

# Geochemical control on spatial variability of fluoride concentrations in groundwater from rural areas of Gujrat in Punjab, Pakistan

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Received: 9 February 2016 / Accepted: 3 October 2016 / Published online: 18 October 2016  
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**Abstract** Spatial variability and geochemical factors controlling fluoride ( $F^-$ ) concentrations were evaluated in five villages of subdistrict Gujrat in Pakistan. Groundwater samples ( $n = 70$ ) were collected along the River Chenab and examined for  $F^-$  concentrations. The average  $F^-$  concentrations in groundwater of village Chhani Nikoani (1.8 mg/L) and Dhool Khurd (2.2 mg/L) were crossing the World Health Organization (WHO) permissible limit of 1.5 mg/L, while village Kalra Khasa, Ghazi Chak and Kula Chor were below the WHO guidelines. About 64 % of the samples contain fluoride concentrations that exceed the 1.5 mg/L drinking water standard set by WHO. Spatially  $F^-$  concentrations in groundwater increased as moving away from the River Chenab because more residence time for water–rock interaction was available. High  $F^-$  concentrations were associated with high electric conductivity (EC), total dissolved solids (TDS), pH and  $Na^+$  values. The overall groundwater quality is controlled by silicate mineral weathering and less by evaporation. Fluoride originates from anion exchange ( $OH^-$  for  $F^-$ ) on clays and

weathered micas under high pH conditions. High fluoride levels are associated with  $NaCl$ - and  $NaHCO_3$ -type water produced by calcite precipitation and/or base ion exchange. The groundwater with higher fluoride concentrations is accompanied by lower  $Ca^{+2}$  levels. This study enhances our understanding on geochemical behavior of F and highlights the importance of spatial variability on F release in aquifers of Punjab in Pakistan, as well as in other countries of Asia region.

**Keywords** Groundwater · Soil · Fluoride · Clay · Spatial variability · Gujrat · Pakistan

## Introduction

Fluoride ( $F^-$ ) is an important nourishing constituent for health which is present in groundwater as free fluoride ions. It begins to affect human health as its concentration exceeds World Health Organization (WHO) guideline for  $F^-$  in drinking water (Saxena and Ahmed 2003). When  $F^-$  exceeds value of 1.5 mg/L WHO guideline for  $F^-$  in drinking water, it results in dental and skeletal fluorosis, crippled limbs, rheumatic pain, the calcification of ligaments stiffness, and the rigidity of the joints (Ayoob and Gupta 2006). It can adversely affect the kidneys, liver, gastrointestinal tract as well as the nervous, immune, and reproductive systems disorders (Ibrahim 2011).

The problem of fluorosis develops extensively in many areas of the world, such as in Argentina, Bangladesh, China (Guo et al. 2007), India (Jacks et al. 2005), Japan, Morocco, New Zealand, South African Countries, Thailand and Middle East countries, and USA (Rafique et al. 2009). In Pakistan, the high  $F^-$  concentrations in groundwater have been reported from Karachi (Siddique et al. 2006), Lahore

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(Farooqi et al. 2007), Peshawar (Shah and Danishwar 2003), and Thar Desert (Rafique et al. 2008).

Fluoride has affinities for rocks and occurs in  $F^-$ -bearing minerals that lead to transportation of substantial amount of  $F^-$  into the groundwater (Lunshan et al. 2007). Hence, groundwater with high  $F^-$  concentrations is probable in areas where  $F^-$ -bearing minerals are abundant (Shaji et al. 2007). Common natural sources of  $F^-$  in groundwater are the dissolution of  $F^-$ -bearing minerals like fluorspar and fluorapatite and some micas weathered from silicates (Guo et al. 2007). The dissolution of  $F^-$ -bearing minerals not only produces kaolinite but also discharges cations, such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$ , causing an increase in TDS which indirectly affect  $F^-$  concentration in groundwater (Li et al. 2015). Fluoride-bearing minerals occur in deep soils, when soluble  $F^-$  concentration is higher in deep soil than in surface soils, and it follows the geological source of  $F^-$  contamination (Jayawardana et al. 2012).

Higher concentrations of  $F^-$  usually occur due to water–rock interaction of fluorite, fluorapatite, and cryolite or any  $F^-$ -bearing mineral which results in  $Ca^{2+}$  depletion of groundwater due to common ion effect (Chae et al. 2007). The levels of dissolved  $F^-$  are generally linked with the pH value and water type, although the depth and temperature of groundwater and climatic factors like evaporation/precipitation also play significant roles (Rafique et al. 2015). Ion exchange in which  $OH^-$  replaces  $F^-$  in groundwater on certain clay minerals or weathered micas (Rafique et al. 2009). Higher  $F^-$  concentrations are associated with both  $NaCl$ - and  $NaHCO_3$ -type waters, and lower  $F^-$  concentrations are linked with  $CaHCO_3$ - and  $CaMgCl$ -type waters, where greater  $Ca^{2+}$  levels lead to precipitation of fluorite (Rafique et al. 2015). The clay proportion of soil has positive relation with  $F^-$  concentrations in soil than silt and negative relation with sand (Farooqi et al. 2009).

The groundwater flow rate is higher in areas nearby river, residence time is lower, and there is a less time of contact between water and  $F^-$ -bearing rocks. This led to lower concentrations of  $F^-$  in the groundwater. However, in the central basin areas, groundwater had moved a longer distance and thus had a higher residence time (Li et al. 2015). This indicates that groundwater is more enriched in  $F^-$  along the flow path away from river. As a result,  $F^-$  concentrations got increased (Basharat 2012).

Gujrat has been famous for the production of low-temperature pottery and ceramic goods. Gujrat is also known in the world for its clay which is used to produce quality pottery since ages. The clay content of soil of Gujrat varied along with increasing distance from River Chenab as subdistrict Gujrat is located near River Chenab. Sandy loams are more abundant near river that has negative relation with  $F^-$  concentrations (Farooqi et al. 2009), while

moving away from river, silty loams and clayey soil are evident that has capacity to hold higher  $F^-$  concentrations (Ashraf and Ahmad 2008).

Groundwater in semiarid areas surrounding Gujrat is known to have  $F^-$  concentrations that go above the guideline for drinking water 1.5 mg/L set by WHO (Rafique et al. 2008). The percentile  $F^-$  contribution in lowering the water quality of areas around Gujrat, i.e., Sargodha (7 %), Faisalabad (16 %), Lahore (18 %) and Kasur (18 %) is comparatively high than Gujrat (2 %) which indicate certain geological factors that are controlling  $F^-$  enrichment in groundwater of Punjab (Pakistan Council of Research in Water Resources 2010).

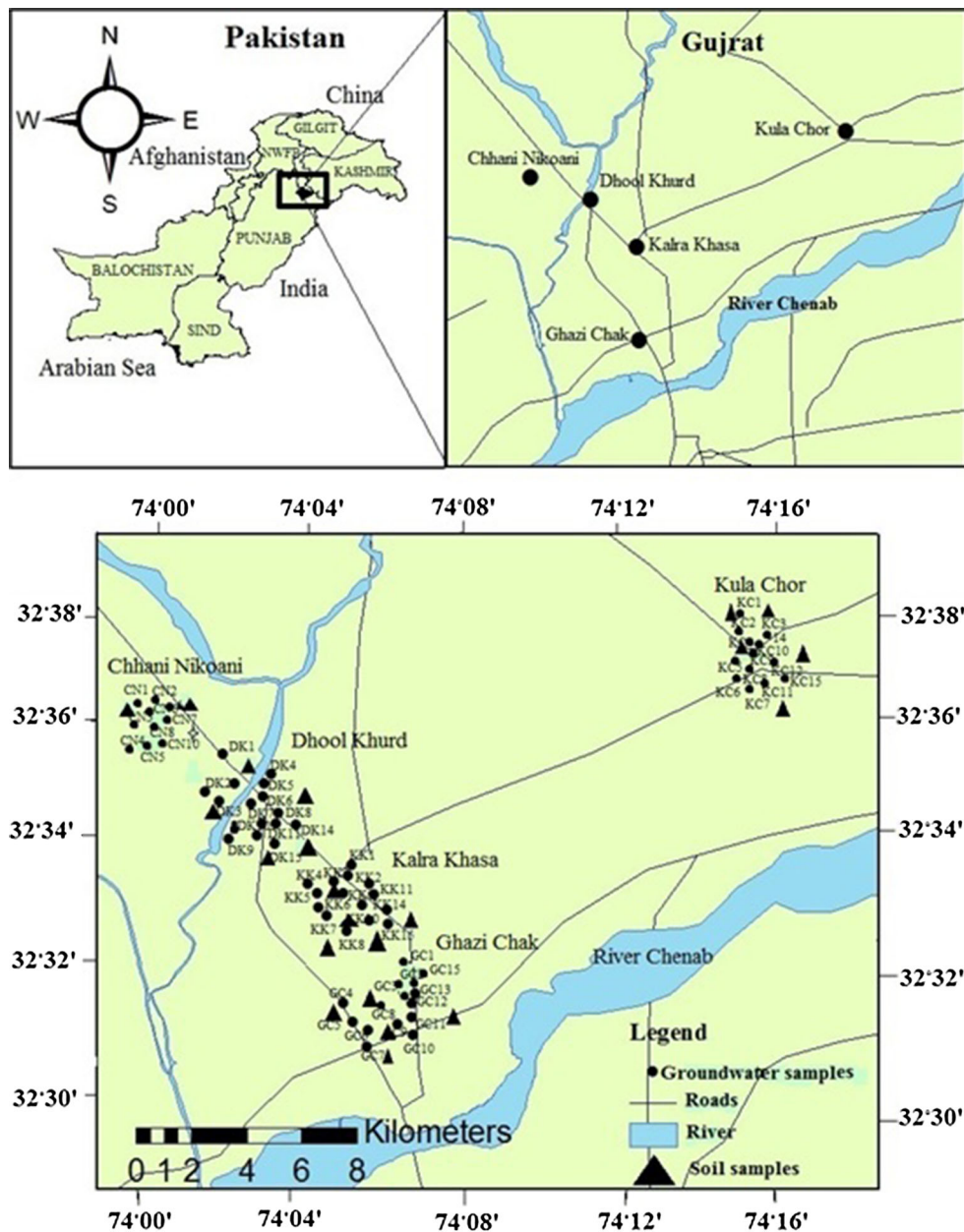
The present study evaluates groundwater quality in a region where screening by Pakistan Council of Research in Water Resources (PCRWR) reported fluoride in groundwater, and the area is known for its high class of clay minerals and was undertaken to define the sources of dissolved fluoride and the geochemical processes that influence its occurrence. The aim is to identify geochemical relationships that influence in understanding the origin of high fluoride established on measures of the overall water quality. This study was the first attempt to analyze  $F^-$  and to predict its geochemistry controlling the  $F^-$  concentrations.

## Materials and methods

### Study area

#### *Location and hydrometeorology*

District Gujrat (Fig. 1) including an area of approximately 1254 km<sup>2</sup> was selected as the study area for this study. It is located in the semiarid zone of Punjab, Pakistan between 32.5738N and 74.0789E. For political and administrative purposes, the whole district is divided into three subdistricts (Kharian, Sarai Alamgir, and Gujrat); subdistrict Gujrat was selected for study. Climate of the study area is tropical with an average annual rainfall of 670 mm, 70 % of which occurs between June and September. The wet season starts from end June and lasts up to the start of November, whereas the rest of the months are generally dry. The temperature rises to maximum of 48.2 °C in summer and drops to a minimum of 2 °C during winter (Gujrat city profile). The main rivers of the study area are River Jhelum and River Chenab. The study area falls within the area of upper Chaj Doab and sandwiched between these two rivers but more influenced by River Chenab, having a distance of 12 km. Gujrat is populated with 270,000 people and majorly drained by River Chenab (Ashraf and Ahmad 2008).



**Fig. 1** Map of study area with location of groundwater and soil sampling points, circles represent groundwater sampling points, and triangles represents soil sampling points

*Geological and hydrogeological setting*

The soil loams of the Gujrat are composed of silty and sandy alluvial substantial (Ashraf and Ahmad 2008). Punjab Province is drained by five major rivers that flow down from high range mountains of Himalaya. The sediments carried along with these rivers water from the massive alluvial basin of the aquifer that contains material washed down from the Himalaya Mountains were set down. Study area contains more than 500-m-thick Quaternary deposition (Ashraf and Ahmad 2008). The alluvium

material consists of sand and silt and minute amounts of gravel and clay, set down by the Indus River by its present and ancestral offshoots. In harmony with their mode of deposition by large continually flowing rivers, the alluvial depositions are heterogeneous by nature, and individual layers have restricted horizontal and vertical continuity (Greenman et al. 1967).

In general, unconfined aquifers and some confined aquifers are present in the study area (Basharat 2012). Groundwater table is declining with increasing population and over abstraction (81 % annual abstraction) of

groundwater than recharge (Mahmood et al. 2011). Aesthetically acceptable water starts below the depth of 50 feet (Ashraf and Ahmad 2008). The direction of groundwater flow is from recharge zone, foothills of Himalaya toward discharge plain area of Gujrat. Flow direction of groundwater in the study area also got affected by River Chenab's fluctuating flow during rainy and dry season (Mahmood et al. 2011).

### Sampling

Groundwater samples were collected from five villages of subdistrict Gujrat during October 2014. To cover entire subdistrict Gujrat, five random villages were selected (Fig. 1). From these villages, in total 70 groundwater samples were collected. In Dhool Khurd (DK), Kalra Khasa (KK), Ghazi Chak (GC), and Kula Chor (KC), 15 groundwater samples were collected from each village at the depth of 14–105, 7–105, 8–122, and 11–75 m, respectively. From village Chhani Nikoani (CN), 10 groundwater samples were collected at the depth of 20–90 m because the area is sparsely populated compared to other villages. From each village Dhool Khurd (DK), Kalra Khasa (KK), Ghazi Chak (GC), and Kula Chor (KC), total 10 soil samples (each composite of 3) were collected in polyethylene zipper bags (five from surface and five from subsurface), while from village Chhani Nikoani (CN), four soil samples were collected (two from surface and two from subsurface). Soil sampler (hand Augur) was used for surface (0–5 cm) and subsurface (35–40 cm) soil samples collection.

Groundwater samples were collected in 300-mL polyethylene bottles that had been pre-washed with dilute (1 %) nitric acid according to standard methods (Greenberg et al. 1998). Prior to sample collection the pump was flushed for 5 min. The bottles were first rinsed with groundwater and then completely filled and sealed with caps to avoid the oxidation of redox-sensitive constituents. At each sampling point, two samples were collected. One was preserved by acidifying to the pH value of <2 with ultra-pure HNO<sub>3</sub> for the later analysis of cations, while the other was stored without acid for the later analysis of anions in the environmental geochemistry laboratory. The exact sampling coordinates were identified using a GPS unit.

### Analytical techniques

Temperature and pH were measured by digital pH meter, oxidation reduction potential (Eh) by Eh meter, conductivity, and total dissolved solids (TDS) were measured in the field using digital meter. In laboratory, water samples were analyzed for alkalinity as HCO<sub>3</sub><sup>-</sup> by acid–base titration, sulfates by titration with barium chloride method,

chlorides by silver nitrate titrimetric method, nitrates by phenol disulphonic method, and phosphates by ammonium molybdate method (APHA 1995). Similarly, acidified samples were analyzed for major cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) using Sequential Flame Atomic Absorption Spectrophotometer (Varian Spectra AA-240) under standard operating conditions having  $r > 0.99$ .

Fluoride was analyzed by using fluoride ion-selective electrode Orion 9609 with ion analyzer EA 940 by diluting water sample with total ionic strength adjustment buffer (TISAB) in ratio 1:1 to avoid dissociation of fluoride complexes with other metals present in samples that can hinder the F analysis (Greenberg et al. 1998). High levels of precision and accuracy were maintained during all phases of laboratory analysis, which included blank and spiked samples to ensure the reliability of each method. The ionic balance error (IBE) values were within an acceptable limit of ±5 % (Domenico 1990; Mandel 1981) for all samples.

Soil samples were grounded followed by sieving through 200-mm mesh. The pH value of soil samples was determined with pH meter in ratio of 1:5 soil to water, while the soluble fluoride concentrations were determined in same ratio with ion-selective meter same as that of water. Minerals were identified by X-ray diffraction spectroscopy (XRD).

All scientific and statistical computations were made by using IBM SPSS statistics version 20, XLSTAT Pro v7 5.2, PHREEQC, and Arc GIS 10 software. Multivariate statistical methods were used for interpretation and classification of large environmental datasets. The normality of data under variables was checked by Kolmogorov–Smirnov test. Principal component analysis (PCA) was employed on the dataset to reduce the analytical data collected from each village. For mineral speciation, saturation indices were used to analyze the degree of equilibrium between mineral species and water.

Reagents, procedural blanks, and samples were measured three times, and the average of three values was used. For QC/QA, Standard Reference Materials (JSL-1 & JSD-1) was used and the recovery was found 98 % using the same procedure and reagents. Arsenic was measured by using the atomic absorption graphite technique at Geo-science Advanced Research Laboratories.

## Results and discussion

### Overall groundwater quality

Table 1 shows the chemical parameters measured in the groundwater samples collected at the CN, DK, KK, GC and KC. The pH of the samples varied from 7.8 to 8.7, 7.1 to

**Table 1** Basic statistical parameters in groundwater of subdistrict Gujrat

Parameters	WHO guideline	Descriptive statistics	Chhani Nikoani (CN)	Dhool Khurd (DK)	Kalra Khasa (KK)	Ghazi Chak (GC)	Kula Chor (KC)
Depth (m)	–	Range	20–90	14–105	7–105	8–122	11–75
		Mean	55	45	49	59	22
		SD	97.87	112.8	109.1	118.6	57.1
Temperature (°C)	–	Range	21.6–22.3	22.1–22.6	21.4–27	21–21.9	21.9–22.7
		Mean	21.9	22.3	22	21.3	22.3
		SD	0.19	0.15	1.39	0.22	0.23
pH	6.5–9	Range	7.8–8.7	7.1–8.9	7.2–8.5	7–8	7.1–8.6
		Mean	8.2	8	7.8	7.4	7.8
		SD	0.30	0.62	0.48	0.36	0.44
EC (mS/cm)	0.250	Range	0.51–2.28	0.16–1.72	0.19–1.72	0.13–1.86	0.2–3.34
		Mean	0.97	1.01	0.71	0.72	1.23
		SD	0.48	0.37	0.62	0.73	0.94
TDS	1000	Range	342–1528	107–1152	127–1152	87–1246	134–2238
		Mean	651.91	680	481.9	485	827.6
		SD	323	254.2	419.2	494.1	633.1
HCO <sub>3</sub> <sup>-</sup>	500	Range	450–550	200–950	300–700	250–600	250–900
		Mean	500	493	433.4	423.3	581.6
		SD	33.4	194.4	130.4	133.4	174.3
Cl <sup>-</sup>	250	Range	213–958	35.5–603	46.2–674	35.5–355	17.8–603
		Mean	450	220.1	291.1	179.8	353.5
		SD	216.2	160	168.3	96	181.2
F <sup>-</sup>	1.5	Range	0.6–4	0.3–6.4	0.4–2.6	0.6–1.9	0.5–3.3
		Mean	1.8	2.2	1.3	0.9	1.45
		SD	1.03	1.71	0.78	0.36	0.84
SO <sub>4</sub> <sup>2-</sup>	500	Range	34.4–111	34.9–108	33.3–127	34.8–133	43.7–132
		Mean	60.15	56.76	84.51	71.08	86.74
		SD	23.56	18.46	33.26	30.81	29.92
PO <sub>4</sub> <sup>3-</sup>	0.01	Range	7.7–10.6	6.8–10.3	4.3–11.8	6.2–9.82	0.59–9.93
		Mean	9.02	8.28	8.28	8.02	7.09
		SD	1.18	1	1.95	1.10	2.80
NO <sub>3</sub> <sup>-</sup>	50	Range	bdl-31.5	21–22.8	21.7–25	22.7–24	21.6–61.7
		Mean	21.7	21.88	22.71	23.23	36.28
		SD	8.14	0.31	1.13	0.50	15.47
Na <sup>+</sup>	200	Range	199–529	135–217	150–243	73.9–301	218–327
		Mean	398	173	195	156	291
		SD	113.2	23.9	26.4	78.9	32.8
K <sup>+</sup>	12	Range	0.66–2.62	0.60–4.40	1.11–52.9	0.04–12.3	0.9–9.9
		Mean	1.38	2.12	7.53	3.57	4.79
		SD	0.85	1.38	13.3	3	3.3
Ca <sup>2+</sup>	100–150	Range	12.6–101	13.3–160	26.6–256	1.12–128	23.3–168
		Mean	46.26	54.50	56.9	56.7	66.6
		SD	53.57	65.68	63.7	45.01	44.24
Mg <sup>2+</sup>	50–75	Range	9.69–53.6	9.14–79	12.2–98.4	0.38–56.3	16.3–86.1
		Mean	25.76	29.53	22.89	30.39	49.1
		SD	17.3	27.31	23.63	14.84	22.45
Ion balance error	>±3 %	Mean	-0.651	-1.544	-0.010	-2.242	-0.646

All concentrations are in mg/L except where mentioned, number of samples collected (N) = 15 except for CN = 10

SD standard deviation

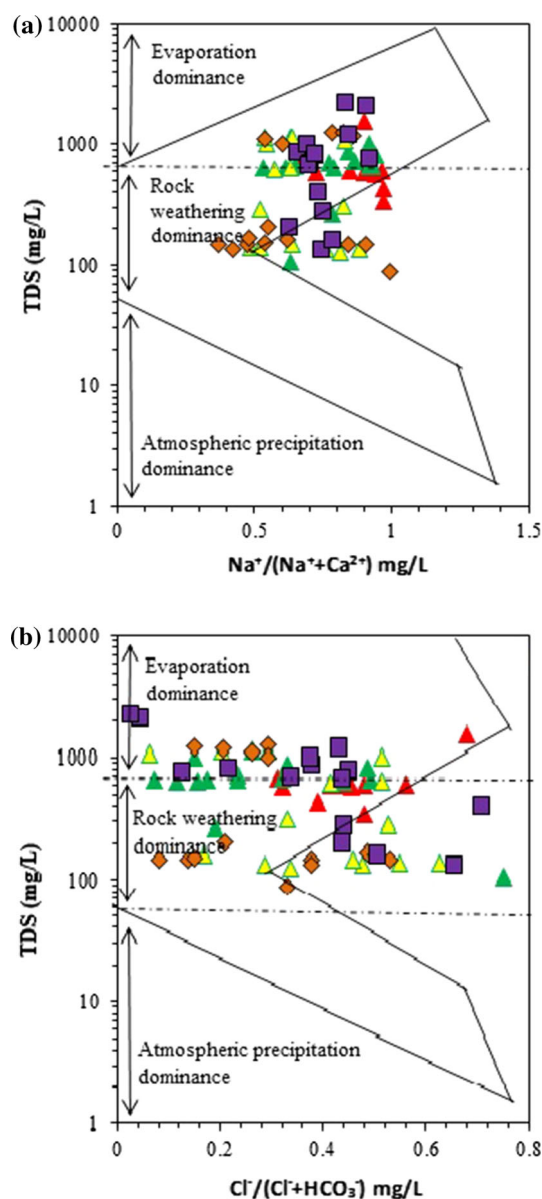
8.9, 7.2 to 8.5, 7.0 to 8.0, and 7.1 to 8.6 at CN, DK, KK, GC, and KC, respectively. Since pH usually has no direct impact on consumers, no health-based guideline value has been proposed for pH by WHO (WHO 2011). The TDS of the samples varied from 342 to 1528, 107 to 1152, 127 to 1152, 87 to 1246, and 134 to 2238 at CN, DK, KK, GC, and KC, respectively. The palatability of water with a total TDS level of less than about 600 mg/L is generally considered to be good; drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L (WHO 2011).

In almost all of the groundwater samples, the EC and TDS measurements were higher than the WHO guidelines. The EC measurements ranged from 0.13 to 3.34 mS/cm, and the TDS measurements ranged from 87 to 2238 mg/L. Soluble electrolytes and high salinity are generally the main cause of elevated EC and TDS in groundwater (Brahman et al. 2013). It is clear that much of the groundwater in this region is unacceptable for drinking in terms of high EC and TDS.

Sodium was the major cation, with concentration ranging from 73.9 to 529 mg/L. The average concentration of  $\text{Na}^+$  in groundwater samples from Chhani Nikoani (398 mg/L) and Kula Chor (291 mg/L) was higher than WHO guideline (200 mg/L), while the average concentration of  $\text{Na}^+$  in samples of other villages was within the WHO guideline. The  $\text{Na}^+$  naturally occurs in water; sometimes, mineral deposits enhance its concentration in groundwater to unacceptable levels (Rafique et al. 2015). Potassium concentration varied from 0.04 to 52.9 mg/L with 95 % of the samples were below the WHO guideline for  $\text{K}^+$  in drinking water (12 mg/L) and 5 % of samples contained  $\text{K}^+$  higher than the WHO guideline. The  $\text{Ca}^{2+}$  concentration ranged from 1.12 to 256 mg/L in groundwater of present study area. Most of the samples (90 %) had  $\text{Ca}^{2+}$  concentrations under the WHO guideline (100–150 mg/L), while few (10 %) had  $\text{Ca}^{2+}$  values above the WHO guideline. Magnesium concentration ranged from 0.38 to 98.4 mg/L. Around 8 % of the samples had  $\text{Mg}^{2+}$  concentration above WHO guideline, while 90 % had  $\text{Mg}^{2+}$  concentration below WHO guideline.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are relatively lower in the groundwater of the study area. Chloride ( $\text{Cl}^-$ ) and  $\text{HCO}_3^-$  were the dominant anions in groundwater samples.  $\text{Cl}^-$  ranged from 200 to 950 mg/L and  $\text{HCO}_3^-$  ranged from 17.8–958 mg/L. Fifty percent of the groundwater samples contained  $\text{Cl}^-$  above the WHO guideline. The  $\text{HCO}_3^-$  concentrations were more than WHO guideline (500 mg/L) in 33 % of samples. Higher values of  $\text{Cl}^-$  might be due to the presence of geologic deposits containing halite in the groundwater of study area (Srinivasamoorthy et al. 2008). And high concentrations of  $\text{HCO}_3^-$  in few samples are linked to pH and weathering of

carbonaceous minerals (Kumar 2014). Sulfate ( $\text{SO}_4^{2-}$ ) concentration ranged from 33.3 to 133 mg/L.

Data were plotted on diagrams developed by Gibbs (1970) for the purpose of understanding the dominant control(s) on water quality (Fig. 2a, b; Table 1). These plots suggest 60 % contribution of rock weathering and 40 % evaporation in controlling groundwater chemistry for an area which is semiarid. It signifies the water–rock interaction phenomena which got affected by residence time. The dominance of NaCl-type groundwater is the resultant of evaporation, which assists to increase the ionic



**Fig. 2** Gibbs plot which illustrate the dominant processes that control the chemistry of groundwater samples, **a** for cations, **b** for anions. Symbols are as described in Fig. 3

strength of the groundwater. Primarily, it also increases the minerals solubility in groundwater, including those that release fluoride into groundwater. However, as the dissolved species concentrations continue to increase, the groundwater becomes supersaturated with respect to minerals that are less soluble, which ultimately precipitate out from groundwater (Rafique et al. 2015).

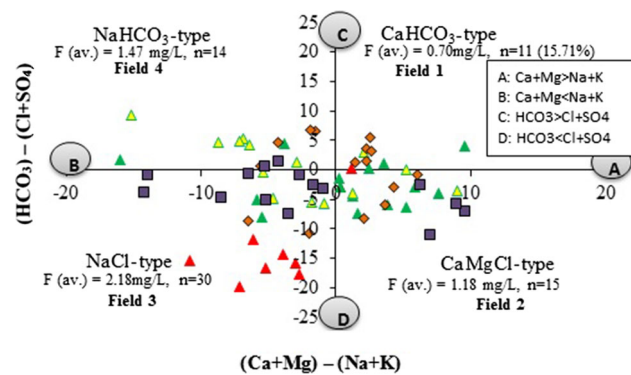
Chadha (1999) proposed a hydrogeochemical classification scheme for water by plotting the difference between  $(CO_3 + HCO_3)$  and  $(Cl + SO_4)$  concentrations in meq/L expressed as percent versus  $(Ca + Mg)$  and  $(Na + K)$  concentrations in meq/L also expressed as percent (Chadha 1999). This classification is a modified version of the Piper diagram (Piper 1944). The resulting diagram has four fields, representing four types of hydrogeochemical processes (Fig. 3). Nearly, 43 % ( $N = 30$ ) of the samples collected from the study area belong to NaCl-type water affected by evaporation. Rest 21 % ( $N = 15$ ) belong to CaMgCl-type waters, 14 % ( $N = 20$ ) with are  $NaHCO_3$ -type water, and 16 % ( $N = 11$ ) classified as  $CaHCO_3$ -type waters (Fig. 3). Water quality produced by either base ion exchange ( $NaHCO_3$ ) or reverse ion exchange ( $CaMgCl$ ) type waters would only occur where the aquifer includes the proper clay minerals. Carbonate minerals are prevalent within the study area (Naseem et al. 2010). Moreover, high Na/Ca ratio for Field 4 samples means that Na increased and calcium decreased through base ion exchange or calcite precipitation. The relatively low  $Ca/(Ca + SO_4)$  ratios and high sodium for Field 3 and Field 4 samples support the conclusion that ion exchange is influencing groundwater chemistry at the locations where these samples were collected (Edmunds and Smedley 2005; Chae et al. 2006; Guo et al. 2007). The  $NaHCO_3$ -type water that is undersaturated with respect to calcite which is due to the

exchange of calcium and magnesium ions in solution for sodium on clays or other secondary minerals.

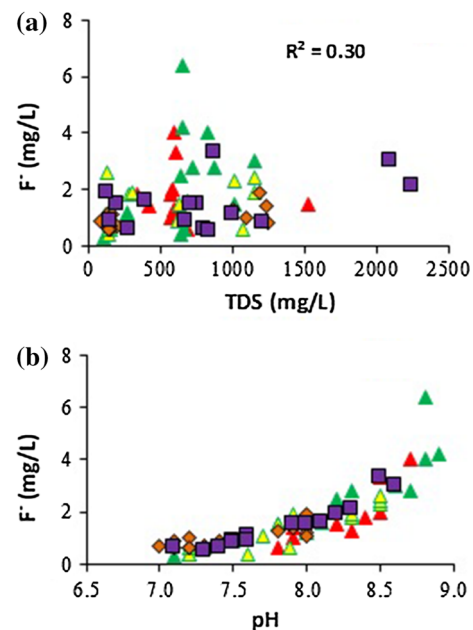
### Spatial distribution of fluoride and role of geochemical control

The  $F^-$  concentrations from study area Gujrat varied from 0.3 to 6.4 mg/L. The mean  $F^-$  concentration in groundwater samples from village Chhani Nikoani (1.8 mg/L) and Dhool Khurd (2.2 mg/L) was exceeding WHO drinking water standard of 1.5 mg/L. According to classification used by (Nagendra Rao 2003), about 48 % of groundwater samples from village Chhani Nikoani and Dhool Khurd had  $F^-$  concentrations below WHO standard, while 32 % of samples were within range of 1.6–3.0 mg/L which can cause dental fluorosis, and remaining 20 % of samples had  $F^-$  concentrations of 3.1–7.0 mg/L which can cause skeletal fluorosis in humans (Nagendra Rao 2003). The mean  $F^-$  concentration in groundwater samples from village Kalra Khasa (1.3 mg/L), Ghazi Chak (0.9 mg/L), and Kula Chor (1.45 mg/L) was mostly below WHO standard. Overall, about 73 % of samples had  $F^-$  concentrations below WHO standards, while remaining 22 % of samples from these villages were within range of 1.6–3.0 mg/L which can cause dental fluorosis, and remaining 5 % of samples were within the range of 3.1–7.0 mg/L, which lead to skeletal fluorosis (Nagendra Rao 2003).

A slight positive correlation ( $R^2 = 0.30$ ) between  $F^-$  concentration and TDS was observed (Fig. 4a). In the study



**Fig. 3** Chadha diagram showing groundwater samples classification taken from the study area (after Chadha 1999). Field 1:  $CaHCO_3$ -type waters, reflecting recharge and weathering. Field 2:  $CaMgCl$ -type waters, reflecting reverse ion exchange. Field 3: NaCl-type waters, reflecting evaporation or mixing with seawater. Field 4:  $NaHCO_3$ -type waters, reflecting base ion exchange (Symbols same as used in Fig. 2)



**Fig. 4** Relationship of  $F^-$  with a TDS, b with  $pH^+$  in groundwater of study area Gujrat. Symbol for different villages is as described in Fig. 2

area, high TDS values were observed in few samples from village Chhani Nikoani, Dhool Khurd, and Kula Chor with comparatively high  $F^-$  concentrations, while village Kalra Khasa and Ghazi Chak had low TDS values with comparatively lower concentrations of  $F^-$  to other villages. Similar results of correlation between  $F^-$  and TDS were reported from Nagar Parkar (Rafique et al. 2009).

Figure 3 shows that higher  $F^-$  concentrations are associated with both NaCl (Field 3) and  $NaHCO_3$  (Field 4), and the samples plotted in Fields 3 and 4 of Fig. 3 are relatively depleted in calcium and show evidence of base ion exchange (as described in “Overall groundwater quality” section), and lower  $F^-$  concentrations are linked with  $CaHCO_3$ - and  $CaMgCl$ -type waters, where greater  $Ca^{2+}$  levels lead to precipitation of fluorite (Rafique et al. 2015).

The  $NaHCO_3$ -type water is result of the removal of  $Ca^{2+}$  and  $Mg^{2+}$  from groundwater by  $Na^+$  ion exchange with  $F^-$  on clay minerals. This shows cation exchange reaction is important in controlling  $F^-$  chemistry in groundwater (Chae et al. 2007; Rafique et al. 2015) where  $Ca^{2+}$  has been replaced with  $Na^+$  in waters containing high  $F^-$ . The dominance of NaCl-type groundwater (Fig. 3) is due to evaporation, which may increase the ionic strength of the water. The concentration of dissolved mineral got increased because of evaporation, and groundwater becomes saturated with respect to the least soluble minerals, which ultimately precipitate out from groundwater. Hence NaCl water type can affect  $F^-$  concentration in groundwater due to minerals precipitation (Rafique et al. 2015). In the current study, NaCl type of water contains the highest concentration of  $F^-$  as indicated before in Fig. 3.

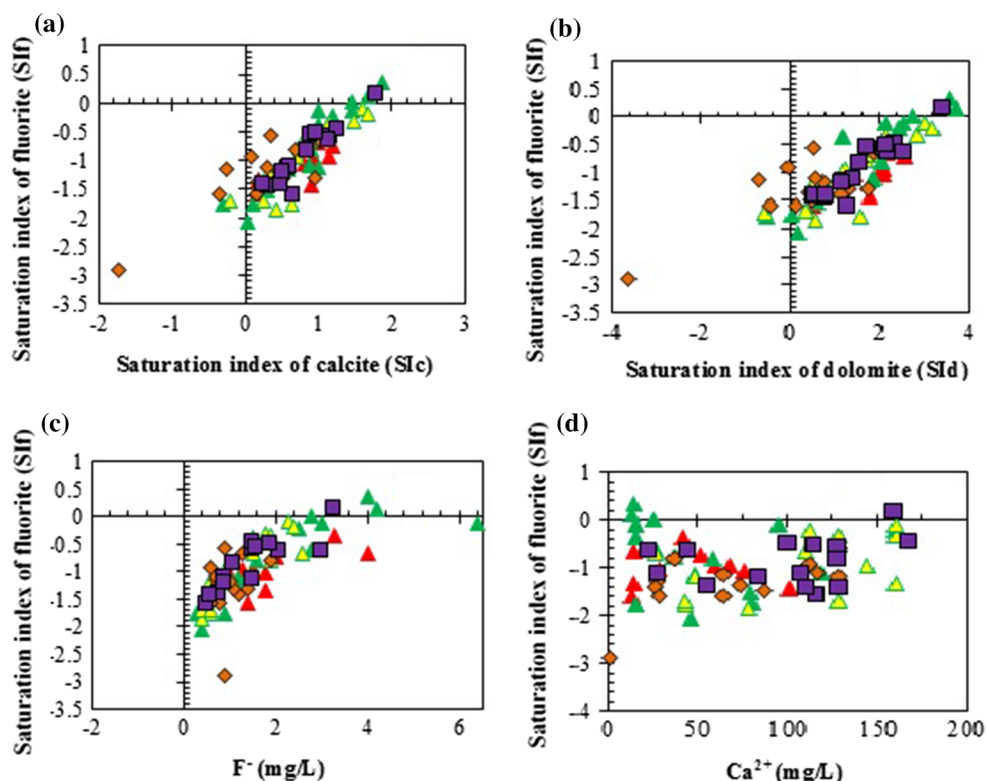
Fluoride-rich groundwater in many regions of the world is often of  $NaHCO_3$  type with low concentrations of  $Ca^{2+}$  and alkaline pH values (Li et al. 2011). The present study shows positive correlation with pH. A positive correlation ( $R^2 = 0.85$ ) between  $F^-$  concentration and pH was observed (Fig. 4b). Similar positive correlation of pH with  $F^-$  concentration was observed in different regions of the world (Valenzuela-Vasquez et al. 2006; Farooqi et al. 2007; Rafique et al. 2009; Wang et al. 2009; Mamatha and Rao 2010; Li et al. 2011). Groundwater samples from present study area have pH range from 7.1 to 8.6. Water with pH value  $<7$  rarely have detectable  $F^-$  concentration (Genxu and Guodong 2001). The  $F^-$  and  $OH^-$  have similar sizes of their ionic radii and could play substitute role for each other in minerals. Clay particles have ability to adsorb  $F^-$  ions, with increasing pH the  $F^-$  ions got displaced by  $OH^-$  ions, ultimately releasing  $F^-$  ions into groundwater (Genxu and Guodong 2001). This relationship might explain the high  $F^-$  concentrations in samples from village Chhani Nikoani and Dhool Khurd with pH value from 7.8 to 8.9.

High pH would also favor calcite precipitation (thereby increasing fluorite solubility). The solubility of calcite ( $CaCO_3$ ) is of particular importance, because it shares a common ion with fluorite ( $CaF_2$ ), which normally controls the upper limit of dissolved fluoride. Figure 5a–d plots the calcite and fluorite saturation indices. This plot shows that groundwater in the study area has evolved to the point where all samples with high fluoride are supersaturated with respect to calcite, which should favor the removal of calcium from solution and allow fluoride concentrations to increase (Kundu et al. 2001). Assuming that  $NaHCO_3$ -type waters were produced by base ion exchange (the removal of Ca and Mg from solution in exchange for Na on clay minerals), the net result is the same as described above for NaCl-type waters. As  $Ca^{2+}$  concentrations are decreased, the groundwater is able to contain higher levels of fluoride before saturation with respect to fluorite is reached. This interpretation is supported by the fact that fluoride concentrations are generally lower in the  $CaHCO_3$ - and  $CaMgCl$ -type waters, where higher  $Ca^{2+}$  levels lead to fluorite precipitation.

#### Statistical verification of correlation among physicochemical parameters

The correlation matrix for physicochemical parameters is given in Table 2. For statistical verification of these correlations, PCA was applied on groundwater dataset. The PCA plot is powerful recognition technique that explains characteristics of samples and distribution of intercorrelated parameters (Brahman et al. 2013). PCA plot was drawn for dataset of present study to verify the intercorrelation with physicochemical parameters. The PCA plot with two component axes explained 71.4 % of variance in data set. The first component axes explained 50.86 % of variance in data, while second component axes explained 20.54 % of variance in data. Parameters distribution in upper right side of plot was more enriched with  $Na^+$ ,  $K^+$ ,  $F^-$ , pH, EC, and TDS which indicate geological sources of these components (Fig. 6). High  $F^-$  groundwater is generally characterized by  $Na^+$  rich and  $Ca^{2+}$  poor with comparatively high pH values and  $HCO_3^-$  concentrations (Li et al. 2015), as a result of natural processes of evaporation, dissolution of minerals, and cation exchange. The results of present study show high values for  $Na^+$ , TDS, EC, pH and  $HCO_3^-$  which might lead to  $F^-$ -rich groundwater. The first component axes showed negative loadings for  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Cl^-$  which indicate climatic effects. The current study was observed to have lower values for  $Ca^{2+}$  and  $Mg^{2+}$  which lead to  $F^-$ -rich groundwater (Li et al. 2011). Water type is very important in controlling  $F^-$  enrichment;  $NaHCO_3$  type support high concentrations of  $F^-$  in groundwater (Li et al. 2011). Figure 6 illustrates the  $Na^+$  value was more inclined toward  $Cl^-$  than toward





**Fig. 5** Relationship between various chemical components of groundwater samples. **a** Fluorite and calcite saturation index, **b** fluorite and dolomite saturation index, **c** fluorite saturation index and  $F^-$ , **d** fluorite saturation index and  $Ca^{2+}$

**Table 2** Correlation matrix of physicochemical parameters in groundwater of study area Gujrat

Variables	Depth	Temp	pH	EC	TDS	$HCO_3^-$	$Cl^-$	$F^-$	$SO_4^{2-}$	$PO_4^{3-}$	$NO_3^-$	$Ca^{2+}$	$Mg^{2+}$	$Na^+$	$K^+$
Depth (m)	<b>1</b>														
Temp (°C)	-0.05	<b>1</b>													
pH	0.03	0.06	<b>1</b>												
EC (mS/cm)	<b>-0.46</b>	0.02	<b>0.35</b>	<b>1</b>											
TDS	<b>-0.46</b>	0.02	<b>0.35</b>	<b>1</b>	<b>1</b>										
$HCO_3^-$	<b>-0.36</b>	0.03	0.1	<b>0.52</b>	<b>0.52</b>	<b>1</b>									
$Cl^-$	0.19	0.2	0.08	-0.13	-0.13	-0.15	<b>1</b>								
$F^-$	-0.01	0.11	<b>0.85</b>	<b>0.3</b>	<b>0.3</b>	0.05	-0.02	<b>1</b>							
$SO_4^{2-}$	0.12	0.14	<b>-0.31</b>	<b>-0.58</b>	<b>-0.58</b>	<b>-0.27</b>	0.15	<b>-0.25</b>	<b>1</b>						
$PO_4^{3-}$	0.06	<b>-0.26</b>	0.16	-0.06	-0.06	0.07	-0.02	0.15	-0.2	<b>1</b>					
$NO_3^-$	<b>-0.34</b>	-0.13	-0.01	0.21	0.21	0.13	-0.02	-0.03	-0.03	0.12	<b>1</b>				
$Ca^{2+}$	0.03	0.12	<b>-0.3</b>	-0.14	-0.14	0.07	<b>0.4</b>	<b>-0.3</b>	0.16	-0.1	-0.05	<b>1</b>			
$Mg^{2+}$	-0.05	0.08	<b>-0.29</b>	-0.09	-0.09	0.09	<b>0.43</b>	<b>-0.32</b>	0.16	-0.06	-0.01	<b>0.75</b>	<b>1</b>		
$Na^+$	-0.02	0.1	<b>0.26</b>	0.13	0.13	0.18	<b>0.59</b>	0.11	0.1	0.05	0.18	-0.15	-0.07	<b>1</b>	
$K^+$	-0.19	-0.09	-0.18	0.08	0.08	0.12	-0.01	-0.12	-0.04	0.18	0.06	<b>0.25</b>	0.16	-0.1	<b>1</b>

Values in bold are different from 0 with a significance. Level alpha = 0.05, all ions in (mg/L)

$HCO_3^-$ , indicating dominance of NaCl water type that can limit  $F^-$  concentrations in groundwater. NaCl water type can affect  $F^-$  concentrations in groundwater due to minerals precipitation (Rafique et al. 2015). The second

component axes of PCA showed positive loadings for all parameters which indicate natural source, i.e., mineral weathering as source of contamination (Mamatha and Rao 2010).

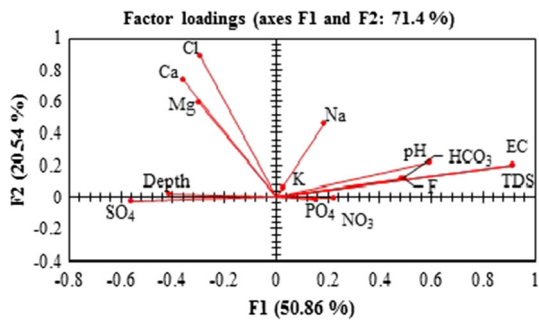


Fig. 6 PCA plot for distribution of  $F^-$  and physicochemical parameters in groundwater of Gujrat

### Spatial distribution of fluoride and role of local geology

The spatial distribution of categorized  $F^-$  concentrations along with River Chenab is presented in Fig. 7. The  $F^-$  concentrations in groundwater of study area were decreased while moving away from the River Chenab. Northwestern villages Chhani Nikoani and Dhool Khurd had more  $F^-$  concentrations, located away from River Chenab. While southwestern villages Kalra Khasa and Ghazi Chak were observed to have low  $F^-$  concentrations, located nearer to River Chenab. A northwestern village

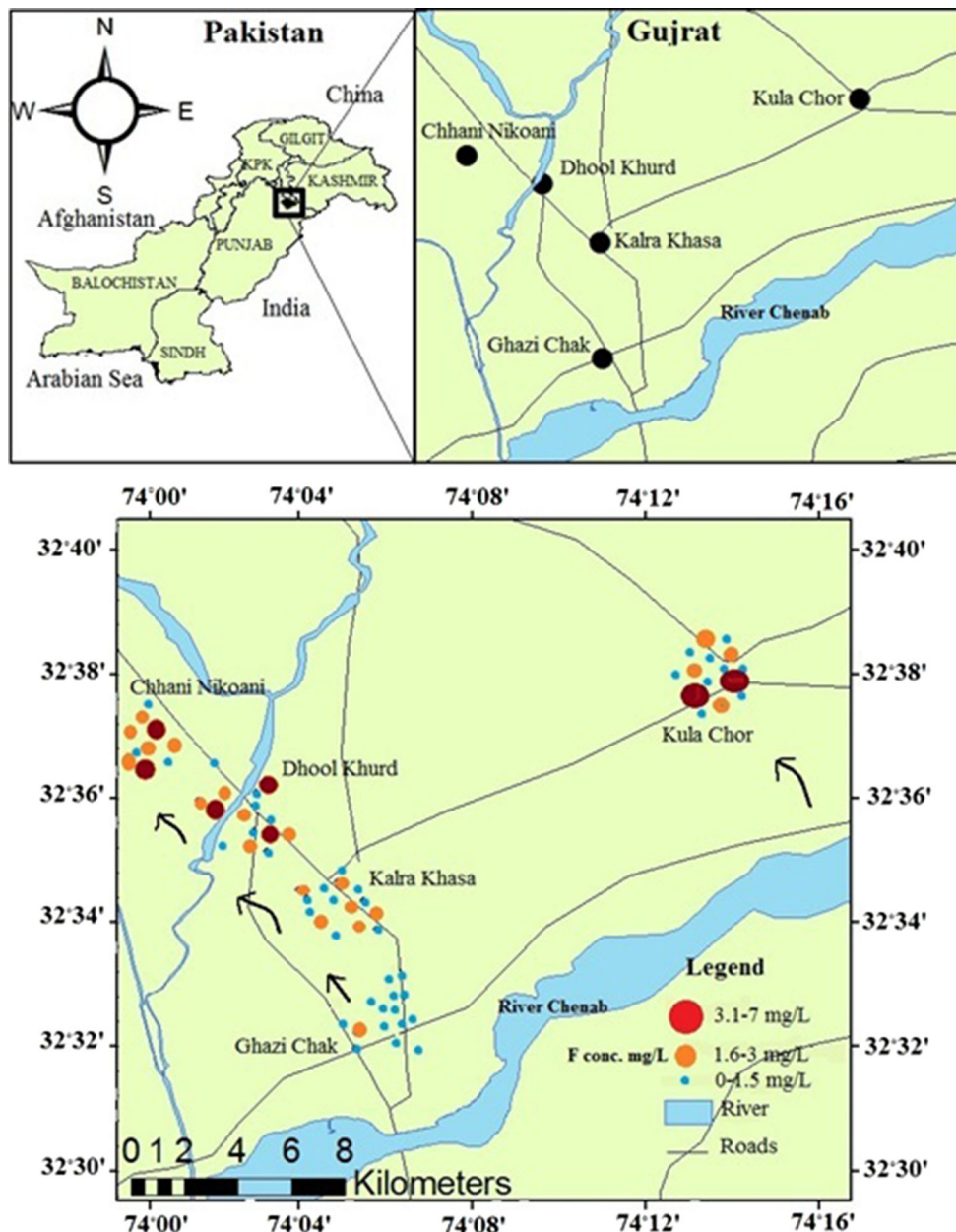
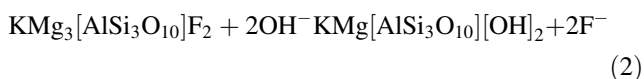
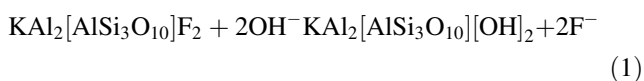


Fig. 7 Spatial distribution of  $F^-$  concentrations in groundwater samples from study area Gujrat

also observed to have comparatively more F<sup>-</sup> concentrations, which was located away from River Chenab. The higher F<sup>-</sup> concentrations in groundwater were analyzed in villages away from River Chenab, while villages nearer to River Chenab had lower concentrations. This obvious spatial distribution patterns reflect the geochemical controls on its occurrence and are clearly linked to the interpolation of groundwater flow regime, high rate of groundwater flow made harder to lose F<sup>-</sup> from its mineral rock (Kausar et al. 2003; Chae et al. 2007; Currell et al. 2011; Dey et al. 2012; Li et al. 2015). Sites nearer to River Chenab had high groundwater flow rate, lower residence time, and less time for contact between water- and F<sup>-</sup>-bearing minerals. Hence, decreased concentrations of F<sup>-</sup> were observed in nearby sites of river. However, when moved away from River, residence time was increased which led to increased F<sup>-</sup> concentrations in groundwater (Li et al. 2015). Similar trend of F<sup>-</sup> concentrations with flow regime of groundwater was reported from many regions of the world (Suthar et al. 2008; Rango et al. 2009; Naseem et al. 2010; Yitbarek et al. 2012; Su et al. 2013; Li et al. 2015).

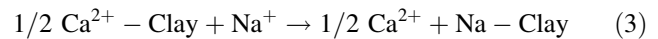
XRD and thin sections were used to analyze minerals present in the soils of the study area (Fig. 8a, b). The results inferred that F<sup>-</sup>-bearing minerals were not identified by XRD pattern. The main mineral was quartz, with muscovite and biotite identified in three villages with relatively higher F<sup>-</sup> concentrations and not detected in Ghazi Chak and Kula Chor. Muscovite and biotite might be the source of F<sup>-</sup> in these villages by the following reaction (1 and 2). High alkalinity values and Na<sup>+</sup> in groundwater have more OH<sup>-</sup> ions which can replace with F<sup>-</sup> content of F<sup>-</sup>-bearing minerals, increasing its concentrations in groundwater (Guo et al. 2007).



Weathering of muscovite and biotite was major source of F<sup>-</sup> content in groundwater other than geochemical factors (Kumar et al. 2015). The muscovite and biotite which is considered as the major source of F<sup>-</sup> in groundwater is detected by the petrographic thin sections (Fig. 8a) and by XRD (Fig. 8b).

Although the F<sup>-</sup> concentrations exceeded the WHO guideline in 23 % of samples, the concentrations are lower as compared to other reported areas in Pakistan (Table 3). Water-soluble F<sup>-</sup> concentration was measured in soil samples. The descriptive statistical summary of surface and subsurface soil samples from each village is given in Table 4. The mean value of F<sup>-</sup> in surface soil (0–5 cm)

samples from all villages was 1.29 mg/Kg, while in subsurface soil (35–40 cm) samples was 1.53 mg/Kg. Water-soluble F<sup>-</sup> from all villages also showed a positive correlation with pH ( $R^2 = 0.64$ , Fig. 9a) as that in groundwater. Soil pH is an important factor in controlling F<sup>-</sup> concentrations (Loganathan et al. 2003) The F<sup>-</sup> enrichment of groundwater occurs with increasing alkalinity of soil and releases F<sup>-</sup> into water as result of ion exchange reaction (Sheikhy et al. 2014). Increasing alkalinity of soil causes desorption of Ca<sup>2+</sup>, and data points shifted to right after ion exchange reaction with Na<sup>+</sup>.

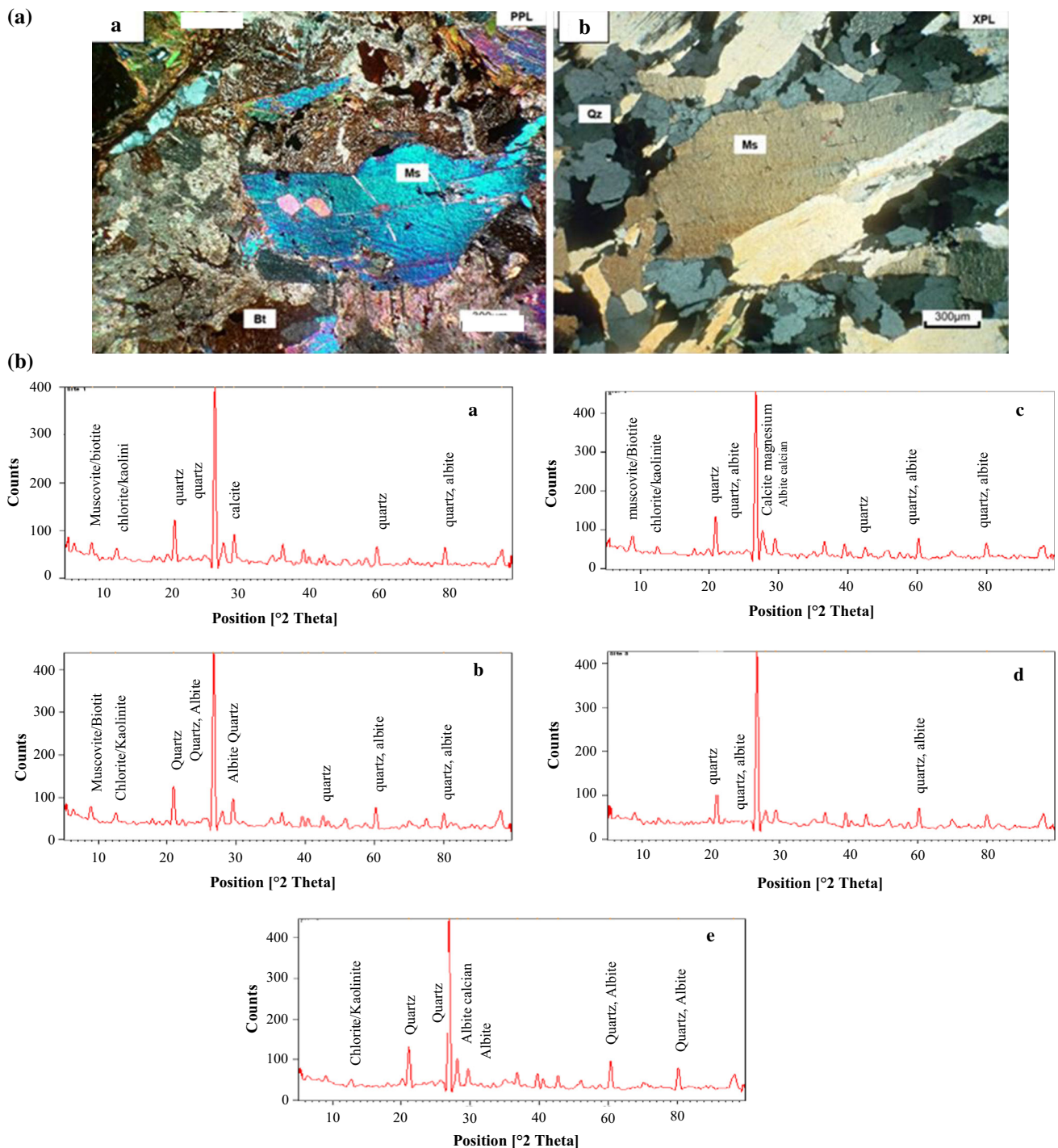


Mostly, sandy loams were found in all villages except Chhani Nikoani which is silty loam. Different soil fractions have different effects on F<sup>-</sup> concentrations. Fluoride showed a strong negative correlation with sand ( $R^2 = -0.58$ , Fig. 9b), weak correlation with silt ( $R^2 = 0.08$ , Fig. 9c), and clay fraction was positively correlated ( $R^2 = 0.35$ ) with F<sup>-</sup> concentrations (Fig. 9d). This positive correlation indicates that clay particles, which occur at low concentrations in sandy loam soils, have great capability to bound F<sup>-</sup> on their surface. The clay content was evenly distributed in all villages except Kula Chor which have less percentage of clay particles in its soil samples.

A negative correlation was observed between groundwater F<sup>-</sup> concentrations and soil F<sup>-</sup> concentrations from same study area (Fig. 10). More F<sup>-</sup> concentration in soil samples as compared to water samples from village Chhani Nikoani, Dhool Khurd, and Ghazi Chak was observed. This is due to more percentage of clay content in soil of these villages, which have capability to adsorb F<sup>-</sup> on surface (Guo et al. 2007). Less F<sup>-</sup> concentration in soil sample as compared to water samples from village Kalra Khasa and Kula Chor was observed. The presence of more percentage of sand particles as compared to silt and clay particles have less holding capability and might result in F<sup>-</sup> release from soil into groundwater (Li et al. 2011).

## Conclusions

The groundwater occurring in district Gujrat has been found unsuitable (23 %) for drinking as a result of high total dissolved solids and the occurrence of elevated fluoride concentrations; 23 % of the samples collected in this study contain fluoride concentrations that exceed the WHO permissible limit of 1.5 mg/L. This study reveals the fact that fluoride originates from the weathering of minerals in the aquifer matrix and possibly the exchange of OH<sup>-</sup> for F<sup>-</sup> on clay minerals and weathered micas under high pH conditions. Rock weathering is the dominant process



**Fig. 8** Relationship between **a**  $F^-$  and pH, **b**  $F^-$  and sand %, **c**  $F^-$  and silt %, **d**  $F^-$  and clay % of soil samples. Symbols are same as used in Fig. 3

affecting groundwater quality, of 57 % of the samples, and second process is evaporation. As the ionic strength of groundwater increases through evaporation, minerals are

initially more soluble, but finally the solubility limits for non-evaporite minerals are reached, causing precipitation which is best shown by the saturation indices of the

**Table 3** Reported F<sup>-</sup> concentrations in different areas of Pakistan

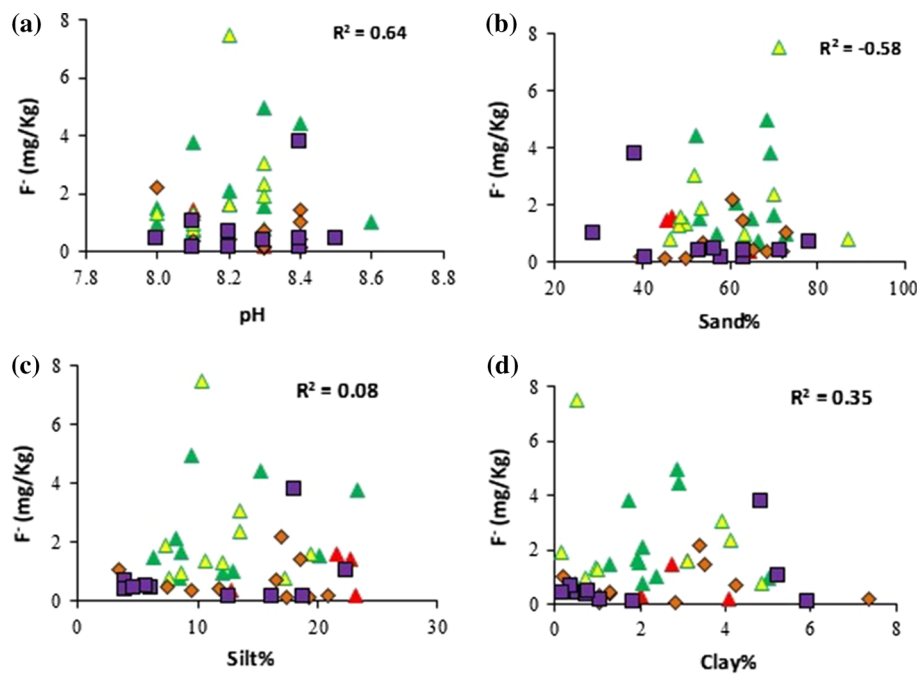
City/region	Year	Matrices	Max. concentration	Health effects	WHO guideline	References
Faisalabad	2002	Water	1.15 mg/L	Dental caries reduction	1.5 mg/L	Kausar et al. (2003)
Lahore	2007	Water	22.8 mg/L	Skeletal fluorosis		Farooqi et al. (2007)
Mithi	2006	Water	11.6 mg/L	Skeletal fluorosis		Rafique et al. (2008)
Nowshera	2010	Water	7.90 mg/L	Osteoporosis		Anjum et al. (2013)
Naranji Kando	1998	Water	13.52 mg/L	Skeletal fluorosis		Shah and Danishwar (2003)
Nagarparker	2007	Water	7.85 mg/L	Osteoporosis		Rafique et al. (2009)
Tharparker	2009	Water	7.85 mg/L	Osteoporosis		Naseem et al. (2010)
Umarkot	2014	Water	44.4 mg/L	Growth retardation		Rafique et al. (2015)
Gujrat	2010	Water	- <sup>a</sup>	Many cases of fluorosis		PCRWR (2010)
Gujrat	2015	Water	6.4 mg/L	Dental fluorosis		This study

<sup>a</sup> No fluoride concentrations provided and, report shows 2 % samples exceeded the WHO limit

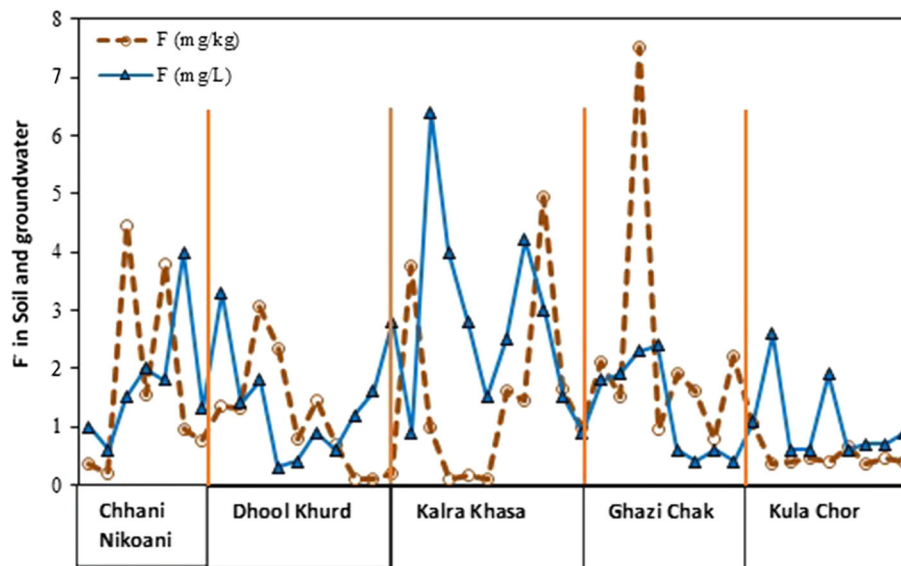
**Table 4** Statistical summary of pH, EC, F<sup>-</sup> and soil fractions from surface and subsurface soil samples from Gujrat

Sampling sites	Descriptive statistics	pH	EC (mS/cm)	F <sup>-</sup> (mg/Kg)	Sand (%)	Silt (%)	Clay (%)	Lithology
<i>Surface soil (0–5 cm)</i>								
Chhani Nikoani (N 2)	Range	8.3–8.4	9.4–9.9	0.20–0.35	40.03–64.55	12.08–23.24	2.02–4.1	Silt loam
	Mean	8.35	9.69	0.27	52.29	18.08	3.06	
	SD	0.07	0.41	0.1	17.3	7.38	1.47	
Dhool Khurd (N 5)	Range	8.1–8.4	9.9–10	0.75–4.45	45.7–69.2	15.2–23.3	1.74–3.12	Sandy loam
	Mean	8.2	10.02	2.3	55.78	20.6	2.49	
	SD	0.13	0.02	1.7	10.7	3.26	0.6	
Kalra Khasa (N 5)	Range	8–8.6	9.6–10	0.8–3.05	56.8–72.7	8.5–13.02	1.9–5.01	Sandy loam
	Mean	8.2	9.9	1.7	67.01	10.3	2.85	
	SD Range	0.23	0.13	0.91	6.1	2.08	1.26	
Ghazi Chak (N 5)	Range	8–8.3	9.9–10	0.10–1.4	48.2–61.3	6.3–13.5	0.95–3.91	Sandy loam
	Mean	8.1	10.01	0.51	52.9	10.1	1.85	
	SD	0.13	0.02	0.58	5.04	2.91	1.23	
Kula Chor (N 5)	Range	8.1–8.3	9.9–10	0.1–3.7	53.4–87.1	7.3–13.5	0.14–4.12	Sandy loam
	Mean	8.2	9.9	1.02	69.1	9.5	1.19	
	SD	0.1	0.02	1.57	12.3	2.56	1.64	
<i>Subsurface soil (35–40 cm)</i>								
Chhani Nikoani (N 2)	Range	8.2–8.3	9.9–10	1.45–1.6	46.4–48.6	17.2–19.4	3.1–4.8	Sandy loam
	Mean	8.2	9.9	1.5	47.5	18.3	3.9	
	SD	0.07	0.01	0.1	1.58	1.54	1.24	
Dhool Khurd (N 5)	Range	8.3–8.4	9.9–10	1–4.9	39.5–62.9	16.5–20.9	1.04–7.3	Sandy loam
	Mean	8.3	10	2.24	50.2	18.5	3.8	
	SD	0.05	0.01	1.56	8.85	1.71	2.31	
Kalra Khasa (N 5)	Range	8–8.4	9.9–10	0.8–7.5	60.6–72.6	3.5–16.9	0.18–3.38	Sandy loam
	Mean	8.2	10.04	2.5	67.7	9.8	1.43	
	SD	0.17	0.15	2.8	4.96	4.99	1.17	
Ghazi Chak (N 5)	Range	8.1–8.4	9.9–10	0.35–2.2	28.8–63.2	12.7–22.4	1.08–5.9	Silt loam
	Mean	8.2	9.9	0.89	45.9	17.7	3.81	
	SD	0.15	0.03	0.78	14.3	3.56	2.19	
Kula Chor (N 5)	Range	8–8.5	10–10	0.3–0.6	52.9–78.3	3.9–6.24	0.18–0.8	Sandy loam
	Mean	8.2	10	0.45	64.5	4.9	0.54	
	SD	0.19	0.01	0.11	10.4	0.9	0.25	

N number of samples, SD standard deviation



**Fig. 9** Combined trend of  $F^-$  concentration in groundwater and soil samples taken from same points



**Fig. 10** Comparison of fluoride concentrations in soil and water of the study area

samples from the study area which are supersaturated with respect to calcite containing high fluoride, and it is likely that the removal of calcium from solution and permits fluoride concentrations to increase. Some calcium is removed from solution through base ion exchange, thus increasing the fluoride concentrations associated with

$NaCl$ - and  $NaHCO_3$ -type water. Spatial distribution and relatively lower concentrations in the area and presence of clay minerals also suggest the role of local geology and rock–water interaction in controlling the fluoride concentrations.

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