

# Chapter 16

## A Comparative Analysis of Fluoride Contamination in a Part of Western India and Indus River Basin

Shubhangi, Anand Kumar, Akanksha Balha, Sonal Bindal and Chander Kumar Singh

**Abstract** Fast-growing population, water demand, and the presence of inorganic contaminants in groundwater of arid and semiarid region have created a need for quality assurance before the domestic water supply. Altogether, 30 water samples were collected from Jaisalmer (10 samples each from Jaisalmer and Pokhran blocks) and Bhatinda (10 samples) districts of Rajasthan and Punjab, respectively, and analyzed for major ions and water quality parameters. Results suggest that most of the groundwater samples are alkaline in nature with high electrical conductivity. Based on the mean value, most of the ions such as  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{F}^-$  are found to be above the WHO guideline for drinking water. Geochemical modeling and conventional graphical plots are used to decipher the groundwater chemistry.  $\text{Mg-HCO}_3$  is found as the most dominant water type followed by  $\text{Na-HCO}_3$  and  $\text{Na-Cl}$  in Bhatinda, while in Jaisalmer and Pokhran  $\text{Na-Cl}$  is found as the most dominant water type except one sample which shows water facies of  $\text{Na-HCO}_3$  type. Fluoride is found as the major contaminant in all the three regions as F varied from 1.9 to 4.5 mg/L in Jaisalmer, while in Pokhran and Bhatinda it has varied between 1.1 and 6.1 mg/L and 0.8 and 4.0 mg/L, respectively. About 60% of the samples from Bhatinda, 100% samples in Jaisalmer, and 90% of the samples from Pokhran contain  $\text{F} > 1.5$  mg/L. Most of the samples are undersaturated with fluorite and gypsum while oversaturated with calcite and dolomite suggesting dissolution of fluorite as a major contributor for high  $\text{F}^-$  in groundwater of the study areas.

**Keywords** Fluoride · Groundwater · Arid and semiarid regions

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## 16.1 Introduction

The occurrence of fluorine, a naturally found element in earth's crust as fluoride ( $F^-$ ) ions in groundwater, has become a global public health concern. Due to high electronegativity and reactivity, fluorine is mostly found as fluoride mineral complexes and under favorable conditions this moves from aquifer minerals to groundwater. Fluoride is an essential part of human diet as a daily dose of 0.5–1.0 ppm is required for proper development and mineralization of bones and enamels of teeth. Consumption of fluoride through groundwater is reported as the tow edge knife as both low and high fluorides affect human health adversely (Hussain et al. 2002, 2004). It has been found that the deficiency of fluoride leads to dental caries, formation of enamel, and bone fragility (Cao et al. 2000; Ayenew 2008), while the high concentration of fluoride ( $>1.5$  ppm) is also toxic as its prolonged consumption causes lack of enamel formation, molting of teeth, bone fragility, and at the severe stage it may cause bilateral lameness and stiffness of gait depending on the level and period of exposure (Edmunds and Smedley 2005; Singh et al. 2011, 2013).

Fluoride is widely distributed in several naturally occurring minerals, such as fluorite ( $CaF_2$ ), cryolite ( $Na_3AlF_6$ ), topaz, tourmaline, and micas, where it is found in combination with silicates, but particularly in association with phosphorus as fluorapatite [ $Ca_5(PO_4)_3F$ ]. Human interference in groundwater is almost negligible; therefore, hydrogeochemical process including mineral weathering, precipitation, dissolution, ion-exchange, oxidation, reduction, and residence time determines the extent of fluoride contamination (Barbecot et al. 2000; Reghunathet al. 2002; Singh et al. 2011; Rina et al. 2012; Kumar et al. 2015). The concentration of fluoride in groundwater depends on the various factors including types of aquifer minerals, interaction between groundwater and aquifer minerals, climatic condition, chemistry in recharge area, and intermixing of water.

In India (Chap. 1, Fig. 1.6), the problem is acute in states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, Assam, and Uttar Pradesh (Godfrey et al. 2006; Ayoob and Gupta 2006; Sharma et al. 2007; Khaiwal and Garg 2007; SIHFW 2008; Hussain et al. 2012; Singh and Mukherjee 2015). The effect of fluoride on human health is more severe in semiarid and arid regions because of extreme climatic conditions favor the dissolution of fluorite in groundwater. It has been reported that 30 districts of Rajasthan and 11 districts of Punjab are fluoride affected (CGWB 2009). Several methods including multivariate statistical analysis, geochemical modeling, inverse geochemical modeling, conventional plots (Yidana and Yidana 2010; Singh et al. 2011; Machiwal and Jha 2015), geochemical modeling (Yidana et al. 2008), stable isotopes (Barbieri et al. 2005; Carucci et al. 2012), redox indicator, and structural equation modeling (Belkhiri and Narany 2015) are widely used to investigate the geochemical evolution and hydrochemical processes controlling the chemical characteristics and fluoride contamination in groundwater. With the above background, this study is an

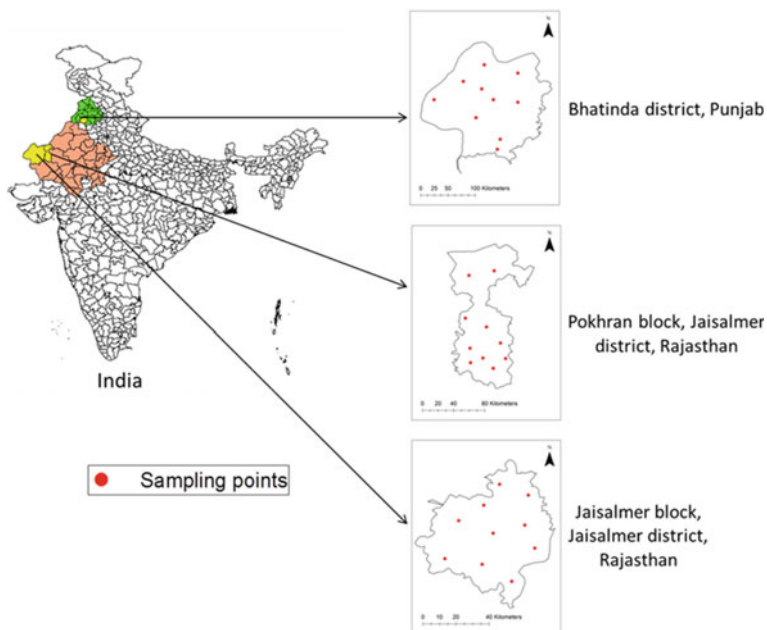
attempt to compare the major hydrogeochemical process responsible for fluoride enrichment in groundwater of the study area. More related information regarding groundwater of South Asia is available in Mukherjee (2018).

## 16.2 Materials and Methods

### 16.2.1 Study Area

The study area is situated in the northwestern region of India and includes Bhatinda district of Punjab state and two administrative blocks of the Jaisalmer district of Rajasthan state, namely Jaisalmer and Pokhran (Fig. 16.1)

The Jaisalmer block is located between 70.80°E and 71.58°E longitudes and between 26.41°N and 27.20°N latitudes, covering approximately an area of 3850 km<sup>2</sup>. The Pokhran block is located between 71.39°E and 72.09°E longitudes and between 26.32°N and 27.54°N latitudes, covering an area of approximately 6000 km<sup>2</sup> amid the Thar Desert, while Bhatinda lies between 29.55° and 30.6° north latitude and 74.63° to 75.76° east longitudes in Punjab very close to the Thar Desert. The Jaisalmer district lies in the arid region as the annual rainfall varies from 450 mm at the eastern margin to 100 mm at the western margin of the district.



**Fig. 16.1** Study area with sampling location

The mean maximum temperature varies from 40 to 45 °C and minimum temperature varies from 3 to 10 °C. The evapotranspiration rate is very high, i.e., approximately 3–20 times higher than precipitation. Bhatinda district also lies in the semiarid climatic zone with the annual rainfall of around 450 mm.

Geologically, Pokhran and Jaisalmer are overlaid by the vast blanket of young unconsolidated alluvium including blown sand of the Thar Desert of western Rajasthan. The important lithological formations in the region are sedimentary rocks comprising of sandstone, limestone, and shales. Carbonate rocks such as limestone, marble, and dolomite are dominant rocks in the region. The various geological formations of Jaisalmer and Pokhran are consolidated, semiconsolidated, and unconsolidated, while Bhatinda has both unconfined and confined aquifers covered with Indo-Gangetic alluvial plain of Quaternary age.

### ***16.2.2 Sample Collection and Analysis***

A random sampling plan was adopted, and altogether 30 samples, out of which 20 from Jaisalmer and Pokhran blocks of Jaisalmer district of Rajasthan and 10 from the Bhatinda district of Punjab, have been collected. The tube wells were pumped for 3–5 min to avoid any interference of iron cast pipes, the samples were collected in polypropylene bottles, and the location was geocoded using global positioning system (Garmin GPS). Samples are mostly collected from the tube wells and deep to shallow hand pumps which are the major source of drinking water. The pH, total dissolved solid (TDS), and electrical conductivity (EC) of the water samples were measured at sampling sites with the help of portable pH, TDS, and EC electrodes (Oakton Probe).

The water samples were collected in the 100 mL bottles, one of them was acidified using  $\text{HNO}_3$  for cation analysis, and the other unacidified bottle was also filled with the sample for anion analysis. The samples were stored in an icebox, carried to the laboratory, and kept at 4 °C for further chemical analysis. Immediately after the water samples were transported to the laboratory, the major cations were ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) analyzed using an atomic absorption spectrometer Thermo Fisher Scientific M series AAS graphite furnace (GFAAS), and the major anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) were analyzed using an ion chromatograph (Dionex). Bicarbonate ( $\text{HCO}_3^-$ ) was determined by titration using standard procedures as described in standard methods for the examination of water and wastewater (APHA 2007). The analytical precision of the ions analyzed was determined by calculating the normalized ionic charge balance error, which varied within  $\pm 5\%$ . Saturation index and major water types have been calculated using PHREEQC. Saturation index was calculated using the following formula:

$$SI = \log \frac{IAP}{K_f} \quad (16.1)$$

where IAP is the ion activity product of dissociation of the mineral in the aqueous solution, and  $K_f$  is the equilibrium solubility product of the mineral.

## 16.3 Result and Discussion

### 16.3.1 Distribution of Major Ions

Water quality parameters with the basic statistics have been summarized in Table 16.1. pH of all the water samples indicates alkaline condition in the study area. pH of the water samples in Jaisalmer varied from 7.7 to 8.2 with the mean value of 8.0, while in Pokhran and Bhatinda it varied from 7.6 to 8.5 and 8.2 to 8.9 with the mean value of 7.9 and 8.6, respectively. Based on the mean value of pH, highest pH has been observed in Bhatinda. High concentration of pH in groundwater suggests high interaction between rainwater and the soil in the region. Enhanced dissolution imparts alkalinity in the aquifer system.

Large variation in EC concentration has been observed in all three regions. In Jaisalmer, the concentration of EC varied from 1600 to 3600  $\mu\text{S}/\text{cm}$  with the mean value of 2460  $\mu\text{S}/\text{cm}$ . The EC in Pokhran varied from 1790 to 12,000  $\mu\text{S}/\text{cm}$ , and in Bhatinda, it varied from 280 to 2410  $\mu\text{S}/\text{cm}$  with the mean value of 3919 and 1479  $\mu\text{S}/\text{cm}$ , respectively. The high EC and TDS value indicates high salinity in groundwater. The study area lies in arid to semiarid region where evaporation is very high thus results in increased salt concentration. Wide variation in water quality parameters suggests that the hydrogeochemistry of the area is not homogenous, and it has been affected by the climatic factors including rock–water interaction as well as anthropogenic inputs. Only four samples (all from Bhatinda) out of 30 collected have EC value <1500 which falls within the WHO prescribed limit for drinking water (WHO 2009).

$\text{Na}^+$  is found as the most dominant cation in all three sampled areas followed by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  in Pokhran and Jaisalmer and  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in Bhatinda. The concentration of  $\text{Na}^+$  in Jaisalmer varied from 239 to 670 mg/L with mean value 416.4 mg/L. The concentration of Na in Pokhran varied from 215 to 1068 mg/L, while in Bhatinda it varied from 34 to 312 mg/L with the mean value 588.1 and 129.2 mg/L, respectively.  $\text{Na}^+$  is considered as conservative in nature, and it binds with the clay minerals (Subramanian and Saxena 1983). Concentration of  $\text{Ca}^{2+}$  in Jaisalmer varied from 40 to 108 mg/L with an average value of 70.3 mg/L, while in Pokhran and Bhatinda the values ranged between 30–125 and 12–88 mg/L with an average of 84.1 and 38.6 mg/L, respectively. The highest concentration of  $\text{Ca}^{2+}$  is found in Pokhran and the lowest is observed in Bhatinda. The concentration of  $\text{Mg}^{2+}$  in the groundwater varied from 23 to 48.6 mg/L in Jaisalmer, while in Pokhran and Bhatinda it varied from 12.1 to 68.6 mg/L and 21.0 to 113.0 mg/L, respectively.

**Table 16.1** Descriptive statistics of the samples from study area with WHO (2009) guideline

Variable	Pokhran					Jaisalmer					Bhatinda					WHO (2009)
	Min	Max	Mean	Std. deviation		Min	Max	Mean	Std. deviation		Min	Max	Mean	Std. deviation		
pH	7.6	8.5	8.0	0.2		7.7	8.2	7.9	0.1		8.2	8.9	8.6	0.2		6.5-8
EC	1790.0	12000.0	3919.0	3080.6		1600.0	3600.0	2460.0	826.2		280.0	2410.0	1479.0	854.0		-
TDS	1206.0	3118.0	1959.6	654.2		810.0	2211.0	1414.1	537.4		80.0	2100.0	713.0	665.1		500
Na	215.0	1068.0	588.1	325.7		239.0	670.0	416.4	169.1		34.0	312.0	129.2	109.3		200
K	6.6	54.8	22.5	15.0		6.0	17.8	12.6	3.4		8.0	150.0	56.0	53.8		30
Ca	30.0	125.0	84.1	26.6		40.0	108.0	70.3	18.5		12.0	88.0	38.6	28.5		200
Mg	12.1	68.6	37.9	17.6		23.0	48.6	34.0	8.2		21.0	113.0	44.0	29.9		150
Cl	368.0	1395.0	635.6	324.0		172.0	652.0	428.6	156.4		45.0	593.0	259.1	205.1		250
SO <sub>4</sub>	81.0	374.0	188.0	89.7		93.0	417.0	184.8	97.6		0.05	0.4	0.2	0.1		250
HCO <sub>3</sub>	183.0	1220.0	544.7	332.4		242.0	610.0	409.1	109.8		379.0	654.0	553.4	105.4		600
NO <sub>3</sub>	29.7	304.4	170.2	103.5		5.00	360.2	86.2	135.4		1.1	7.9	4.7	2.5		50
F	1.1	6.1	4.0	1.5		1.9	4.5	2.7	0.8		0.8	4.0	1.8	1.0		1.5

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  along with  $\text{HCO}_3^-$  determine the hardness of the groundwater. At soil zone, precipitation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  occurs due to temporary hardness, and these precipitated salts might get leached from the soil zone with rainwater or irrigation water and contribute high concentration of these ions in groundwater.  $\text{K}^+$  concentration in Jaisalmer varied from 6 to 17.8 mg/L with an average of 12.6 mg/L, while in Pokhran and Bhatinda the values range between 6.6–54.8 and 8–150 mg/L with average values of 22.5 and 56 mg/L, respectively. The highest concentration of  $\text{K}^+$  was found in Bhatinda. Weathering of  $\text{K}^+$  bearing minerals, i.e., K-feldspar might be responsible for the  $\text{K}^+$  concentration in groundwater. Anthropogenic activities as use of synthetic fertilizers might also contribute  $\text{K}^+$  in groundwater.

Among anions the  $\text{Cl}^-$  is the most dominant based on the mean values in Jaisalmer and Pokhran followed by  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{F}^-$ , while in Bhatinda  $\text{HCO}_3^-$  is the most dominant anion followed by  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ , and  $\text{SO}_4^{2-}$ . The concentration of  $\text{Cl}^-$  in Jaisalmer varied from 172 to 652 mg/L with an average of 428.6 mg/L, while in Pokhran and Bhatinda the concentration varied from 368–1395 and 45–593 mg/L with an average of 635.6 and 205.1 mg/L, respectively. The maximum  $\text{Cl}^-$  concentration is found in the Pokhran and Jaisalmer where the temperature is found to be high during most of the time in year compared to Bhatinda, high concentration of  $\text{Cl}^-$  might be due to high evaporation rate in these regions.  $\text{HCO}_3^-$  concentration varied from 242 to 610 mg/L with an average value of 409.1 mg/L in Jaisalmer, while in the Pokhran and Bhatinda it varied from 183 to 1220 mg/L and 379–654 mg/L with average values of 544.7 and 553.4 mg/L. High  $\text{HCO}_3^-$  concentration indicates the presence of carbonate minerals. Weathering of silicate and carbonate minerals along with degradation of organic matter might contribute high concentration of  $\text{HCO}_3^-$  ions in groundwater (Rina et al. 2012). The concentration of  $\text{NO}_3^-$  is found highest in groundwater samples collected from Pokhran as the concentration ranges from 29.7 to 304.4 mg/L with an average of 170.2 mg/L, while in Jaisalmer and Bhatinda the concentration of  $\text{NO}_3^-$  varied from 5 to 360 mg/L and 1.1 to 7.9 mg/L with an average of 4.7 mg/L. Very low concentration of  $\text{SO}_4^{2-}$  is observed in Bhatinda where the concentration of  $\text{SO}_4^{2-}$  varied from 0.05 to 0.4 mg/L, while in Pokhran and Jaisalmer the concentration of  $\text{SO}_4^{2-}$  is comparatively high as the concentration varied from 81.37 mg/L in Pokhran and 93–417 mg/L in Jaisalmer, respectively. Dissolution of minerals such as gypsum and anhydrite might contribute  $\text{SO}_4^{2-}$  in groundwater, while anthropogenic activities as use of fertilizers and leaching of municipal waste or agricultural runoff might contribute high concentration of  $\text{NO}_3^-$  in groundwater, whereas the anthropogenic inputs in desertic regions are very less, however, the high  $\text{NO}_3^-$  can be observed as it has accumulation over the long periods of climatic phenomena of lightening and rainfall (Walvoord et al. 2003).

Fluoride is found as the major contaminant with severe health risk in all three regions as the concentration of F varied from 1.9 to 4.5 mg/L in Jaisalmer, while in Pokhran and Bhatinda it has been found to vary between 1.1–6.1 and 0.8–4.0 mg/L,

respectively. In semiarid and arid regions, the weathering of fluoride-containing rocks (fluorite) is the major source of  $F^-$  in groundwater. However, high pH along with high  $HCO_3^-$  favors the dissolution of fluorite-bearing minerals.

### 16.3.2 Correlation Between Major Ions

The correlation matrix ( $p < 0.05$ ) for all the water quality parameters has been analyzed to decipher the relationship among the major ions present in the study area (Table 16.2). Correlation between water quality variables gives an insight of the major hydrogeochemical process which controls the chemical characteristics of the groundwater. In Pokhran, pH is strongly correlated with  $K^+$ , while  $Na^+$  shows strong correlation with  $Cl^-$  and moderate correlation with  $SO_4^{2-}$ ,  $HCO_3^-$ , and  $NO_3^-$ .  $K^+$  shows moderate positive correlation with  $NO_3^-$ . In Jaisalmer, pH is strongly correlated with  $Ca^{2+}$ , while  $Na^+$  is strongly correlated with  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$ . Positive correlation between  $Cl^-$  and  $Na^+$  with EC shows that dissolution of ions from rocks is a major controlling factor of EC. In Bhatinda,  $Na^+$  shows strong and positive correlation with  $K^+$  and  $Cl^-$  and moderate correlation with  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $HCO_3^-$ . A strong correlation among  $SO_4^{2-}$  and  $NO_3^-$  in Bhatinda indicates agricultural activities and seepages from the drainage as major contributor of these ions in groundwater.

### 16.3.3 Hydrogeochemical Processes

#### 16.3.3.1 Weathering and Dissolution

Plot between  $Ca^{2+}/Na^+$  and  $HCO_3^-/Na^+$ , i.e.,  $Na^+$  normalized  $Ca^{2+}$  versus  $HCO_3^-$  graph, is used to identify the dominance of hydrogeochemical process, i.e., influence of silicate weathering, evaporate dissolution, or carbonate weathering on groundwater chemistry. Figure 16.2a indicates that chemical characteristics of most of the water samples from all three locations have been influenced by the evaporate dissolution. In Fig. 16.2b,  $Na^+$  normalized  $Ca^{2+}$  versus  $Mg^{2+}$  graph indicates that most of the  $Mg^{2+}$  is derived due to evaporate dissolution. The scatter plot between  $Ca^{2+} + Mg^{2+}$  and  $SO_4^{2-} + HCO_3^-$  identifies the ion-exchange is the dominant process. The samples close to equiline (1:1 line) indicate the dissolution of dolomite, calcite, or gypsum as the dominant process in the aquifer (Fig. 16.2c). If ion-exchange is the major process, then it will shift the points away from the equiline, i.e., toward right while if reverse ion-exchange is dominant, then it tends to shift the points left to equiline due to excess of  $Ca^{2+} + Mg^{2+}$  ions (Singh et al. 2013). The scatter plot between  $Ca^{2+} + Mg^{2+}$  and  $SO_4^{2-} + HCO_3^-$  indicates that most of the water samples of Bhatinda are below equiline which indicates



**Table 16.2** Correlation analysis of physicochemical parameters from different regions

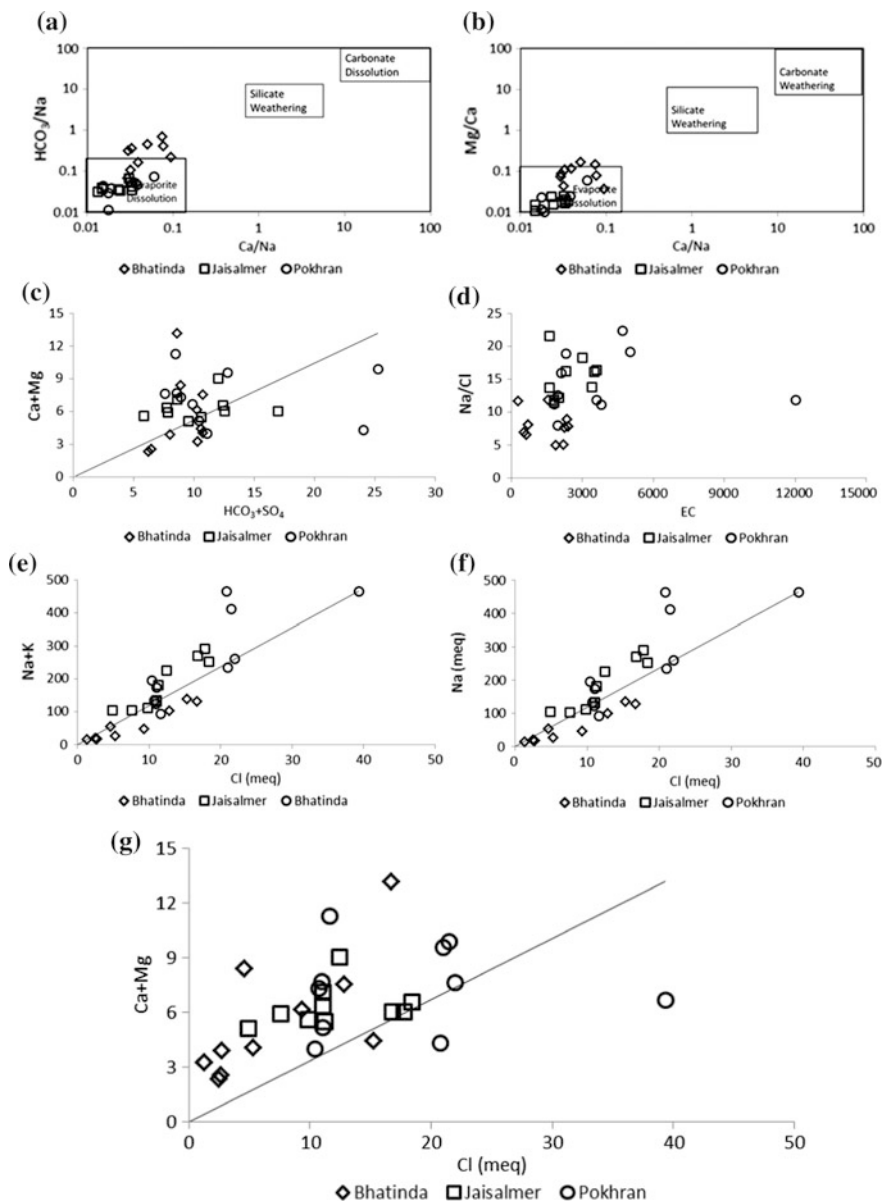
	pH	EC	TDS	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	F
<i>Bhatinda</i>												
pH	<b>1</b>											
EC	-0.053	<b>1</b>										
TDS	0.239	<b>0.792</b>	<b>1</b>									
Na	-0.232	<b>0.804</b>	<b>0.730</b>	<b>1</b>								
K	-0.159	<b>0.843</b>	<b>0.755</b>	<b>0.911</b>	<b>1</b>							
Ca	-0.193	<b>0.678</b>	0.232	0.380	<b>0.554</b>	<b>1</b>						
Mg	- <b>0.681</b>	0.460	0.085	<b>0.690</b>	<b>0.532</b>	0.428	<b>1</b>					
Cl	-0.135	<b>0.881</b>	<b>0.729</b>	<b>0.962</b>	<b>0.943</b>	<b>0.549</b>	<b>0.619</b>	<b>1</b>				
SO <sub>4</sub>	0.290	-0.124	-0.393	-0.140	-0.160	0.199	0.132	-0.076	<b>1</b>			
HCO <sub>3</sub>	0.394	<b>0.608</b>	<b>0.620</b>	0.390	<b>0.528</b>	0.429	0.048	0.439	0.319	<b>1</b>		
NO <sub>3</sub>	0.407	-0.323	- <b>0.561</b>	- <b>0.581</b>	- <b>0.547</b>	0.142	-0.209	-0.474	<b>0.746</b>	0.076	<b>1</b>	
F	<b>0.541</b>	0.210	0.053	-0.287	-0.001	0.368	-0.409	-0.084	0.344	<b>0.523</b>	<b>0.536</b>	<b>1</b>
<i>Pokhran</i>												
pH	<b>1</b>											
EC	- <b>0.083</b>	<b>1</b>										
TDS	<b>0.410</b>	- <b>0.060</b>	<b>1</b>									
Na	<b>0.174</b>	<b>0.790</b>	<b>0.450</b>	<b>1</b>								
K	<b>0.713</b>	- <b>0.134</b>	<b>0.266</b>	- <b>0.078</b>	<b>1</b>							
Ca	<b>0.192</b>	- <b>0.027</b>	<b>0.474</b>	- <b>0.052</b>	<b>0.405</b>	<b>1</b>						
Mg	- <b>0.299</b>	- <b>0.081</b>	- <b>0.005</b>	- <b>0.341</b>	- <b>0.174</b>	<b>0.487</b>	<b>1</b>					
Cl	- <b>0.068</b>	<b>0.962</b>	<b>0.073</b>	<b>0.809</b>	- <b>0.073</b>	<b>0.061</b>	<b>0.006</b>	<b>1</b>				
SO <sub>4</sub>	<b>0.451</b>	<b>0.166</b>	<b>0.639</b>	<b>0.510</b>	- <b>0.001</b>	<b>0.290</b>	<b>0.113</b>	<b>0.314</b>	<b>1</b>			
HCO <sub>3</sub>	<b>0.323</b>	<b>0.162</b>	<b>0.753</b>	<b>0.649</b>	- <b>0.068</b>	<b>0.065</b>	- <b>0.318</b>	<b>0.136</b>	<b>0.456</b>	<b>1</b>		

(continued)

Table 16.2 (continued)

	pH	EC	TDS	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub>	F
NO <sub>3</sub>	<b>0.470</b>	<b>0.247</b>	<b>0.653</b>	<b>0.559</b>	<b>0.586</b>	<b>0.264</b>	<b>-0.421</b>	<b>0.321</b>	<b>0.280</b>	<b>0.452</b>	<b>1</b>	
F	<b>0.140</b>	<b>-0.023</b>	<b>0.596</b>	<b>0.242</b>	<b>0.324</b>	<b>0.441</b>	<b>-0.211</b>	<b>-0.060</b>	<b>-0.079</b>	<b>0.584</b>	<b>0.669</b>	<b>1</b>
<i>Jaisalmer</i>												
pH	<b>1</b>											
EC	-0.115	<b>1</b>										
TDS	-0.012	<b>0.974</b>	<b>1</b>									
Na	-0.176	<b>0.993</b>	<b>0.978</b>	<b>1</b>								
K	0.179	0.316	0.268	0.261	<b>1</b>							
Ca	<b>0.707</b>	-0.048	0.032	-0.090	-0.203	<b>1</b>						
Mg	-0.129	<b>0.550</b>	<b>0.645</b>	<b>0.583</b>	0.209	-0.079	<b>1</b>					
Cl	-0.232	<b>0.926</b>	<b>0.869</b>	<b>0.918</b>	0.235	-0.086	<b>0.530</b>	<b>1</b>				
SO <sub>4</sub>	0.037	<b>0.696</b>	<b>0.738</b>	<b>0.722</b>	0.362	-0.072	0.285	<b>0.565</b>	<b>1</b>			
HCO <sub>3</sub>	-0.245	<b>0.763</b>	<b>0.677</b>	<b>0.753</b>	0.146	0.085	0.199	<b>0.629</b>	0.455	<b>1</b>		
NO <sub>3</sub>	0.329	<b>0.512</b>	<b>0.657</b>	<b>0.526</b>	0.012	0.167	<b>0.718</b>	0.341	0.284	0.146	<b>1</b>	
F	-0.289	0.393	0.360	0.430	0.462	-0.477	0.059	0.358	<b>0.753</b>	0.220	-0.143	<b>1</b>

Bold shows moderate to good correlation



**Fig. 16.2** a  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$  versus  $\text{HCO}_3^-$  scatter plot; b  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$  versus  $\text{Mg}^{2+}$  scatter plot; c  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{SO}_4^{2-} + \text{HCO}_3^-$  scatter plot; d  $\text{Na}^+/\text{Cl}^-$  versus EC scatter plot; e scatter plot between  $\text{Na}^+$  versus  $\text{Cl}^-$ ; f scatter plot between  $\text{Na}^+ + \text{K}^+$  versus  $\text{Cl}^-$ ; g. scatter plot between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{Cl}^-$

ion-exchange as a major process in this region, while the samples from Pokhran show reverse ion-exchange as a major process.

Ratio of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  determines the dissolution of calcite and dolomite; if the value of  $\text{Ca}/\text{Mg}$  is below 1, it indicates dissolution of dolomite and values  $>1$  indicates dissolution of calcite. In this study, most of the water samples collected from Bhatinda show  $\text{Ca}/\text{Mg}$  value  $< 1$  indicating dissolution of dolomite while in Jaisalmer and Pokhran the value of  $\text{Ca}/\text{Mg} > 1$  indicating calcite dissolution.

### 16.3.3.2 Evaporation

Evaporation plays an important role in determining the concentration of ions in groundwater system.  $\text{Na}^+/\text{Cl}^-$  versus EC plot is the effective indicator of evaporation (Fig. 16.2d). If halite dissolution is the dominant process, then in that case the value of  $\text{Na}^+/\text{Cl}^-$  ratio will be 1. High value of  $\text{Na}/\text{Cl}$  indicates  $\text{Na}^+$  might be released from the silicate weathering. The scatter plot between  $\text{Na}^+ + \text{K}^+$  versus  $\text{Cl}^-$  indicates the dominance of silicate weathering; samples above 1:1 lines indicate excess of cations due to weathering of silicate minerals. The plot between  $(\text{Na}^+ + \text{K}^+)$  versus  $\text{Cl}^-$  indicates that most of the water samples from Bhatinda are below equiline, while the samples from Pokhran and Jaisalmer are above the equiline. It suggests that the groundwater quality in Jaisalmer and Pokhran is influenced by the silicate weathering or the excess of cations might be due to the presence of saline soil. In Jaisalmer and Pokhran, high concentration of  $\text{Na}^+$  is observed while low  $\text{K}^+$  which might be because of resistance of potassium to chemical weathering.

### 16.3.3.3 Ion-Exchange

The  $\text{Na}^+$  versus  $\text{Cl}^-$  scatter plot indicates that most of the samples from Bhatinda are below the equiline suggesting evaporation as a dominant process, while the samples from the Jaisalmer and Pokhran are above the equiline suggesting that the silicate weathering might be contributing the excess of cation in groundwater. Exchange of cations might also act as an alternative source of excess of  $\text{Na}^+$  as the area is in arid region where alkaline soil is common. The scatter plot between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{Cl}^-$  indicates ion-exchange as most of the samples from all the regions are above equiline.

## 16.4 Geochemical Modeling

### 16.4.1 Hydrochemical Facies

Hydrochemical facies are used to identify the overall chemical characteristics of the aquifer. It indicates the effects of interaction between the water and aquifer minerals within the lithological framework. Na–Cl is found as the most dominant hydrochemical facies in Jaisalmer and Pokhran area, while in Bhatinda Na–HCO<sub>3</sub> and Mg–HCO<sub>3</sub> are the most dominant facies (Fig. 16.3 and Table 16.3). The flow path of groundwater, residence time, interaction between groundwater and aquifer minerals, and chemical process within the aquifer system determine the type of the water. Piper trilinear diagram also suggests Na<sup>+</sup> and Ca<sup>2+</sup> as dominant cationic species and Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> as dominant anionic species. The low concentration of Ca<sup>2+</sup> might be due to the precipitation of Ca<sup>2+</sup> as carbonate (Gaciri and Davis 1993). Ion-exchange between Ca<sup>2+</sup> and Na<sup>+</sup> due to the movement of groundwater in the weathering zone may also result in high F<sup>-</sup> associated with high Na<sup>+</sup> and low Ca<sup>2+</sup> concentration (Tamta 1994).

### 16.4.2 Saturation Indices

Saturation indices are used to determine the reactivity of the minerals in groundwater. Positive value of saturation indices (SI) indicates oversaturation of the minerals, while the negative value of SI indicates undersaturation. When the solution will be undersaturated in terms of any minerals, it will tend to dissolve; while if the solution is oversaturated, that mineral will precipitate. In this study, all the samples from Bhatinda are found to be undersaturated with fluorite and gypsum while oversaturated with dolomite and calcite, whereas in Jaisalmer all except one sample is undersaturated with fluorite and oversaturated with dolomite and calcite. In Pokhran, most of the water samples, 7 out of 10, are oversaturated with fluorite and all samples are oversaturated with respect to dolomite and calcite. This region lies in the arid climatic zone with high temperature and less rainfall which is responsible for the precipitation of these minerals in groundwater. It also indicates that the water has enough residence time to reach up to mineral equilibrium. The samples with high F<sup>-</sup> are undersaturated with fluorite and indicate dissolution of fluorite as a major source of fluoride in groundwater. Oversaturation of calcite and therefore precipitation of Ca in alkaline environment favor the dissolution of fluorite (Adriano 1986). Increase in concentration of HCO<sub>3</sub> ions, pH, and temperature can result in the precipitation of calcite (Hounslow 1995).

### 16.5 Fluoride Enrichment

Fluoride is an essential element for formation of bone and enamel of teeth; a daily intake of 0.5 mg of  $F^-$  is essential for healthy diet, but once the concentration increases above 1.5 mg/L it adversely affects the human health. In present study out of total 30 collected samples from three areas, only five samples are having  $F < 1.5$  mg/L, which indicates sever health implications. It has been reported that lower pH value prevents the dissolution of fluorite minerals, while the high pH value favors the dissolution of fluorite (Adriano 1986). In arid and semiarid regions, less rain and high evaporation play an important role in dissolution of fluorite in groundwater (Farooqi et al. 2007; Singh and Mukherjee 2015). In alkaline environment, hydroxyl ions replace  $F^-$  from fluorite-bearing minerals, and high TDS enhances the ionic strength of the solution which favors the dissolution of fluorite. In granitic or sandstone dominant aquifers, dissolution of fluorite can be a possible reason for the presence of fluoride in groundwater. The hydrolysis of aluminosilicate in aquifers produces bicarbonate ion, which might enhance the dissolution of fluorite in groundwater.

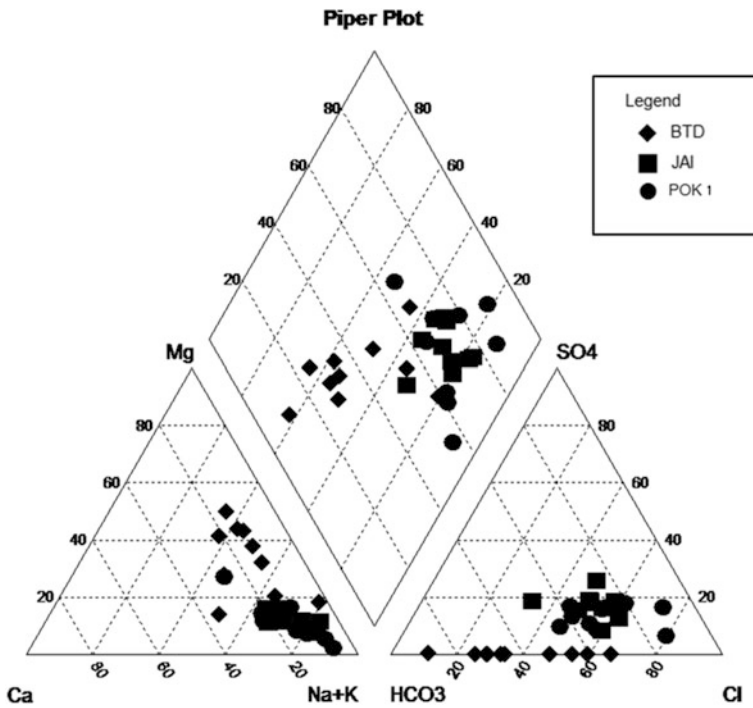
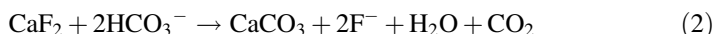


Fig. 16.3 Piper plot of Bhatinda, Jaisalmer, and Pokhran

**Table 16.3** Major water facies and their distribution

Water type	Total no of sample	Jaisalmer	Pokhran	Bhatinda
Mg–Na–HCO <sub>3</sub> –Cl	3	0	0	3
Na–Cl–HCO <sub>3</sub>	12	5	5	2
Mg–HCO <sub>3</sub>	1	0	0	1
Na–HCO <sub>3</sub> –Cl	1	0	0	1
Na–Ca–HCO <sub>3</sub> –Cl	2	1	0	1
Na–Mg–Cl–HCO <sub>3</sub>	1	0	0	1
Na–Cl–SO <sub>4</sub> –HCO <sub>3</sub>	1	1	0	0
Na–Ca–Cl–HCO <sub>3</sub>	1	3	2	0
Na–Cl	5	0	2	0
Na–Mg–Ca–Cl–HCO <sub>3</sub>	2	0	1	0
Na–Mg–HCO <sub>3</sub> –Cl	1	0	0	1



Along with high pH, Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are found making it favorable for dissolution of fluorite (Singh et al. 2013). However, other minerals and ionic constituents of water may influence the dissolution of fluorite in groundwater (Table 16.4).

## 16.6 Conclusion

The conventional graphical plot along with the geochemical modeling helps in understanding the geochemical process leading to fluoride enrichment in groundwater of the study area. Groundwater is the only source of portable water supply in arid and semiarid regions of India. High concentration of fluoride in the well water is a severe public health concern. The anthropogenic influence of fluoride in groundwater is not much possible in these regions thus the high fluoride in groundwater is mostly of geogenic nature. The study suggests that water samples from Bhatinda are less saline in comparison with the Jaisalmer and Pokhran.

**Table 16.4** Saturation indices of water samples

Sample no	SI (Calcite)	SI (Dolomite)	SI (Gypsum)	SI (Fluorite)
BTD 1	0.8409	2.2897	-5.1374	-1.3318
BTD 2	0.9099	2.423	-5.026	-1.0761
BTD 3	1.2503	2.8901	-4.5678	-0.9933
BTD 4	1.5672	3.2515	-4.4698	-0.1366
BTD 5	0.8996	2.3508	-4.7714	-1.4558
BTD 6	1.855	3.4058	-4.3443	-0.1066
BTD 7	0.3954	1.3264	-5.5443	-1.8284
BTD 8	1.2994	2.808	-5.1591	-0.4183
BTD 9	1.0653	2.5981	-4.341	-1.0246
BTD 10	0.9843	2.8721	-5.4883	-2.0074
JAI 1	0.78	1.4536	-1.295	0.0842
JAI 2	0.3381	0.7609	-1.6484	-0.1166
JAI 3	0.2573	0.8883	-1.7564	-0.5195
JAI 4	0.6765	1.1948	-1.6705	-0.5045
JAI 5	0.6886	1.3476	-1.7254	-0.2034
JAI 6	0.6824	1.1464	-1.7646	-0.4029
JAI 7	0.6863	1.2332	-1.5207	-0.4481
JAI 8	1.1026	2.1054	-1.4141	-0.4811
JAI 9	0.4746	1.0387	-1.6681	-0.3009
JAI 10	0.7229	1.3928	-1.7638	-0.4952
POK 1	1.1512	1.8648	-1.7407	0.2395
POK 2	0.4499	0.7862	-1.4516	0.0748
POK 3	1.6229	3.0907	-1.2511	0.4148
POK 4	1.2482	2.3845	-1.568	0.151
POK 5	0.6317	1.0639	-1.5646	-0.3054
POK 6	0.7676	1.7277	-1.401	-1.0869
POK 7	0.6049	1.1655	-1.7915	-0.1531
POK 8	0.4686	1.2319	-2.0574	-0.5088
POK 9	0.9947	1.754	-1.6971	0.3371
POK 10	0.5732	1.2197	-1.7376	0.5254

Extreme climate along with the geochemical process is the main controlling factor governing the fluoride concentration in groundwater in both of these regions. Weathering of silicate minerals along with evaporate dissolution is the major hydrogeological process in Bhatinda, while in Jaisalmer and Pokhran the chemical characteristics of groundwater are evolved mainly because of evaporate dissolution. High-temperature low precipitation, ion-exchange, and highly alkaline condition along with weathering and dissolution of fluoride-containing minerals are responsible for fluoride contamination in groundwater.



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