.

The highly folded metamorphosed rocks of the Delhi super group form the main part of the mountains and consist of quartzite, mica schist and gneiss (Singh et al.

1972; Wasson et al. 1984; Sundaram and Pareek 1995). Alwar group and Ajabgarh group consist mostly of calc-silicates, quartzites, grits and schistose rocks. The other important lithological formations consist of a thick series of sedimentary rocks comprising sandstone, limestone and shales. Of special interest are the Bap (Jodhpur district) and Pokhran (Jaisalmer district) beds of Upper Carboniferous age, which have now been exploited for ground water. Two types of porous formations are found from hydrogeological point of view i.e. unconsolidated formations and semi-consolidated formations. The semi consolidated formations belonging to palaeozoic, mesozoic and coenozoic groups are composed of siltstone, claystone, sandstone, shale conglomerate and limestone. Sandstone and limestones form the main aquifers in the district. Sandstones are the most potential aquifers in the Pokhran area of Jaisalmer. Igneous and metamorphic rocks of lower proterozoic age comprising of slate, quartzite, phyllite, schist and gneiss are also found in the area. This igneous suite consisting of basalt and rhyolite is overlain by the sandstone and limestone of the Marwar supergroup. The Palaeozoic Bap boulder bed along with dolomite and minor shale overlie the Marwar rocks (Deotare et al. 1998). Carbonate rocks (limestone, marble and dolomite) are also present. A total of 16 water samples were collected in the month of April 2010 in polypropylene bottles (Tarsons)

Fig. 1 Study area



from shallow hand pumps and tube wells, which are the only available water sources for drinking and other domestic use in the area. The study area lies in periphery of Thar Desert so it was not possible to collect more number of samples due to very limited number of tubewells/borewells. The pH, total dissolved solids (TDS) and electrical conductivity (EC) of the collected water samples were measured in the field using portable pH meter, TDS meter and electrical conductivity meter (Hanna). The samples were acidified using HNO_3 (Ultrapure Merck) for cation analysis. The samples were stored in ice box and were carried to the laboratory and kept at 4°C for further chemical analysis. Groundwater samples were collected from various localities of Pokhran block of the Thar Desert and analyzed for fluoride ion along with other chemical parameters. Other major parameters F^- , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-} were analyzed according to the standard procedures described in standard methods for the examination of water and wastewater (APHA 2005) immediately after the water samples were transported to the laboratory. The water quality parameters were used in Phreeqc to calculate the SI values and the processes responsible for fluoride enrichment in groundwater. Saturation indexes (SI) are used to evaluate the degree of equilibrium between water and respective mineral. Changes in saturation state are useful to distinguish different stages of hydrochemical evolution and help identify which geochemical reactions are important in controlling water chemistry (Coetsiers and Walraevens 2006, Langmuir 1997). The saturation index of a mineral can be obtained using following equation (Garrels and Mackenzie 1967),

$$\text{SI} = \log(\text{IAP}/K_t)$$

where, IAP = ion activity product of the dissociated mineral, K_t = equilibrium solubility at mineral temperature. $\text{SI} < 0$, indicates that the groundwater is under-saturated with respect to that particular mineral. Such a value could reflect

the character of water from a formation with insufficient amount of the mineral for solution or short residence time and $\text{SI} > 0$ specifies that the groundwater is oversaturated with respect to the particular mineral and therefore incapable of dissolving more of the mineral. Such an index value reflects groundwater discharging from an aquifer containing ample amount of the mineral with sufficient resident time to reach equilibrium.

Results and Discussion

The statistical parameter (mean, range standard deviation, minimum, maximum etc.) of various physico-chemical parameters that were analyzed with are given in Table 1. The fluoride concentration in water samples varied between 0.76–4.74 mg/L with mean value of 2.19 mg/L. It was observed that 87.50% of the samples exceeded the maximum desirable limit of BIS (Bureau of Indian Standards) and nearly 62.5% of the samples exceeded the maximum desirable limit of WHO (World Health Organization) standards. Fluorine is the most electronegative element and thus it reacts immediately to form fluoride compounds and therefore making presence of free fluorine an obsolete possibility but under favorable physico-chemical conditions with long residence time it may occur as dissolved form in groundwater (Handa 1975; Salve et al. 2008).

At acidic pH the fluoride is adsorbed on the surface of the clay. A higher value of pH favours the enrichment of fluoride in groundwater. The OH^- in groundwater with high value of pH can replace the exchangeable fluoride of fluoride containing minerals (biotite/muscovite) thus can increase the concentration of fluoride in groundwater.

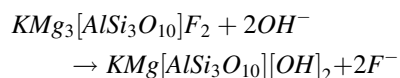
The hydroxyl ions replace fluoride from the Biotite and muscovite as shown below:

Table 1 Statistics of physical and chemical parameters of groundwater samples

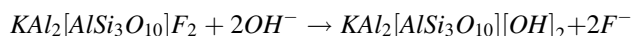
Variable	Mean	St. dev	Minimum	Median	Maximum	Range	Skewness	Kurtosis
pH	8.175	0.2176	7.9	8.15	8.5	0.6	0.19	−1.47
EC	1691.3	374	890	1745	2230	1340	−1.04	1.36
TDS	1534	464	520	1580	2140	1620	−1.18	1.49
HCO_3^-	436.9	101.4	341.3	381.6	622.5	281.3	0.8	−0.96
F^-	2.194	1.384	0.76	1.725	4.74	3.98	0.99	−0.48
Cl^-	434.9	135.3	122	456.1	616.8	494.8	−1.48	2.57
SO_4^{2-}	135.1	52.9	31.3	138.6	210.2	178.9	−0.39	−0.1
Na^+	111.9	53.6	38.5	102	232.7	194.2	1.37	1.88
K^+	11.5	13.97	1.02	7.49	44.83	43.81	1.78	2.34
Ca^{2+}	51.76	23.99	7.21	54.83	82.62	75.41	−0.45	−0.45
Mg^{2+}	35.68	15.29	9.29	37.5	60.04	50.75	−0.13	−0.57

Concentration in mg/L except EC ($\mu\text{S}/\text{cm}$) and pH

Biotite



Muscovite



In granitic or sandstone dominant aquifers dissolution of fluoride can be possible reason for presence of fluoride in groundwater. The hydrolysis of alumino-silicate minerals in the hard rock aquifers produces bicarbonate ion, which can enhance fluorite dissolution as below



Water with high F^- concentration can form in the areas where alkaline (carbonate rocks) waters are in contact with fluoride bearing minerals. Fluoride concentration is generally independent of other water soluble components but a noticeable correlation exists between F^- and pH. The fluoride solubility is lowest in the pH range of 5–6.5 (Adriano 1986). At higher pH ionic exchange occurs between F^- and OH^- ions (illite, mica and amphiboles) resulting in increase of F^- ion concentration in groundwater. The presence of high HCO_3^- , Na^+ and pH favors the release of F^- from aquifer matrix into groundwater. It was observed that the groundwater in the study area was alkaline at all the places as the pH value of groundwater in the study area varied from 7.9 to 8.5 with a mean value of 8.18. The alkaline nature of the groundwater favors the solubility of fluoride bearing minerals. In an alkaline environment the fluoride ions are desorbed thus supplementing the dissolution of fluoride bearing minerals.

A correlation matrix was generated for the water quality parameters that were analyzed to find out the possible relationship among the various ions and their concentration (Table 2). The matrix plot was also plotted to decipher the possible relation between various parameters (Fig. 2). The

correlation matrix generated showed strong correlation of fluoride with pH, EC and TDS and strong negative correlation with Ca. Strong correlation of F and pH ($r = 0.65$) showed that fluoride in groundwater has resulted from leaching of fluoride containing minerals. Fluoride exhibits positive correlation ($r = 0.41$) with bicarbonate ion. It shows a positive correlation with Na^+ but higher negative correlation ($r = -0.70$) with Ca^{2+} , indicating that it has higher affinity for sodium than calcium. Thus, the F^- content shows an increase with Na^+ and decrease with Ca^{2+} due to dominance of ion-exchange process. During ion-exchange process calcium ions in water may react with clay minerals (sodium-montmorillonite) to release sodium ions and thus increasing concentration of Na^+ ions in groundwater (Hounslow 1995). The low concentration of Ca^{2+} reflects its precipitation as carbonate (Gaciri and Davis 1993). Ion exchange between Ca^{2+} and Na^+ due to the movement of groundwater in the weathering zone may also result in high F^- associated with high Na^+ and low Ca^{2+} concentration.

Increase in concentration of HCO_3^- ions, pH and temperature can result in precipitation of calcite (Hounslow 1995). A positive correlation between Cl^- and Na^+ with EC shows that dissolution of ions from rocks is a major controlling factor of EC.

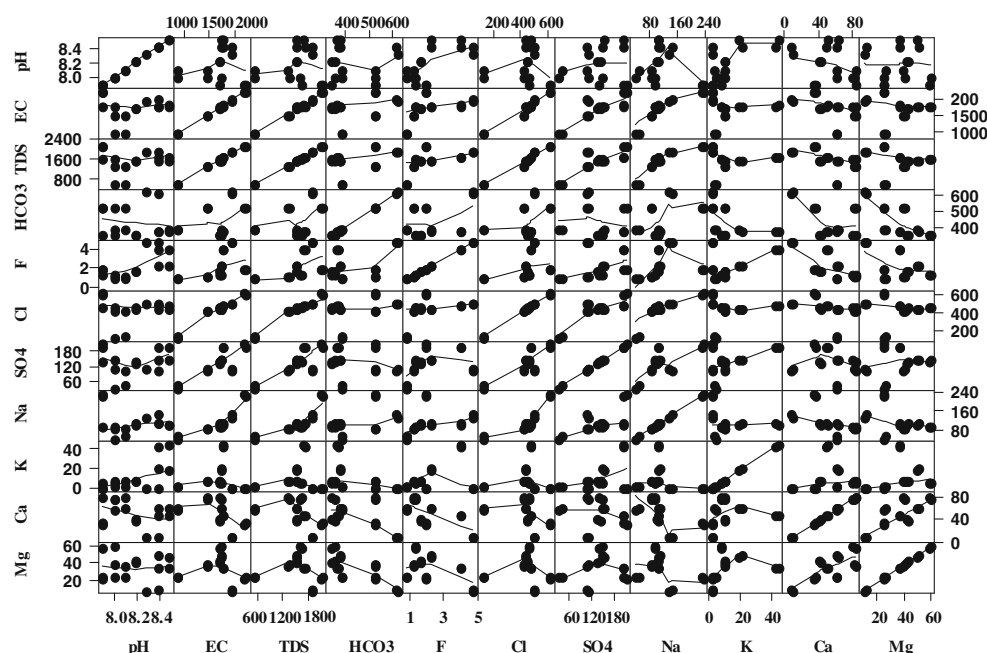
The HCO_3^-/Ca^{2+} ratio at all the places was found to be greater than 1, suggesting favorability of chemical conditions for the fluoride dissolution processes (Saxena and Ahmed 2003). Further it was noticed that the ratio of Na^+/Ca^{2+} at 75% of all sampling locations was greater than 1 indicating low calcium activity. A high concentration of sodium favors dissolution of fluoride bearing minerals at higher pH (Shaji et al. 2007).

The anthropogenic origin of fluoride in the study area can completely be ruled out as the area has neither industries nor much human settlements except very few in northern parts so as to consider the discharge from these as potential sources of fluoride input in groundwater as contaminant.

Table 2 Correlation matrix of physico-chemical parameters of groundwater samples (values in bold indicate significant correlation)

	pH	EC	TDS	HCO_3^-	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
pH	1.000										
EC	0.100	1.000									
TDS	0.105	0.994	1.000								
HCO_3^-	-0.087	0.360	0.392	1.000							
F^-	0.688	0.513	0.558	0.411	1.000						
Cl^-	0.047	0.979	0.983	0.348	0.444	1.000					
SO_4^{2-}	0.141	0.819	0.808	-0.065	0.342	0.842	1.000				
Na^+	-0.179	0.862	0.833	0.500	0.311	0.815	0.680	1.000			
K^+	0.647	0.069	0.092	-0.441	0.403	0.109	0.495	-0.188	1.000		
Ca^{2+}	-0.325	-0.493	-0.489	-0.515	-0.714	-0.373	-0.176	-0.564	0.129	1.000	
Mg^{2+}	-0.066	-0.068	-0.083	-0.738	-0.478	0.016	0.213	-0.349	0.289	0.762	1.000

Fig. 2 Matrix Plot of all physico-chemical parameters analyzed



Thus high concentration of fluoride is geogenic in origin, i.e. local hydro-geological conditions in the area are responsible for its higher concentration in groundwater. The granite of the study area contains abundant F^- bearing minerals and during weathering, F^- has leached out and got dissolved in groundwater. The F-content of groundwater varies greatly depending on the geological settings, type of rocks and climate. Another major possibility of fluoride enrichment can be attributed to evaporation. Since the study area lies in arid to semiarid environment and the temperature in summers is very high and rainfall is very less so due to evaporation the groundwater becomes oversaturated with calcite thus precipitating calcite which in turn reduces calcium content and thus promotes dissolution of fluorite. Fluoride ion is positively correlated with calcium ions before the water is saturated with fluorite. After oversaturation the concentration of Ca^{2+} ions overrides the solubility limit of fluorite as fluorite dissolution is suppressed by common ion effect and the correlation between the two ions (Ca^{2+} and F^-) becomes negative (Handa 1975). Datta et al. (1996) also reported evaporation as a major process enriching fluoride content in groundwater in Rajasthan. The fluoride concentration in groundwater is mainly governed by two processes (i) oversaturation of calcite due to evaporation and (ii) calcium ion exchange process. The high rate of evaporation in arid to semi-arid climatic condition of the study area might have enhanced the calcite precipitation in an alkaline environment of groundwater and thus creating deficiency of calcium ions and creating an amicable environment for fluorite dissolution.

The sediment samples were analyzed on XRD (PANalytical) and the information about the minerals present

were obtained using X'pert HighScore Plus software. The sediment sample showed the presence of fluorite, calcite and bornite along with major mineral quartz (Fig. 3).

Oversaturation can also be produced by other factors that include incongruent dissolution, common ion effect, and evaporation. Figure 4 shows the SI variation for Anhydrite, Aragonite, Calcite, Dolomite, Fluorite and Gypsum. All the samples are oversaturated with respect to Aragonite, Calcite, Dolomite whereas all the samples are undersaturated with respect to Fluorite and Gypsum and Anhydrite presumably these carbonate mineral phases might have influenced the enrichment of fluoride in the study area. Hydrogeochemical modeling using Phreeqc suggests that sodium has source other than halite-albite, calcium has source other than gypsum-carbonate or silicates and ion exchange, gypsum dissolution are prominent processes occurring in the study area. It can be observed

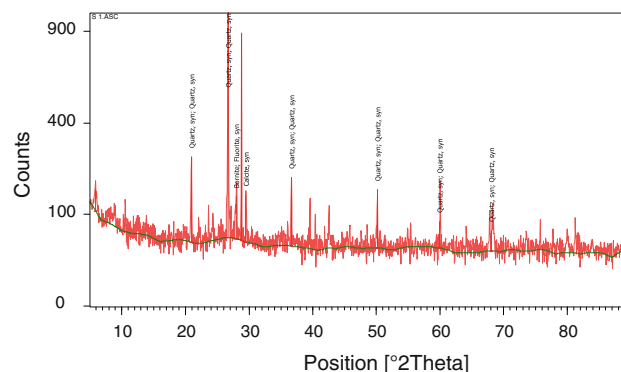


Fig. 3 Diffractogram showing presence of fluorite, calcite and bornite

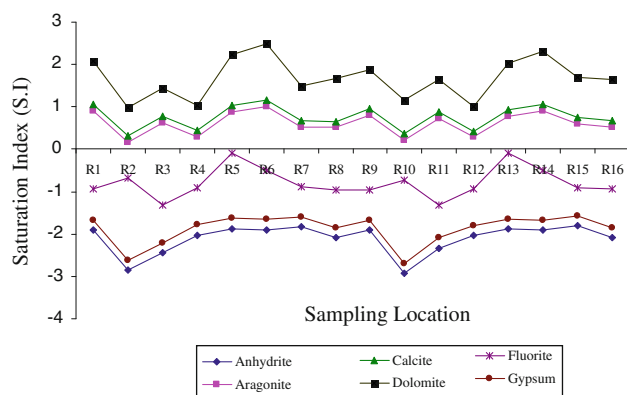


Fig. 4 Saturation index (SI) for Anhydrite, Aragonite, Calcite, Dolomite, Fluorite and Gypsum

from the spatial distribution map of fluoride the concentration of the fluoride is high in northern and north-eastern part of the study area (Fig. 5). The concentration is also high in central part whereas moderate to high concentration is observed in the southern part of the area. The presence of fluorite in sandstone as cement may have imparted the fluoride in groundwater. The increase in concentration of sodium ions increases the solubility of fluoride containing mineral, thus the processes responsible for increase in sodium concentration with decrease in calcium ion concentration have contributed the fluoride in groundwater.

The study of groundwater quality with emphasis on fluoride concentration in Pokhran indicated that the groundwater is alkaline in nature at all the places. It was also found that high concentration of fluoride was substantiated by high concentration of sodium and low concentration of calcium ions in groundwater. The groundwater in the area is brackish and highly contaminated by fluoride. The granitic rocks contain abundant fluoride bearing minerals, which upon weathering are leached out and dissolve in groundwater. It was found that mainly northern and west central part of the study area showed higher concentration

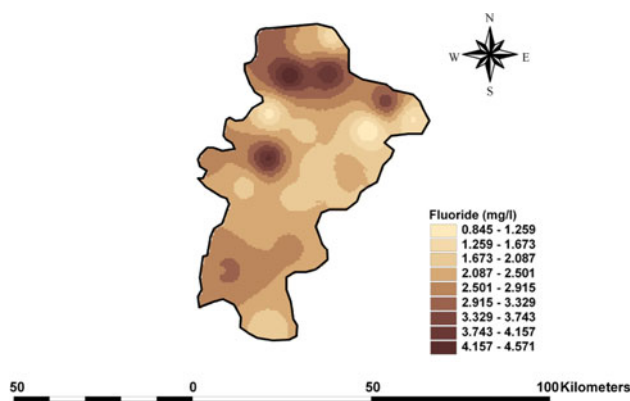


Fig. 5 Spatial Distribution of Fluoride in the study area

of fluoride (above permissible limit of WHO and BIS). Geochemical processes such as ion-exchange, dissolution and weathering are responsible for fluoride contribution in groundwater. Thus low rainfall coupled with high evaporation rate along with highly variable diurnal temperature, which favors water ingestion, and alkaline environment and long residence time favors dissolution of fluoride in groundwater.

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