**ORIGINAL ARTICLE**

# Groundwater fluoride contamination in Coimbatore district: a geochemical characterization, multivariate analysis, and human health risk perspective

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## Abstract

In this paper, fluoride geochemistry and health risk of groundwater in Coimbatore district is studied. The order of dominance of ions were $HCO_3 > Cl > SO_4 > CO_3$ and $Na > Ca > Mg > K$. Alkaline groundwater and the dominance of $HCO_3$ and Na is favourable for the fluoride enrichment. Around 46% of the samples, N–NE regions, have $F^-$ higher than permissible limit of 1.5 mg/L. Pink granites, charnockite and gneisses in lithology is the possible origin of $F^-$. However, $NO_3$ vs F plot shows positive trend in some samples, indicating anthropogenic inputs of $F^-$. Correlation plots of $F^-$ was trending positive with pH, $HCO_3$ and Na and but negative for Ca, indicating the control of these ions in $F^-$ mobility. This result is supported by undersaturation of fluorite and supersaturation of carbonates. Four significant principal components were derived, which have explained 87% of the total variation. PC1 has high factor loadings for EC, Ca, Mg Na, Cl, $SO_4$, $NO_3$ indicating both natural and anthropogenic influences. PC2, PC3 and PC4 have higher loading for pH and $HCO_3$, K and $HCO_3$ and $F^-$, respectively, indicating geogenic factors in the $F^-$ enrichment. Human health risk assessment (HHRA) by ingestion and dermal pathways were calculated using Hazard Quotient HQ and Hazard Index (HI). 27% of males, 36% of females and 39% of the children have HI > 1, posing noncarcinogenic risks.

**Keywords** Fluoride · Geochemistry · Multivariate analysis · Human health risk assessment (HHRA) · Revised permissible limits · Coimbatore

## Introduction

Groundwater is one of the most widely used natural resources and it is serving a major portion of the world's population for safe drinking water. Groundwater contamination is a global issue for human health and thus an important concern in water supply schemes (Sajil Kumar 2017). The consumption of contaminated groundwater may cause serious health effects on human beings and other organisms (Majolagbe et al. 2016). Groundwater contamination occurs due to both natural and manmade activities (Sajil Kumar et al. 2014; Gu et al. 2017). The biggest contaminant sources are industrial pollution, septic tanks, storage tanks for chemicals and oils etc., hazardous wastes, landfills, saline intrusion in coastal areas, atmospheric depositions, and rock–water interactions, among the types of contamination that occur due to natural enrichment, fluoride is one of the major factors. We focus on the enrichment of fluoride in groundwater and its adverse effects on human beings.

High concentration of fluoride in groundwater can cause serious health impacts such as dental skeletal fluorosis in human beings (Ahada and Suthar 2017; Li et al. 2019a, b). The major sources of fluoride in groundwater are marine aerosols, volcanic gases, and fluoride bearing minerals (fluorite, biotite, apatite etc.,). The most important mechanisms that control fluoride in groundwater are ion exchange, dissolution and precipitation of fluoride minerals, sorption processes and human activities (Su et al. 2019). Certain chemical conditions like alkaline pH, bicarbonate, presence of calcium minerals also have a significant role in the presence of fluoride in the aqueous environment (Apambire et al. 1997). Thus Na–Ca ion exchange plays a vital role in fluoride chemistry (Sajil Kumar et al. 2014).

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India is one of the countries in the world that is experiencing the most severe health problems with groundwater contamination, especially with regard to fluoride. The most affected states are Rajasthan, Gujarat, Andhra Pradesh, Karnataka, Tamil Nadu, and Kerala (Indu et al. 2007; Sajil Kumar et al. 2014). It is predicted that around 120 million i.e., 9% of the total population India have an exposure risk due to fluoride (Podgorski et al. 2018). In a study in Telangana, Reddy et al. (2019) reported that the entire state can be classified into four categories very high (17.6%), high (15.8%), medium (32.7%) and low (33.9%) fluoride contamination. Apart from the geological and hydrogeological factors, the dry climate is also acting as an important factor of fluoride enrichment (Gupta et al. 2005; Samal et al. 2020). This information is confirmed from Western Indian states Gujarat (Prajapati et al. 2017), Rajasthan (Kesari et al. 2021) and south Indian states Tamil Nadu (Sajil Kumar 2017) and Andhra Pradesh (Adimalla et al. 2019).

According to the WHO (2011), the permissible level of fluoride in drinking water is 1.5 mg/L, which is an international standard. However, the guideline values in India are proposed and practiced by the Bureau of Indian Standards (BIS 1992). According to BIS standards, the acceptable limit of fluoride is 1 mg/L, and in case of no alternative sources it can be permitted till 1.5 mg/L. The geochemistry and weather conditions of India often favour the enrichment of fluoride in groundwater. The health impacts of fluoride are directly proportional to the daily intake of fluoride into the digestive system. But in different climatic regions the amount of water intake varies considerably, and the ingestion of the fluoride is also varying. Thus, the proposed guideline values do not always highlight the exact conditions. In this study we considered the Bureau of Indian Standards for the analysis.

Groundwater fluoride enrichment is a well discussed topic in Indian as well as global context (Saxena and Ahmed 2001). Several studies have focused on groundwater quality (Ramesh and Elango 2011; Ahmad and Qadir 2011; Aleksis 2011), occurrence and mobility of fluoride in groundwater (Wu et al. 2015), spatial variation mapping using geo-statistics (Choudary et al. 2019; Thapa et al. 2017; Fallahzadeh et al. 2018), multivariate statistical analysis (Salifu et al. 2012; Rashid et al. 2020), and many more. Kumar et al. (2018) studied the dynamics of fluoride contamination in Indo-Gangetic plain using geochemical and isotopic methods. They have reported F levels up to 5.8 mg/L, predominantly controlled by ion exchange and prolonged residence time. Raj and Shaji (2017) identified that the dissolution of fluoride from the minerals is favoured by Na-HCO$_3$ water type with less Ca and alkaline pH and subsequently elevated the F levels up to 2.88 mg/L. Aravinthasamy et al. (2020) studied the fluoride contamination in Shanmunganadhi basin

and identified a considerable variation in pre- and post-monsoon seasons.

In this study, we use the geochemical and multivariate statistical techniques to study the source and mobilization of fluoride in groundwater and evaluate the possible health risks of the same on human beings in the Coimbatore district in Tamil Nadu.

## Materials and methods

### Description of the study area

Coimbatore is mostly bounded by the mountain range Western Ghats in the West and the South, with a general trending slope eastward. A location map of the study area and sampling wells are shown in Fig. 1. This area has a subtropical climate with a wide range from 14° to 40 °C (CGWB 2008; Sajil Kumar and James 2016). This is a monsoon fed area, in which northeast monsoon is dominant over the southwest monsoon and average annual rainfall in Coimbatore is 647 mm. Metamorphic rocks are prominent in Coimbatore, and the most common rock types are charnockite, granites, hornblende–biotite gneiss, sillimanite gneiss with basic and ultra-basic intrusive, crystalline limestone, syenite, pegmatite and quartz veins (Fig. 2). Among these, hornblende–biotite gneiss are most widely seen all over the district. Sedimentary deposits such as colluviums, alluvium and kankar are observed near the aforementioned rivers. Fluvial processes are controlled by geomorphology, structural as well as denudational processes. Several soil types are mostly red calcareous soil, black soil, red non-calcareous soil, alluvial and colluvial soil, brown soil and forest soil. Groundwater is commonly found in fractures and fault regions in the hard rocks and in porous media in the alluviums associated with river systems. However, weathered zones (up to 30 m in depth) are the important aquifers in this region. Two major groundwater flow patterns were identified, one as towards eastern part along with flow paths of the Noyyal River and the other towards SW direction. Detailed information about the study area is reported in earlier studies (CGWB 2008; Sajil Kumar and James 2016).

### Groundwater samples and analytical techniques

Groundwater samples ($n=33$) were collected from the Coimbatore District for hydrochemical analysis. Selected wells were pumped out approximately 10 min, so that the physical parameters such as EC and pH were stabilized. The water level of these wells varied considerably between 8.75 and 38.8 mbgl, with an average 18.09 mbgl. Previously cleaned polythene containers of 1 L capacity were used to store the collected samples. Sample bottles were immediately transferred to the

**Fig. 1** Study area map of Coimbatore district showing sample location
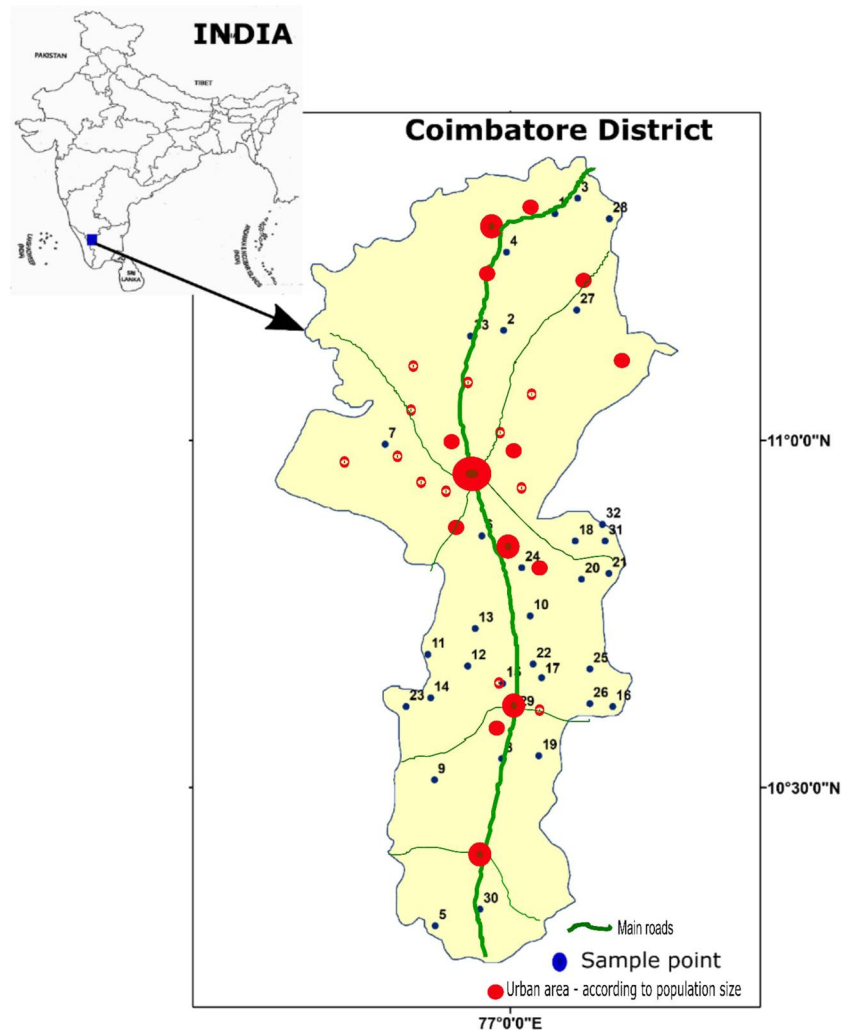


laboratory as soon as the in situ parameters were measured. In the field, EC and pH were measured with portable digital meters. Carbonate and bicarbonate were determined by acid titration using $H_2SO_4$. Chloride concentration was determined using argentometric titration with $AgNO_3$. Sulphate levels in the groundwater were measured using the UV–visible spectrophotometer. Sodium and potassium were analysed using a flame photometer. Among the cations, Ca and Mg were measured using the EDTA titration method, and Na and K with a flame photometer (APHA 1995). Concentrations of fluoride ($F^-$) in the groundwater were measured using a HANNA pH/ISE bench meter, USA (HI 4222). The iron balance error (IBE) has been calculated to check the quality of the analytical data, and which is found to be less than $\pm 5\%$.

## Hydrogeochemical methods and mineral speciation modelling

Hydrogeochemistry was analysed and the interpretations were done piper trilinear plot and bivariate chemical cross plots.

Aqueous speciation modelling was done by the PHREEQC (Appelo and Postma 1999) interphase in the software package Aquachem 4. Saturation indices are a useful tool in the identification of possible geochemical reactions in the groundwater environment. The calculation (see Eq. 1) is as follows,
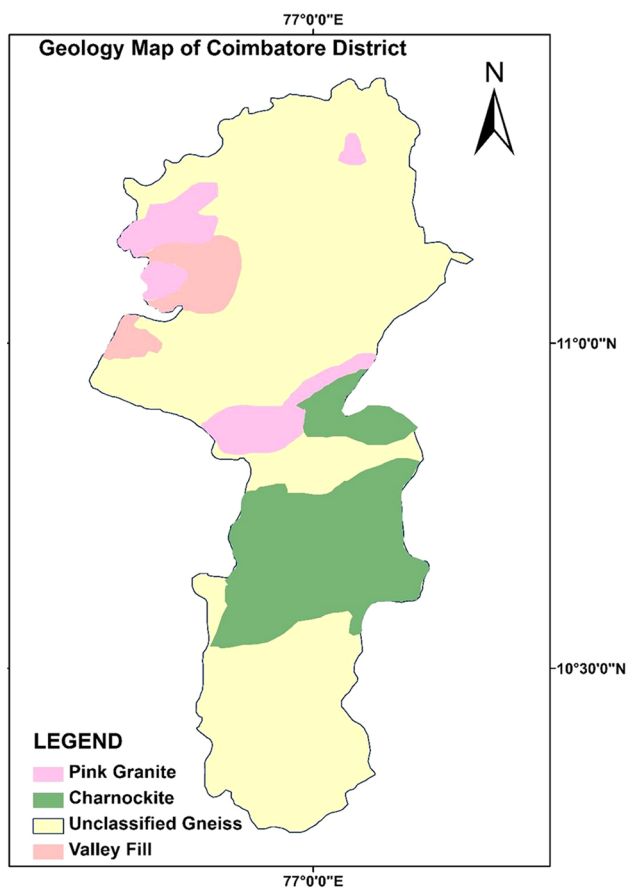
**Fig. 2** Geology map of the study area

$$SI = \log \left( \frac{IAP}{Ksp} \right). \tag{1}$$

Here, where IAP is the ion activity product of the dissociated chemical species in the solution, Ksp is the equilibrium solubility product for the chemical involved at the sample temperature. A positive SI of a mineral indicates that the groundwater is saturated with that mineral and a negative SI shows under saturation of the corresponding mineral.

## Multivariate statistical and geostatistical techniques

In this study, principle component analysis is used as a data reduction technology in which the multidimensional data of groundwater chemistry has been reduced to a less dimensional database, without losing any vital information concerning the hydrochemistry. In the first step, the interconnection between the parameters has been estimated using a correlation matrix. Principle component analysis has been performed using the data analysis package XLSTAT for Windows. The number of influencing principle components was determined based on the Eigen values, and the

extraction of the factors was based on the variances and covariances of the parameters. Finally, by the process of rotation, the loading of each variable on one of the extracted factors is maximized and the loadings of all the other factors are minimized (Sajil Kumar 2019).

Spatial variation maps of fluoride and other related parameters have been done by the Kriging method available in the ArcGIS software.

## Human health risk (HHR) assessment

Adverse effects on human health due to exposure to a certain chemical over a period either by inhalation, ingestion, or dermal pathways need serious attention (USEPA 2014). We studied the health impact of an elevated level of fluoride in drinking water on populations of different age groups such as infants, children and adults. Exposure risk of fluoride by ingestion and dermal pathways using the following Eqs. (2) and (3):

$$CDD_{IN} = (C_{water} \times IR \times EF \times ED)/(BW \times AT) \tag{2}$$

$$CDD_{DE} = (C_{water} \times SA \times KP \times EF \times ED \times ET \times CF)/(BW \times AT). \tag{3}$$

In these equations, $CDD_{IN}$ and $CDD_{DE}$ represent the chronic daily dose by ingestion and dermal effects, respectively ($\mu g/kg$ day). $C_{fw}$ is the concentration of fluoride in groundwater in mg/L. IR represents the ingestion rate of water in L/day (adults = 2.5 L/day; children = 0.78 L/day), SA denotes the exposed skin area in $cm^2$ (adults = 16,600 $cm^2$; children = 12,000 $cm^2$); KP represents the dermal permeability coefficient for water (0.001, it has no unit); and EF is the water exposure frequency (365 days). ED is the yearly exposure duration in years (males = 64, females = 67, and children = 12); ET is the water exposure time in hours/day (0.4 h/day for adults and children); BW is the body weight in kg (65, 55, and 15 for men, women, and children respectively); AT is the average residence time measured in days/year, and CF is the unit-less conversion factor (0.001 for adults and children).

The Hazard Quotient (HQ) of fluoride exposure due to ingestion and dermal pathways was calculated using Eqs. (4) and (5), below:

$$HQ_{IN} = CDD_{IN}/RfD \tag{4}$$

$$HQ_{DE} = CDD_{DE}/RfD. \tag{5}$$

$HQ_{IN}$ denotes the ingestion-based Hazard Quotient and $HQ_{DE}$ is the dermal based Hazard Quotient. RfD is the reference dose of fluoride i.e., 0.04 mg/kg/day (Li et al. 2016). HQ < 1 has negligible non-carcinogenic effects, while on

the other hand HQ > 1 shows significant non-carcinogenic health hazards.

Hazard index (HI) is the total risk of exposure via digestion and dermal pathways

$$HI = HQ_{ingestion} + HQ_{dermal}. \qquad (6)$$

As we discussed for the Hazard Quotient (HQ), a combined exposure dose value less than 1.0 has no significant health impacts over a lifetime of exposure.

# Results and discussions

## General hydrogeochemistry

Physical and chemical characteristics of the groundwater in the Coimbatore District are shown in Table 1. The pH values in the region varied between 7.4 and 8.7, with an average value of 8.25. It is clear from these values that the groundwater is mainly alkaline nature (WHO 2011). The range of conductivity vales (180–6240 μS/cm) suggests that the water chemistry is highly varied within the study area. The TDS values clearly indicate the water quality status, which is widely varied between 100 and 3544 mg/L, with an average concentration of 841 mg/L. The order of dominance of major anions were $HCO_3 > Cl > SO_4 > CO_3$ and the same for cations were $Na > Ca > Mg > K$. Among the anions, bicarbonate dominated the list with a range between 69.3 and 604, and an average of 276.45. Though the maximum concentration of Cl was 1631, the average value is 218 mg/L. The average concentration of $SO_4$ was 70.15 mg/L. The carbonate concentration was negligible in the study area with an average of 7 mg/L. The most dominant cation was Na, which ranged between 7 and 690 mg/L, with an average of 113 mg/L. Figure 3 shows a Box Whisker plot that explains the statistical properties of all the major ions.

A Piper trilinear plot (Piper 1953) is used to understand different water types in the study area (Fig. 4). This shows that the groundwater is mostly dominated by Na and Mg in the cation chemistry and $HCO_3$ and Cl in the anions. The majority of the samples showed the $Na–Mg–HCO_3–Cl$ type of groundwater, which is favourable to fluoride. However, a mixing of Ca and $SO_4$ is also seen in some samples. The groundwater type of each sample is shown in Table 1.

## Fluoride concentrations in groundwater

In the Coimbatore District the values of fluoride concentration ranged between 0.47 and 2.03 mg/L. The international standard value for fluoride in the drinking water is 1.5 mg/L (WHO 2011). The Indian standard value of the maximum permissible limit of fluoride in the drinking is 1.5 mg/L

(BIS 1992) and this is followed in this study. As per the ISI (1983) norms the desirable limit of fluoride in groundwater to maintain the dental and skeletal health is 0.6–1.2 mg/L. Lower than 0.6 mg/L may cause dental caries and higher than 1.5 mg/L may cause dental fluorosis and, in certain cases, skeletal fluorosis. Among the 33 samples analysed, 27% of the samples had a lower fluoride concentration than 0.6 mg/L; 27% of the samples had a concentration between 0.6 and 1.2 mg/L; and the remaining 46% of the samples exceeded the maximum permissible limit 1.5 mg/L. Similar results of elevated concentrations of fluoride in groundwater has been reported from Raebareli district-Uttar Pradesh (Sahu et al. 2017) Karbi Anglong district, Assam (Hanse et al. 2019), Guntur district, Andhra Pradesh (Rao et al. 2020) and Ambadongar South Gujarat (Shirke et al. 2020).

## Spatial variation, geochemical evolution and speciation modelling of fluoride

A spatial variation map of fluoride has been created for the Coimbatore District (Fig. 5). It shows that the groundwater is relatively good in central, southern and southwestern region in the study area. The higher concentrations were observed in the north and north-eastern part of the area and in some patches in the south-eastern and central regions. An earlier study in the district by Sajil Kumar and James (2016) identified the groundwater flow paths and the F-concentration can be seen to increase exactly along the flow paths. The most important sources of fluoride in groundwater are the weathering and dissolution of fluoride rich minerals. The most common fluoride bearing minerals are amphibole, biotite, fluorite and apatite, which exist in hard rocks such as granitic and gneissic rocks (Edmunds and Smedley 2005; Sajil Kumar et al. 2015). Geological formations in the study area show that it is mostly comprising of pink granites, charnockite and unclassified gneisses. These rock types are abundant sources of the above-mentioned fluoride bearing minerals. Under favourable circumstances, i.e. availability fluoride minerals, pH, temperature, anion exchange capacity of aquifer materials, type of geological materials, residence time, porosity, structure, depth, groundwater age and concentration of carbonates and bicarbonates in water (Apambire et al. 1997), the fluoride ions will be released into the groundwater from the aquifers, consequently increasing the $F^-$ in groundwater.

The bivariate plots were created to study the relation between $F^-$ and pH, EC, Na, Ca, $HCO_3$, and $NO_3$. Selection of these parameters was based on inference from earlier studies and their significance in fluoride mobilization. Figure 6 shows the relation between F and pH and it indicates that in many samples, fluoride concentration varies positively with increasing pH. In the study area, all the groundwater samples were alkaline in nature and, under this condition, fluoride

**Table 1** Concentration of chemical characteristics of water types in groundwater samples

| Sample ID | Longitude | Latitude | pH | EC | TDS | TH | Ca | Mg | Na | K | Cl | SO4 | CO3 | HCO3 | NO3 | F | Water types |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 77.07 | 11.33 | 8 | 180 | 100 | 60 | 14 | 6 | 14 | 4 | 14 | 2 | 1 | 69 | 1 | 1.24 | Ca–Na–Mg–HCO3–Cl |
| 2 | 76.99 | 11.16 | 8.4 | 970 | 570 | 230 | 30 | 38 | 106 | 20 | 124 | 58 | 12 | 201 | 18 | 1.6 | Na–Mg–Cl–HCO3 |
| 3 | 77.10 | 11.35 | 8.5 | 750 | 370 | 215 | 38 | 29 | 44 | 18 | 60 | 48 | 5 | 170 | 6 | 1.39 | Mg–Na–Ca–HCO3–Cl |
| 4 | 76.99 | 11.27 | 8.5 | 1020 | 581 | 330 | 40 | 56 | 81 | 16 | 206 | 62 | 18 | 134 | 8 | 1.66 | Mg–Na–Cl–HCO3 |
| 5 | 76.88 | 10.25 | 7.9 | 1430 | 840 | 350 | 60 | 49 | 150 | 35 | 199 | 77 | 0 | 342 | 22 | 0.7 | Na–Mg–Ca–Cl–HCO3 |
| 6 | 76.96 | 10.86 | 8.1 | 1380 | 804 | 450 | 80 | 61 | 97 | 27 | 152 | 110 | 0 | 329 | 25 | 0.49 | Mg–Na–Ca–HCO3–Cl |
| 7 | 76.82 | 10.99 | 7.4 | 850 | 460 | 205 | 20 | 38 | 99 | 10 | 43 | 26 | 1 | 324 | 6 | 0.99 | Na–Mg–HCO3 |
| 8 | 76.99 | 10.54 | 8.6 | 590 | 345 | 185 | 56 | 11 | 35 | 36 | 35 | 10 | 8 | 217 | 6 | 0.47 | Ca–Na–HCO3 |
| 9 | 76.89 | 10.51 | 8.7 | 1360 | 811 | 450 | 60 | 73 | 46 | 102 | 213 | 19 | 24 | 238 | 35 | 0.56 | Mg–Ca–K–Cl–HCO3 |
| 10 | 77.03 | 10.75 | 8.2 | 740 | 393 | 300 | 74 | 28 | 21 | 21 | 32 | 5 | 4 | 291 | 7 | 0.93 | Ca–Mg–HCO3 |
| 11 | 76.88 | 10.69 | 7.6 | 930 | 509 | 285 | 50 | 39 | 76 | 16 | 128 | 34 | 0 | 293 | 4 | 0.67 | Na–Mg–Ca–HCO3–Cl |
| 12 | 76.94 | 10.68 | 8.6 | 830 | 474 | 250 | 46 | 33 | 71 | 16 | 64 | 24 | 9 | 250 | 14 | 1.21 | Na–Mg–Ca–HCO3–Cl |
| 13 | 76.95 | 10.73 | 8.1 | 1780 | 1121 | 340 | 68 | 41 | 161 | 176 | 213 | 29 | 0 | 580 | 32 | 0.71 | Na–K–HCO3–Cl |
| 14 | 76.88 | 10.63 | 8.6 | 730 | 418 | 245 | 50 | 29 | 39 | 35 | 82 | 12 | 8 | 202 | 10 | 0.54 | Ca–Mg–Na–HCO3–Cl |
| 15 | 76.99 | 10.65 | 8.2 | 6240 | 3524 | 1650 | 180 | 292 | 690 | 23 | 1631 | 413 | 0 | 403 | 21 | 2.03 | Na–Mg–Cl |
| 16 | 77.15 | 10.62 | 8.3 | 2590 | 1513 | 960 | 160 | 136 | 138 | 39 | 553 | 120 | 12 | 214 | 56 | 1.01 | Mg–Ca–Na–Cl |
| 17 | 77.05 | 10.66 | 8 | 920 | 521 | 320 | 50 | 47 | 60 | 13 | 117 | 106 | 0 | 214 | 5 | 0.97 | Mg–Na–Ca–HCO3–Cl–SO4 |
| 18 | 77.22 | 10.83 | 7.7 | 2150 | 1247 | 650 | 152 | 66 | 193 | 20 | 404 | 86 | 0 | 403 | 28 | 0.52 | Na–Ca–Mg–Cl–HCO3 |
| 19 | 77.04 | 10.55 | 8.5 | 1070 | 593 | 390 | 56 | 61 | 51 | 27 | 60 | 139 | 18 | 317 | 5 | 1.6 | Mg–Ca–Na–HCO3–SO4 |
| 20 | 77.10 | 10.80 | 8.6 | 780 | 423 | 295 | 64 | 33 | 35 | 22 | 60 | 10 | 10 | 260 | 8 | 0.58 | Ca–Mg–Na–HCO3–Cl |
| 21 | 77.14 | 10.81 | 8.2 | 4380 | 2598 | 1700 | 320 | 219 | 230 | 29 | 695 | 480 | 0 | 506 | 84 | 1.37 | Mg–Ca–Na–Cl–SO4 |
| 22 | 77.03 | 10.68 | 8.4 | 1240 | 682 | 400 | 70 | 55 | 94 | 23 | 149 | 15 | 6 | 445 | 11 | 1.88 | Mg–Na–Ca–HCO3–Cl |
| 23 | 76.85 | 10.62 | 8 | 720 | 385 | 320 | 52 | 46 | 12 | 14 | 82 | 38 | 2 | 178 | 7 | 0.7 | Mg–Ca–HCO3–Cl |
| 24 | 77.02 | 10.82 | 8.2 | 970 | 548 | 290 | 52 | 39 | 78 | 22 | 181 | 62 | 0 | 183 | 5 | 0.48 | Na–Mg–Ca–Cl–HCO3 |
| 25 | 77.12 | 10.67 | 8.5 | 810 | 435 | 245 | 44 | 33 | 69 | 10 | 60 | 91 | 6 | 194 | 8 | 0.8 | Na–Mg–Ca–HCO3–SO4–Cl |
| 26 | 77.12 | 10.62 | 7.9 | 1260 | 741 | 370 | 70 | 47 | 120 | 16 | 145 | 17 | 0 | 403 | 28 | 1.99 | Na–Mg–Ca–HCO3–Cl |
| 27 | 77.10 | 11.19 | 8.5 | 1230 | 739 | 480 | 48 | 87 | 64 | 20 | 238 | 29 | 18 | 146 | 36 | 1.6 | Mg–Na–Ca–HCO3–Cl |
| 28 | 77.23 | 11.33 | 8.4 | 1850 | 1012 | 410 | 64 | 61 | 230 | 23 | 234 | 43 | 12 | 604 | 10 | 1.8 | Na–Mg–HCO3–Cl |
| 29 | 77.01 | 10.61 | 8.3 | 1340 | 822 | 420 | 86 | 50 | 55 | 117 | 142 | 22 | 12 | 427 | 28 | 0.56 | Ca–Mg–K–HCO3–Cl |
| 30 | 76.96 | 10.33 | 8.1 | 240 | 135 | 95 | 26 | 7 | 7 | 11 | 21 | 10 | 1 | 74 | 2 | 0.49 | Ca–Mg–HCO3–Cl |
| 31 | 77.23 | 10.89 | 8.3 | 1190 | 720 | 450 | 48 | 80 | 69 | 20 | 206 | 22 | 6 | 165 | 42 | 1.6 | Mg–Na–Ca–Cl–HCO3 |
| 32 | 77.15 | 10.88 | 8.5 | 3850 | 2768 | 1180 | 184 | 175 | 368 | 18 | 553 | 48 | 18 | 79 | 308 | 1.4 | Na–Mg–Ca–Cl |
| 33 | 76.94 | 11.15 | 8.5 | 960 | 556 | 225 | 32 | 35 | 113 | 15 | 96 | 48 | 18 | 268 | 15 | 1.55 | Na–Mg–HCO3–Cl |
| Min | | | 7.40 | 180 | 100 | 60 | 14 | 6.08 | 7 | 4 | 14 | 2 | 0.00 | 69.30 | 1.00 | 0.47 | |
| Max | | | 8.70 | 6240 | 3524 | 1700 | 320.00 | 291.60 | 690 | 176 | 1631 | 480 | 24 | 604 | 308 | 2.03 | |
| Avg | | | 8.25 | 1434.24 | 841.15 | 446.82 | 74.06 | 63.59 | 112.61 | 30.73 | 217.94 | 70.15 | 6.91 | 276.45 | 27.30 | 1.09 | |
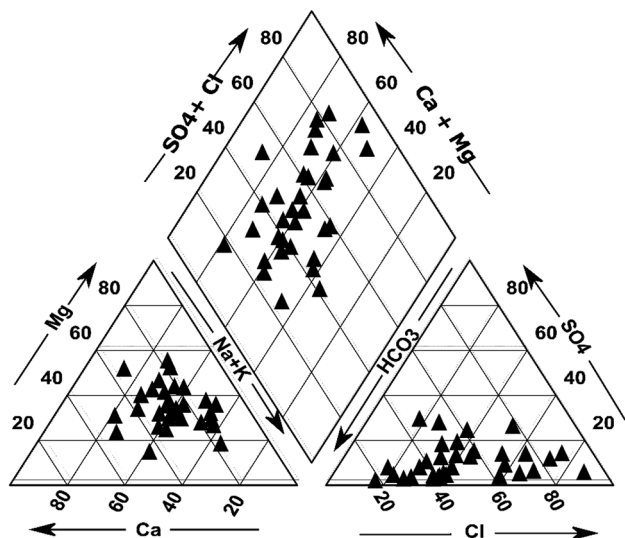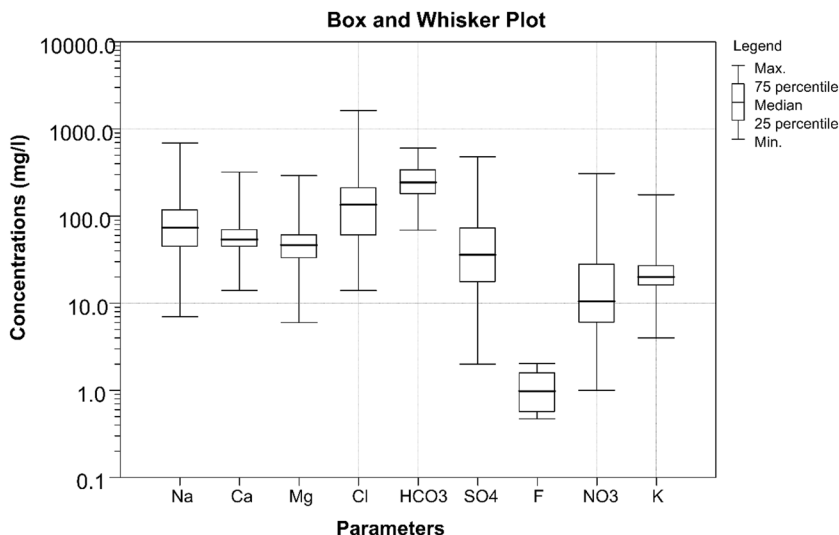
**Fig. 4** Piper diagram showing the water types in the study area

ions will desorb from the mineral phase and subsequently increase the leaching process (Wodeyar and Sreenivsan 1996; Saxena and Ahamed 2001). In addition to this, the relation between F and $HCO_3$ was plotted (see Fig. 7) and shows a relation similar to pH. The possible chemical reaction in an alkaline environment is shown in Eq. (1):

$$CaCO_3(s) + H^+ + 2F^- \rightarrow CaF_2(s) + HCO_3^-. \tag{7}$$
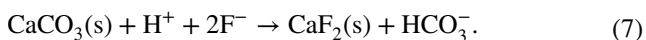
When there is excess $HCO_3$, there is a tendency to react with Ca to form $CaCO_3$. The main reason for this is the greater affinity of $HCO_3$ over calcium to attain stability. In this way more F ions will be released to the solution. Moreover, in the presence of an excess concentration of
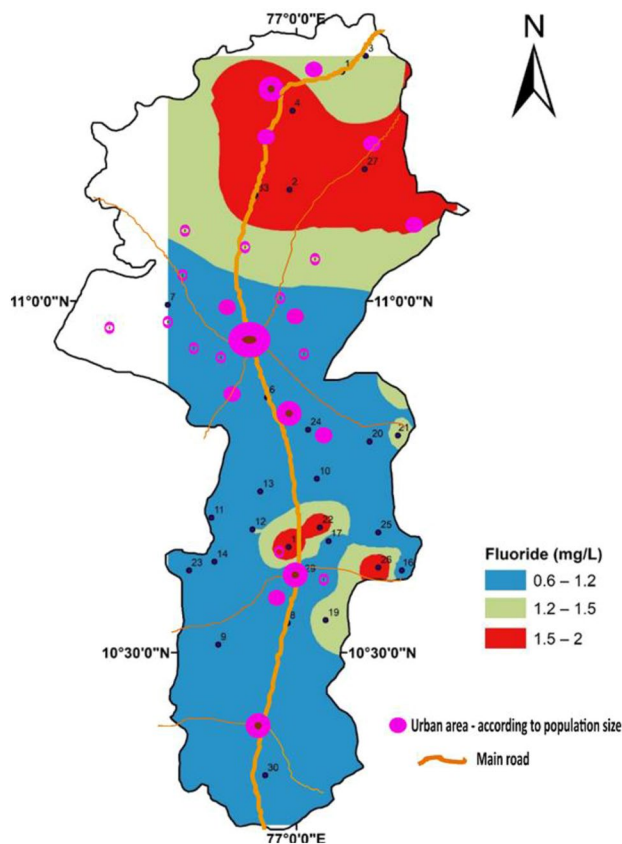


**Fig. 5** Spatial variation of fluoride in groundwater in Coimbatore district

bicarbonate, the number of adsorption sites will decrease and subsequently fluoride will be released into the solution. Thus, those samples that showed a positive relation between F and $HCO_3$, suggest the above-mentioned mechanism.
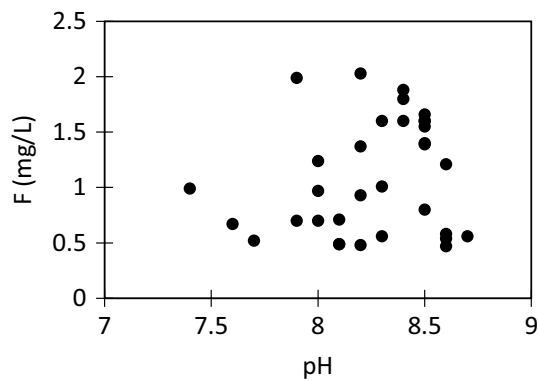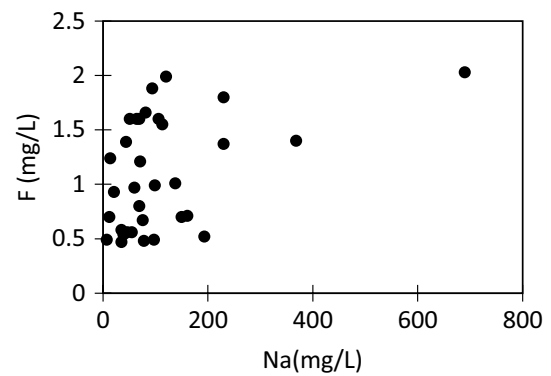
**Fig. 6** Bivariate plot between pH and fluoride
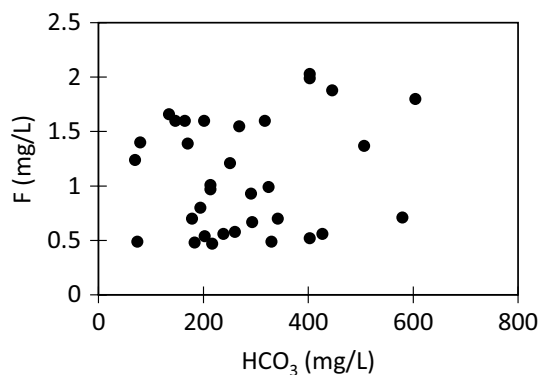


**Fig. 7** Bivariate plot between bicarbonate and fluoride



**Fig. 8** Bivariate plot between calcium and fluoride



**Fig. 9** Bivariate plot between sodium and fluoride
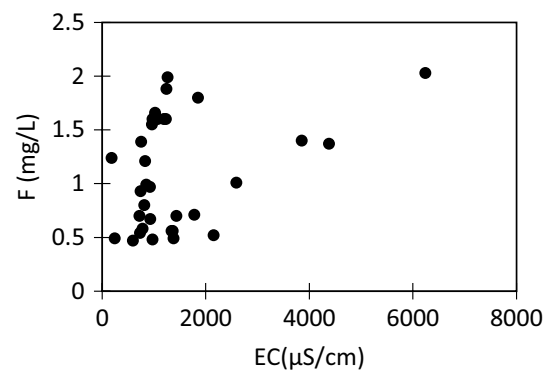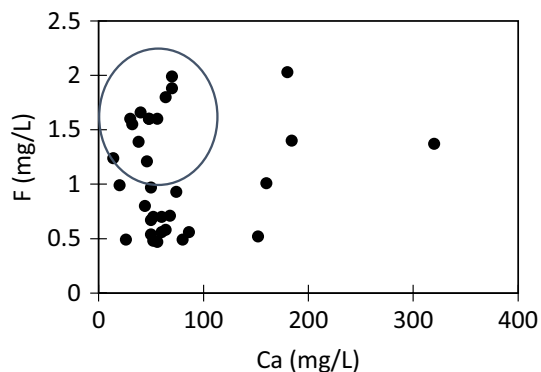


**Fig. 10** Bivariate plot between EC and fluoride

$$Ca^{2+} + 2F^- \rightarrow CaF_2.$$

Figure 9 shows the relation between $Na^+$ and F, revealing that there is a positive relationship between these two ions. The sources of sodium in groundwater can be the weathering of silicate minerals or anthropogenic influences (Sajil Kumar 2013; Li et al. 2019a). There is a dynamic cation exchange between Ca and Na in the groundwater (Li et al. 2018). In general, the Na from the solution will be replaced by the Ca from the aquifers. As the Ca concentration has a controlling nature on the F dynamics, the influence of Na is always an important factor for the mobilization of fluoride (Currell et al. 2011). The relation between EC and F has also been plotted to understand the trend of fluoride in the total ionic concentration of the study area. There are many samples in this study which show a positive relation with F (see Fig. 10).

There are reports on the anthropogenic inputs of fluoride in groundwater (Kumar et al. 2007; Brindha et al. 2011; Kim et al. 2010; Sajil Kumar 2012). There are sources like brick industries, and fertilizers that can bring considerably higher concentrations of fluoride to the groundwater. To

The relation between $Ca^{2+}$ and $F^-$ has been plotted in Fig. 8, which shows that most of the samples having a higher concentration of fluoride have very low calcium concentrations. As the concentration of calcium increased in groundwater, the solubility of fluoride decreased as it combines with $Ca^{2+}$ and precipitate as calcium fluoride ($CaF_2$). This can be expressed in the following equation,
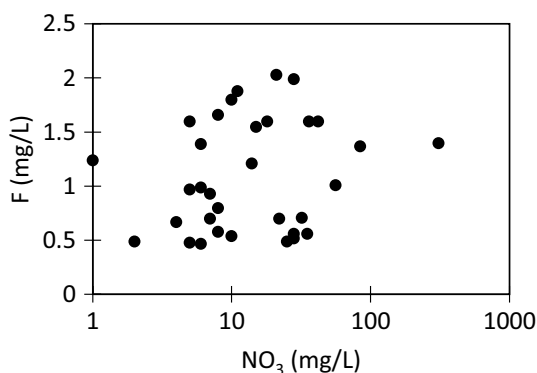
**Fig. 11** Bivariate plot between $NO_3$ and fluoride

understand this, the cross plot between $NO_3$ and F is plotted in Fig. 11. According to this plot, there are samples varying positively with increasing nitrate concentration. Presence of brick industries and extensive usage of fertilizers can be responsible for this. However, this anthropogenic origin of fluoride may be considerably less while compared to the natural sources.

Geochemical modelling was done to understand the chemical equilibrium within the groundwater environment. Saturation Indices (SI) for anhydrite, aragonite, calcite, dolomite, fluorite, gypsum and halite were calculated, and the results were plotted in Fig. 12. Calcite and fluorite are the important minerals in the context of fluoride mobilization (Adimalla 2020). All the samples were undersaturated with respect to fluorite, halite, gypsum and anhydrite. Undersaturated fluorite is a clear indication that the groundwater can dissolve more of this mineral and thus the possibility of increasing the concentration in the solution is greater. Similarly, the sulphate minerals anhydrite and gypsum were also undersaturated. Halite Saturation indices also showed

undersaturation with Na and Cl. An increase in Na concentration in the groundwater may help in the cation exchange process with Ca, and subsequently increase the concentration of fluoride. On the other hand, calcium minerals such as anhydrite, calcite and aragonite were mostly positively saturated (SI > 1) and further dissolution is not possible and will be precipitating as $CaF_2$.

## Principle component analysis (PCA)

A PCA of the Coimbatore District was done on the 33 groundwater samples and 14 parameters. In the initial step, the correlation matrix of each ion was generated (see Fig. 13). Several principle components (PC) were obtained and based on the Eigen value (> 1), four significant PC is extracted (see Table 2). The Eigen values for PCA 1, 2, 3 and 4 were 7.6, 2.0, 1.45, and 1.10, respectively. The highest Eigen values always represent the highest variance within the data (Chabukdhara et al. 2017). The four extracted principle components explained 87.2% of the total variance in the dataset. The highest variance represents the most significant process or mix of processes that control the hydrogeochemistry of the study area (Yidna et al. 2010; Salifu et al. 2012; Gupta et al. 2018). The core application of PCA in this study would be to identify the geochemical processes and the origin of ions in the groundwater.

PC1 has high factor loadings for EC (0.98), TDS (0.98), TH (0.98), Ca (0.89), Mg (0.97), Na (0.88), Cl (0.98), $SO_4$ (0.81), $NO_3$ (0.57), and moderate loading for F (0.31). It is obvious that the EC values directly relate the TDS and TH. Other than the fact that higher factor loadings for Ca and $SO_4$ may be attributed to the dissolution of gypsum and anhydrite, and it may also be noted that both these minerals are undersaturated in all samples. High loadings for Na, Cl and $NO_3$ show the influence of anthropogenic activities.

**Fig. 12** Results of geochemical modelling of 33 groundwater samples in the study area
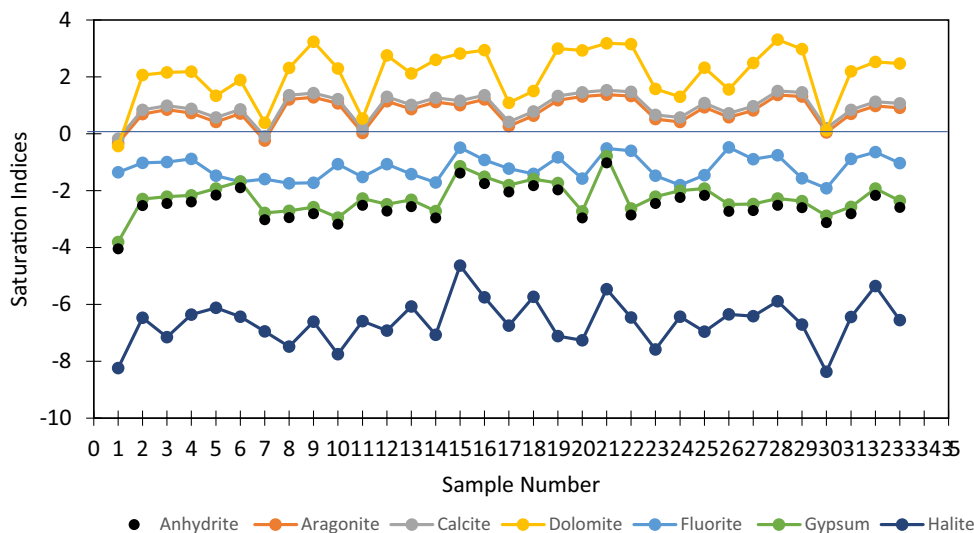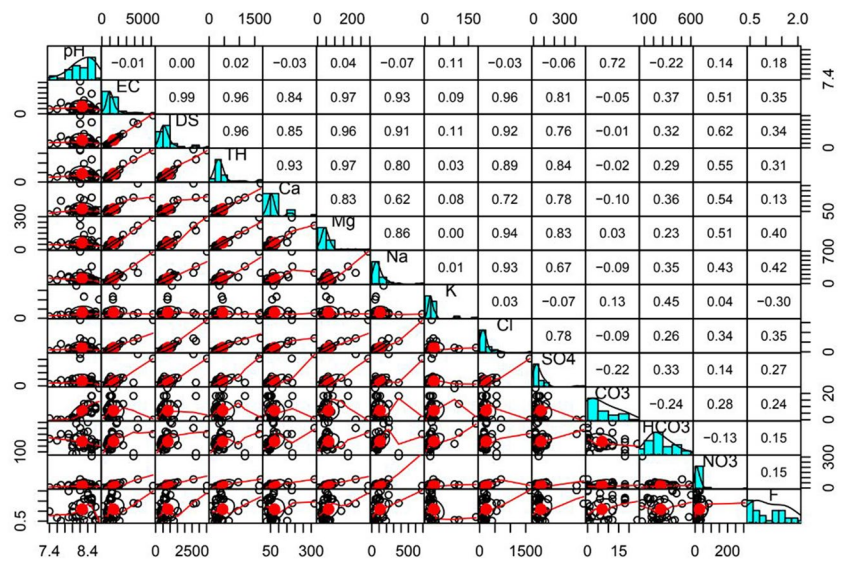
**Fig. 13** Correlation matrix of the physicochemical parameters in the groundwater



In earlier studies, Sajil Kumar and James (2016) reported that the district has contamination sources like industrial effluents from textile and paper industries, intensive irrigation activities with treated wastewater, and uncontrolled application of fertilizers. These are the primary reasons for the higher factor loading in PC1. However, the other sources of Na, Ca and Mg may be due to the weathering of silicate minerals. Weathering and rock–water interaction activities are further proved by the presence of moderate loading for F in PC1. Overall, PC1 is mostly controlled by natural and anthropogenic influences. This component

**Table 2** Principal component analysis of groundwater samples in Coimbatore district

| Parameters | Principal component | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| pH | − 0.027 | 0.872 | 0.01 | 0.09 |
| EC | 0.984 | 0.007 | 0.125 | 0.086 |
| TDS | 0.988 | 0.059 | 0.086 | 0.008 |
| TH | 0.983 | 0.024 | 0.038 | 0.016 |
| Ca | 0.892 | − 0.051 | 0.096 | − 0.161 |
| Mg | 0.973 | 0.068 | 0.001 | 0.124 |
| Na | 0.877 | − 0.042 | 0.089 | 0.228 |
| K | 0.018 | 0.218 | 0.826 | − 0.411 |
| Cl | 0.921 | − 0.049 | 0.07 | 0.188 |
| SO$_4$ | 0.812 | − 0.209 | 0.088 | 0.23 |
| CO$_3$ | − 0.056 | 0.931 | − 0.033 | 0.051 |
| HCO$_3$ | 0.266 | − 0.24 | 0.821 | 0.221 |
| NO$_3$ | 0.598 | 0.378 | − 0.278 | − 0.427 |
| F | 0.31 | 0.27 | − 0.11 | 0.802 |
| % of variance explained | 53.3 | 14.33 | 10.72 | 8.9 |
| Cumulative % variance Explained | 53.30 | 67.6 | 78.4 | 87.2 |

has explained 53.3% of the variance of the total dataset. Additionally, very high loading for TDS in PC1 and negligible loading in the other three groups indicates that the processes evident in this group contribute more to the total ionic concentration of the groundwater in the study area.

PC2 is characterized by high factor loading for pH and CO$_3$. Interestingly Ca, Mg and HCO$_3$ have either very low or negative loadings in this group. Similar results were reported by Rao et al. (2007), who interpreted that this kind of grouping is a process of alkalinity. Though the study area has mostly crystalline rocks, the weathering process can give rise to clay minerals. The reactions which occur during interactions with clay minerals can influence the pH level significantly. During the recharge process, a higher amount of CO$_2$ will be absorbed by water and later converted to HCO$_3$ than during the weathering process (Jacks 1973). Weathering can increase the pH level when a larger amount of HCO$_3$ is converted to CO$_3$ (Berner and Berner 1987; Rao et al. 2007).

PC3 is dominated by potassium (0.82) and bicarbonate (0.82). Potassium is a common constituent of groundwater in semi-arid regions and is present mostly in crystalline rocks. A higher percentage is found in K feldspars (16%) and, following that, in K-Micas (5.2%) (Ahrens 1965). The other possible source of K is the weathering of secondary minerals (i.e. clays) and the most common of them are illite and transitional clay minerals. Co-occurrence of K and HCO$_3$ suggest that they are sourced from the weathering of the above-mentioned minerals.

PC4 has the most significant loading for fluoride (0.80). This suggests that the fluoride ion concentration is sourced from geogenic factors, mostly from F⁻ bearing minerals in the crystalline rocks. This is supported by the positive loading for Na and HCO$_3$ in this group. However, the fact that the loadings of the ions are not strong may

be due to the presence of other dominant processes in the origin of these ions, which has been explained in the earlier sections.

## Human health risk assessment (HRRA)

The groundwater quality assessment in the earlier section shows that the concentration of fluoride in 46% of the samples exceeded the Indian drinking water quality standard of 1.5 mg/L. As there are higher concentration fluoride in the groundwaters, the non-carcinogenic impacts are likely to be dangerous in countries like India, Bangladesh, China and many more. In the HRRA, we have calculated the non-carcinogenic risk through drinking and dermal pathways. For the drinking pathways, chronic daily intake (CDI) has been calculated as per the standard procedure mentioned in the Sect. 3.4. Similarly, the dermal pathway was evaluated using the dermally adsorbed Dose calculations. From these values the Hazard Quotient (HQ) and Hazard Index (HI) were derived. The detailed result for each sample is provided in Table 3.

**Table 3** Human health risk assessment of fluoride in groundwater by Hazard Quotient and Hazard Index

| SI | HQ (oral) | | | H (dermal) | | | Hazard Index (HI) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Male | Female | Child | Male | Female | Child | HI-male | HI-female | HI-children |
| 1 | 0.794872 | 0.939586 | 1.074667 | 0.002111 | 0.002495 | 0.006613 | 0.796983 | 0.942081 | 1.08128 |
| 2 | 1.025641 | 1.212369 | 1.386667 | 0.002724 | 0.003219 | 0.008533 | 1.028365 | 1.215588 | 1.3952 |
| 3 | 0.891026 | 1.053246 | 1.204667 | 0.002367 | 0.002797 | 0.007413 | 0.893392 | 1.056042 | 1.21208 |
| 4 | 1.064103 | 1.257833 | 1.438667 | 0.002826 | 0.00334 | 0.008853 | 1.066929 | 1.261173 | 1.44752 |
| 5 | 0.448718 | 0.530411 | 0.606667 | 0.001192 | 0.001408 | 0.003733 | 0.44991 | 0.53182 | 0.6104 |
| 6 | 0.314103 | 0.371288 | 0.424667 | 0.000834 | 0.000986 | 0.002613 | 0.314937 | 0.372274 | 0.42728 |
| 7 | 0.634615 | 0.750153 | 0.858 | 0.001686 | 0.001992 | 0.00528 | 0.636301 | 0.752145 | 0.86328 |
| 8 | 0.011298 | 0.356133 | 0.407333 | 0.0008 | 0.000946 | 0.002507 | 0.012098 | 0.357079 | 0.40984 |
| 9 | 0.358974 | 0.424329 | 0.485333 | 0.000953 | 0.001127 | 0.002987 | 0.359928 | 0.425456 | 0.48832 |
| 10 | 0.596154 | 0.70469 | 0.806 | 0.001583 | 0.001871 | 0.00496 | 0.597737 | 0.706561 | 0.81096 |
| 11 | 0.429487 | 0.50768 | 0.580667 | 0.001141 | 0.001348 | 0.003573 | 0.430628 | 0.509028 | 0.58424 |
| 12 | 0.775641 | 0.916854 | 1.048667 | 0.00206 | 0.002435 | 0.006453 | 0.777701 | 0.919289 | 1.05512 |
| 13 | 0.455128 | 0.537989 | 0.615333 | 0.001209 | 0.001429 | 0.003787 | 0.456337 | 0.539417 | 0.61912 |
| 14 | 0.012981 | 0.409175 | 0.468 | 0.000919 | 0.001087 | 0.00288 | 0.0139 | 0.410261 | 0.47088 |
| 15 | 1.301282 | 1.538193 | 1.759333 | 0.003456 | 0.004085 | 0.010827 | 1.304738 | 1.542278 | 1.77016 |
| 16 | 0.647436 | 0.765308 | 0.875333 | 0.00172 | 0.002032 | 0.005387 | 0.649155 | 0.76734 | 0.88072 |
| 17 | 0.621795 | 0.734999 | 0.840667 | 0.001651 | 0.001952 | 0.005173 | 0.623446 | 0.736951 | 0.84584 |
| 18 | 0.333333 | 0.39402 | 0.450667 | 0.000885 | 0.001046 | 0.002773 | 0.334219 | 0.395066 | 0.45344 |
| 19 | 1.025641 | 1.212369 | 1.386667 | 0.002724 | 0.003219 | 0.008533 | 1.028365 | 1.215588 | 1.3952 |
| 20 | 0.013942 | 0.439484 | 0.502667 | 0.000987 | 0.001167 | 0.003093 | 0.01493 | 0.440651 | 0.50576 |
| 21 | 0.878205 | 1.038091 | 1.187333 | 0.002333 | 0.002757 | 0.007307 | 0.880538 | 1.040848 | 1.19464 |
| 22 | 1.205128 | 1.424534 | 1.629333 | 0.003201 | 0.003783 | 0.010027 | 1.208329 | 1.428316 | 1.63936 |
| 23 | 0.448718 | 0.530411 | 0.606667 | 0.001192 | 0.001408 | 0.003733 | 0.44991 | 0.53182 | 0.6104 |
| 24 | 0.307692 | 0.363711 | 0.416 | 0.000817 | 0.000966 | 0.00256 | 0.30851 | 0.364677 | 0.41856 |
| 25 | 0.512821 | 0.606185 | 0.693333 | 0.001362 | 0.00161 | 0.004267 | 0.514183 | 0.607794 | 0.6976 |
| 26 | 0.047837 | 1.507884 | 1.724667 | 0.003388 | 0.004004 | 0.010613 | 0.051225 | 1.511888 | 1.73528 |
| 27 | 1.025641 | 1.212369 | 1.386667 | 0.002724 | 0.003219 | 0.008533 | 1.028365 | 1.215588 | 1.3952 |
| 28 | 1.153846 | 1.363915 | 1.56 | 0.003065 | 0.003622 | 0.0096 | 1.156911 | 1.367537 | 1.5696 |
| 29 | 0.358974 | 0.424329 | 0.485333 | 0.000953 | 0.001127 | 0.002987 | 0.359928 | 0.425456 | 0.48832 |
| 30 | 0.314103 | 0.371288 | 0.424667 | 0.000834 | 0.000986 | 0.002613 | 0.314937 | 0.372274 | 0.42728 |
| 31 | 1.025641 | 1.212369 | 1.386667 | 0.002724 | 0.003219 | 0.008533 | 1.028365 | 1.215588 | 1.3952 |
| 32 | 0.033654 | 1.060823 | 1.213333 | 0.002384 | 0.002817 | 0.007467 | 0.036037 | 1.06364 | 1.2208 |
| 33 | 0.99359 | 1.174483 | 1.343333 | 0.002639 | 0.003119 | 0.008267 | 0.996229 | 1.177601 | 1.3516 |
| Min. | **0.011298** | **0.356133** | **0.407333** | **0.0008** | **0.000946** | **0.002507** | **0.012098** | **0.357079** | **0.40984** |
| Max. | **1.301282** | **1.538193** | **1.759333** | **0.003456** | **0.004085** | **0.010827** | **1.304738** | **1.542278** | **1.77016** |
| Avg. | **0.610703** | **0.835452** | **0.955562** | **0.001877** | **0.002219** | **0.00588** | **0.61258** | **0.837671** | **0.961442** |

Bold values indicate the range and average of the human health risk analysis

The health risk of drinking high fluoride groundwater is assessed for the three different age groups and shows that men are less affected than females and children, with a general order of impact of male > female > children. The HQ for men varied between 0.01 and 1.3 with an average of 0.6; for women, it varied between 0.35 and 1.53 with an average 0.83; and for children, it varied between 0.40 and 1.76 with average of 0.95. In this study, the Hazard Quotient from ingestion is prominent (HQ > 1) in 27% of the samples in males, 36% in females and 39% in children's (see Table 4). The variation in the HQ values in adults and children were observed by many researchers from Tunisia (Guissouma et al. 2017), India (Adimalla et al. 2018), Iran (Radfard et al. 2018), China (Li et al. 2018). On the other hand, the HQ values based on dermal contact are well within the threshold value of 1 and there is no potential threat for human beings (please refer to Table 3 for details). Hazard Index (HI) values show the same trend as HQ fluoride as no potential impact via dermal activities has been found. In this study, we understand that the health impact is lowest for men and highest for children. The spatial variation map of HI for males, females and children is shown in Fig. 14.

## Conclusions

Fluoride enrichment in groundwater and the possible human health risks (HHRA) were assessed using classic geochemical methods, multivariate and geostatistical methods. Groundwater was alkaline in all samples, Na and $HCO_3$ were the dominant anion and TDS values varied from 100 to 3544 mg/L, suggesting a significant impact from the anthropogenic activities. The fluoride concentration varied from 0.47 to 2.03 mg/L, with 46% of the samples exceeding 1.2 mg/L. spatial map of fluoride is much higher in the N and NE regions compared to the central regions. Geology of the study area shows the influence of F-minerals like fluorite, mica and amphibole etc. on F levels. However, the concentration of Na, $HCO_3$ and Ca in the groundwater greatly influenced the F-enrichment and its mobility in aquifer matrix. Anthropogenic influences on F-concentration studied with F vs $NO_3$ plot, showed a positive relation in some samples referring to brick and fertilizer industries in the area. Geochemical modelling shows that the groundwater is under-saturated with fluorite and over-saturated with calcite, aragonite and dolomite. It is agreeing with the results of geochemical analysis. PCA showed four significant components, together explaining 87% of the total variance in the data. PC1 had 53.3% of the variance, with higher loading for EC, Ca, Mg, Na, Cl, $SO_4$, and $NO_3$, representing mixed natural

**Table 4**  Details of the HQ and HI values exceeding standard value

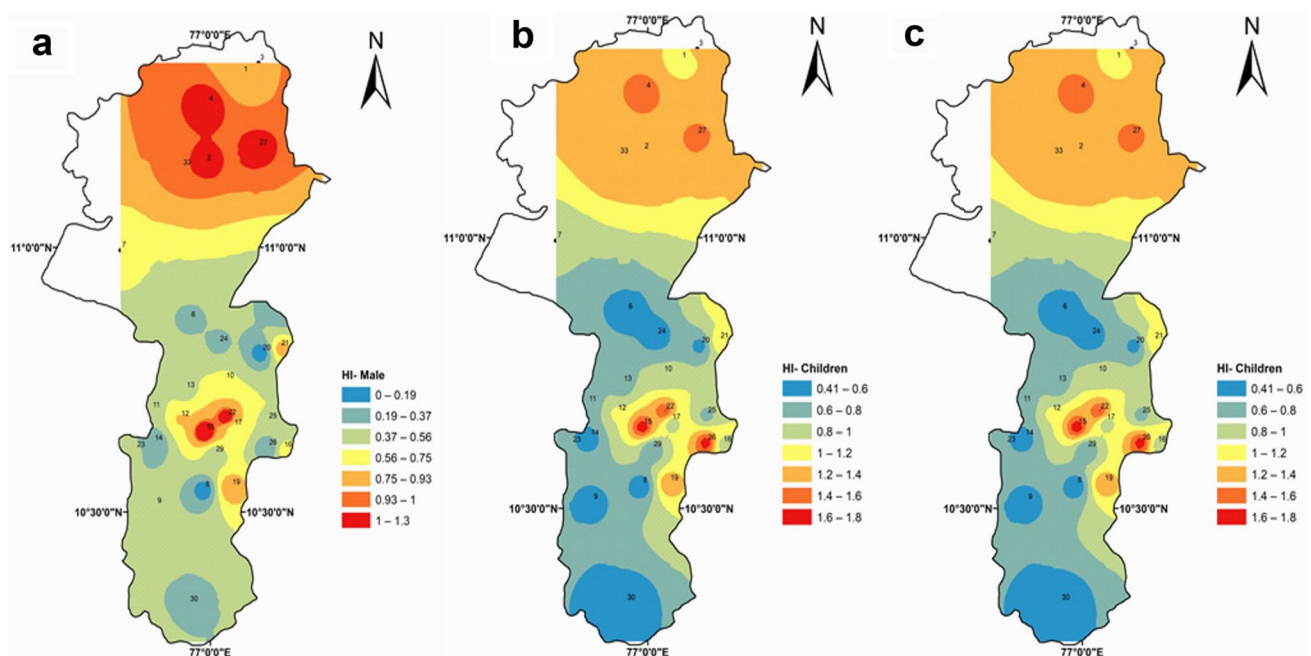|  | HQ-oral > 1 | HQ-dermal > 1 | HI > 1 |
| --- | --- | --- | --- |
| Men | 9 (27%) | 0 | 9 (27%) |
| Women | 12 (36%) | 0 | 12 (36%) |
| Children | 13 (39%) | 0 | 13 (39%) |



**Fig. 14** Spatial variation maps of Hazard Index (HI) for males, females and children

and anthropogenic processes. Factor loading of PC2 (pH and carbonates), PC3 (K and $HCO_3$) and PC4 ($F^-$), respectively. Thus, PC4 exclusively identified as the geogenic influence on enrichment of F. Exposure risk were calculated with Hazard Quotient (HQ) and Hazard Index (HI). The dermal pathway does not pose any non-carcinogenic risk, but the HQ of ingestion poses threats (HQ > 1), in 27% of males, 36% of females and 39% of children. Since the HQ for dermal pathways is negligible, the HQ for ingestion is equal to the HI. The influence of fluoride is severe in children, thus need special care with respect to fluoride contamination.

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