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GEOCHEMISTRY OF FLUORIDES IN GROUNDWATER: SALEM DISTRICT, TAMILNADU, INDIA

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High fluoride in groundwater is a major toxicological and geoenvironmental issue in India. The area selected for study, the Salem district, Tamilnadu State, India, has endemic fluorosis. To determine the geochemistry of fluoride in the local groundwater, samples were collected from major lithological units in the study area (Peninsular gneiss and charnockite) and analyzed for fluoride using standard procedures for two seasons, the pre- and post-monsoon. Higher fluoride was noted in the post-monsoon season in both charnockite (4.02 mg/l) and Peninsular gneiss (2.85 mg/l), indicating the ability of rainwater to dissolve greater concentrations of fluoride to groundwater from the aquifer matrix. Correlation and factor analysis confirms fluoride leaching from the aquifer matrix. Modeling results support the field observations.

INTRODUCTION

Fluorine is widely distributed in the environment and ranks 13th among the other elements in order of abundance in the earths crust. High levels of fluoride in drinking water are found in some countries such as India, China, Japan and parts of the Middle East and Africa. In India its occurrence in aquifer systems is endemic in many areas of Andhra Pradesh, Tamilnadu, Karnataka, Gujarat, Rajasthan, Punjab, Haryana, Bihar and Kerala. Fluoride in groundwater evokes considerable interest due to its unique character as regards to its impact on the physiological system of living beings**.** This is because low doses (<.5 mg/l) can contribute to tooth decay, whereas if consumed in concentrations >.5 mg/l it can cause fluorosis and related diseases. Abnormal levels of fluoride in water are common in fractured hard rock zones which are composed of minerals like topaz, fluorite, flourapatite, villuamite, cryolite and fluoride- replaceable hydroxyl ions in ferro magnesium silicates. Fluorspar occurs in structurally weak planes like shear fracture zones, joints and at the contact of host rock and vein quartz. Rock minerals weather and form calcium and magnesium carbonates, which serve as good sinks for fluoride ions. Fluoride ions from these minerals leach into the groundwater contributing to high fluoride concentrations. The leachable property of fluoride ions is governed by two factors: 1) pH of the leaching solutions and 2) dissolved carbon dioxide in the soil.

The major exposures in the study area are Peninsular gneiss and charnockite which have fluoride bearing minerals that are very susceptible to weathering and leaching processes. In the charnockite, apatite minerals were reported by Srinivasamoorthy (2005). Mica content is significant in the Peninsular gneiss. This study focuses on an area in Tamilnadu, which has been demarcated as an endemic fluorosis zone, to evaluate the fluoride concentrations, its relation to other ions, and its spatial distribution.

REVIEW OF LITERATURE

Fluoride ion, predominantly present in groundwater, is considered a toxicological geoenvironmental issue when present in excess or deficit amounts as it can affect bones and soft tissues like skeletal muscles, erythrocytes, gastrointestinal tissues and ligaments. Lower concentrations of fluoride in groundwater increase risk of tooth decay. High concentrations of fluoride in groundwater from granite and granitoid gneiss and lower concentration from volcanic and sedimentary rocks were identified by Kim (2006) in Korea. Higher fluoride was correlated with high bicarbonates, pH and temperatures of groundwater in Hermosillo city, Mexico, by Valenzuela-Vasquez (2006) who found groundwater residence times and flow were the main factors determining higher concentrations of flouride in groundwater. The spatial variation of fluoride in groundwater was studied in different lithological units by Kumar and Syed (1989) in the Haryana district. They highlight groundwater flow and hydrogeochemical characteristics related to the spatial variation of fluoride content. Srinivasamoorthy (2005) studied the spatial distribution of fluoride in groundwater of the Salem district of Tamilnadu, India, and showed that higher concentrations of fluorides are confined to lithological contacts. River recharge was identified as major source for fluoride in groundwater in part of the Assam district by Babulal et al. (2003). Ramamohana Rao et al. (1996) studied the distribution of fluoride in drinking water in India from the Nalagonda district of Andhrapradesh and identified low Ca^{2+} concentration in rock and soils, and high Na-HCO_3 in soil water as important factors favoring the presence of fluoride in the environment. Thermodynamic stability was used by Jacks (1993) in parts of southern India to identify that major sources of fluorides are from local lithologies. The relationship of fluoride ions in different rock types of the Erode district was studied by Chidambaram et al. (2003). They showed that higher molal ratio and ionic strength are major factors explaining high fluoride in groundwater.

STUDY AREA

The Mettur area selected for study lies in the NW part of Salem district of Tamilnadu, India between north latitudes 11°30’ and 11°57’ and east longitudes 77°45’ and 78°00’ (Figure 1). It falls in the Survey of India map 56 I with a total areal extent of 777.15 km^2. It is bounded by Karnataka on the north and the Erode district on the west. The southern part of the area contains hill ranges and high land areas and the eastern part is low lying floodplain of the river Cauvery. Small hillocks are distributed throughout the study area.

Geological setting

The study area is entirely underlain by Archean crystalline metamorphic complexes. The rocks of this group are highly weathered, jointed and covered by recent valley fills and soil cover in some places. A wide range of rock types occur due to recurring tectonic and magmatic activities in the Precambrian period which resulted in complicated structure and geology. The first major exposure of the district is Peninsular gneiss, which are Meta sedimentary in nature belonging to the Proterozoic – Archean system. Next prominent rock type is charnockite associated with foliated coarse grained garnetiferous leucocratic rocks called leptinites.

Aquifers of the study area

The occurrence and movement of groundwater in a hard rock terrain are restricted to open systems of fractures like fissures and joints in unweathered portions and also the porous zones of

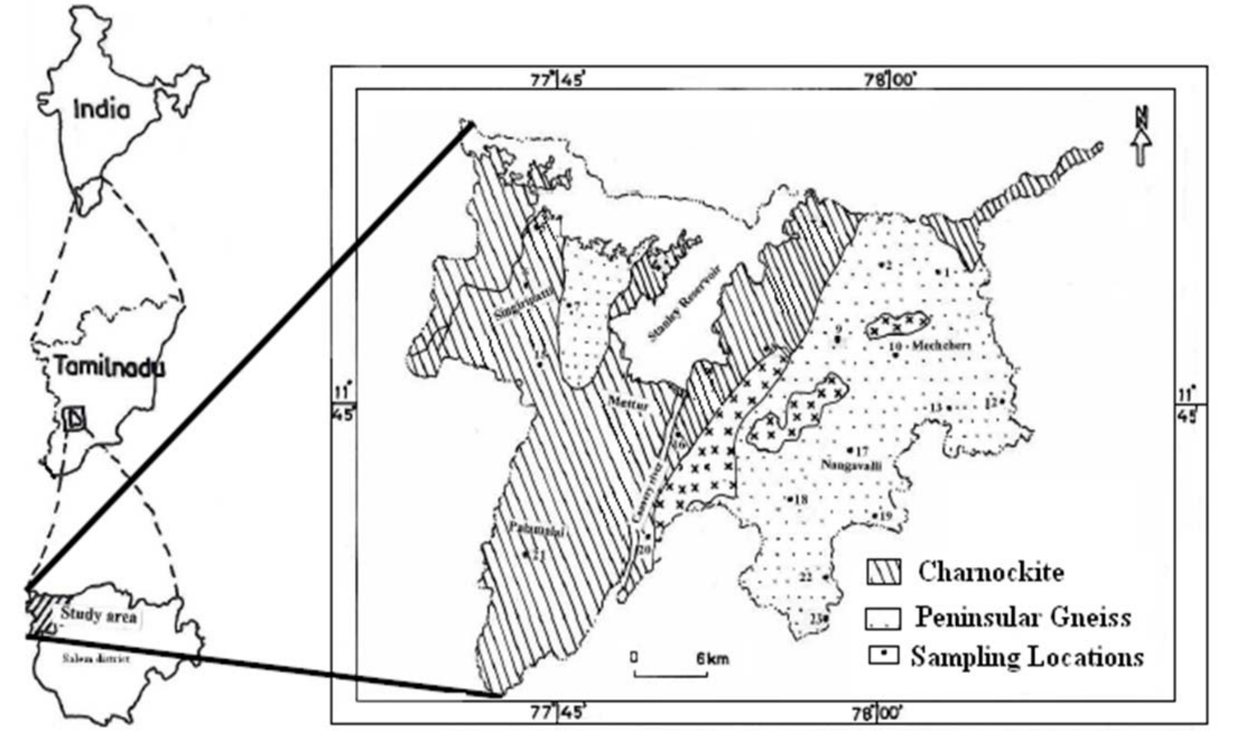

Figure 1. Location, geology, and sampling points of the study area.

weathered formations. The weathered layer in the gneissic terrain of the study area varies in thickness from 2.2 to 50 m. In charnockite, the thickness varied between 5.8 and 55 m. At contacts of gneiss and charnockite, thickness ranged between 9 and 90 m.

MATERIALS AND METHODS

A total of 46 samples representing major lithology of study area were collected for two seasons pre- and post-monsoon (June and December). Water samples were collected in one liter polyethylene bottles with inside stoppers, and brought to the laboratory immediately. Analysis was carried out for major ions using standard procedures (Ramesh and Anbu, 1992). Fluoride ion was determined using the Orion fluoride ion electrode model (94-09, 96-09). Correlation analysis among various parameters was done with the SPSS statistical software package. The geochemical reaction simulation model WATQ4F (Plummer et al., 1976) was used to determine the equilibrium solubility for fluoride.

RESULTS AND DISCUSSION

Total fluoride content during pre-monsoon and post-monsoons from Mettur ranged from 0.37 to 4 mg/l and 0.32 to 3.4 mg/l. A higher concentration was noted in charnockite followed by Peninsular gneiss due to the presence of dominant fluoride bearing minerals like apatite, hornblende and biotite, which have enhanced the fluoride concentration. The statistics of fluoride distribution in groundwater of the Mettur region is shown in Tables 1 and 2. The easy accessibility of circulating rain water to weathered rock due to joints and long term irrigation processes are also common in this region. These are responsible for the leaching of fluoride from parent minerals present in soils and rocks. Further concentration has been brought about due to the semi arid climate of the region and long residence time of groundwater in the aquifer (Wodeyar and Sreenivasan, 1996). The effect of dilution was well noted in the post-monsoon season. A higher concentration of fluoride was seen in charnockite compared to Peninsular gneiss due to the higher degree of weathered zone thickness in the charnockite. On the basis of fluoride concentration three different zones were classified as (1) fluorosis, (2) optimal and (3) deficit. In the pre-monsoon season it was noted that a majority of samples in charnockite and Peninsular gneiss fall in classes 2 and 3 indicating optimal and deficit zones. In the post-monsoon, a majority of samples fall in the optimal and fluorosis zones due to the reasons discussed above (Figure 2 A and B).

Spatial Distribution

The spatial distribution of fluoride in the groundwater (Figure 3 A and B) was mapped to identify regions and locations of widespread fluorosis. During the pre-monsoon in Peninsular gneiss,

Table 1. Statistics for pre-monsoon season.

Ions	pH	EC	Cl	HCO_3	SO_4	PO_4	NO_3	F	H_4SiO_4	Na	K	Mg	Ca	TDS
Max	8	12330	823	447	219	7.65	76.2	2.84	22.4	400	49.3	177	153	1903.4
Min	7	670	35.4	205	0	0	1.24	0.13	1.6	72	1.28	21.6	5.78	682.57
Average	7.48	2318.7	302.23	340.00	97.38	0.79	37.39	0.79	16.40	156.13	17.12	76.70	53.91	1098.8
Standard deviation	0.29	2367.9	203.90	69.80	70.52	1.55	20.34	0.61	4.58	72.28	13.95	39.65	41.44	340.66

Table 2. Statistics for post-monsoon season.

Ions	pH	EC	Cl	HCO_3	SO_4	PO_4	NO_3	F	H_4SiO_4	Na	K	Mg	Ca	TDS
Max	8.4	2035	1057	542	17.7	3.54	27.3	4.02	36.5	296	128	91.3	44.6	1994.5
Min	7.2	600	79.5	142	2.35	0	3.66	0.37	10.8	73.9	1.29	8.79	2	551.9
Average	7.6261	1072.3	331.93	310.91	10.467	0.2917	8.1039	1.327	24.817	133.32	27.988	50.517	11.103	910.78
Standard deviation	0.3222	371.98	210.55	95.922	5.1614	0.9081	5.1794	0.9971	7.7339	55.836	26.643	24.895	9.2704	326.34

fluoride (<0.5 mg/l) was noted in Nangavalli, Mecheri, Potteneri etc., and a higher concentration (1.00 mg/l) was observed in Papambatti. In charnockite (<0.5 mg/l) was noted in Kalnaykanpatti and hot spots (>1.0 mg/l) was observed in Koonandiyur, Gonur and Kunjandiyur. During the post-monsoon fluoride (<0.5mg/l) was noted in Tinnapatti and a maximum of (2.85 mg/l) was noted in Periyasoragai. In charnockite, the minimum was noted at Kaveripuram (<0.5 mg/l) and the highest (4.0 mg/l) was noted in Kunjandiyur. Seasonal fluctuations were higher when compared with lithological influence during both the seasons.

Correlation and Factor analysis

The pH of the circulating water is a factor which controls the leaching of fluoride. A positive correlation between pH and fluoride concentration during the pre-monsoon season indicates higher alkalinity of water promoting the leaching of fluoride to groundwater (Tables 3 and 4). No significant correlation was observed between fluoride and other ions. A good correlation was observed between ions other than fluoride indicating chemical weathering processes activated along with leaching of secondary salt formations may be the major contributors for these ions during the pre-monsoon and post-monsoon seasons.

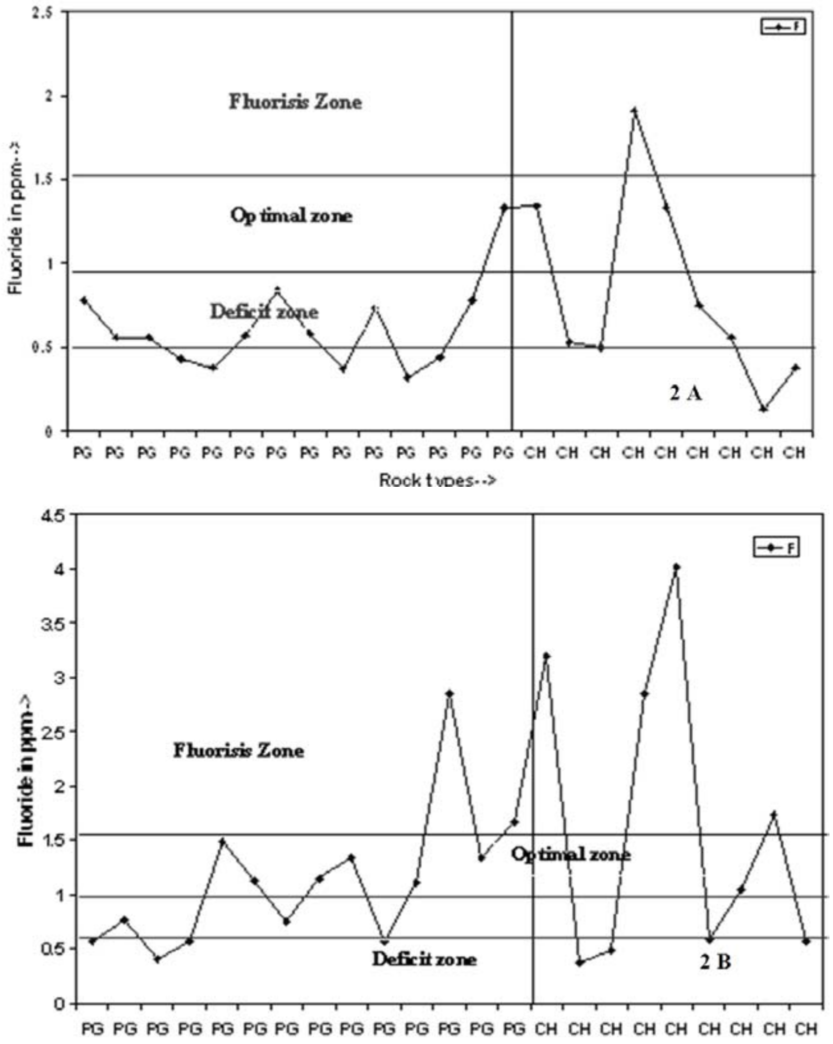

Figure 2 A and B. Zonation of samples during pre- and post-monsoon seasons (PG-Peninsular gneiss, CH-charnockite).

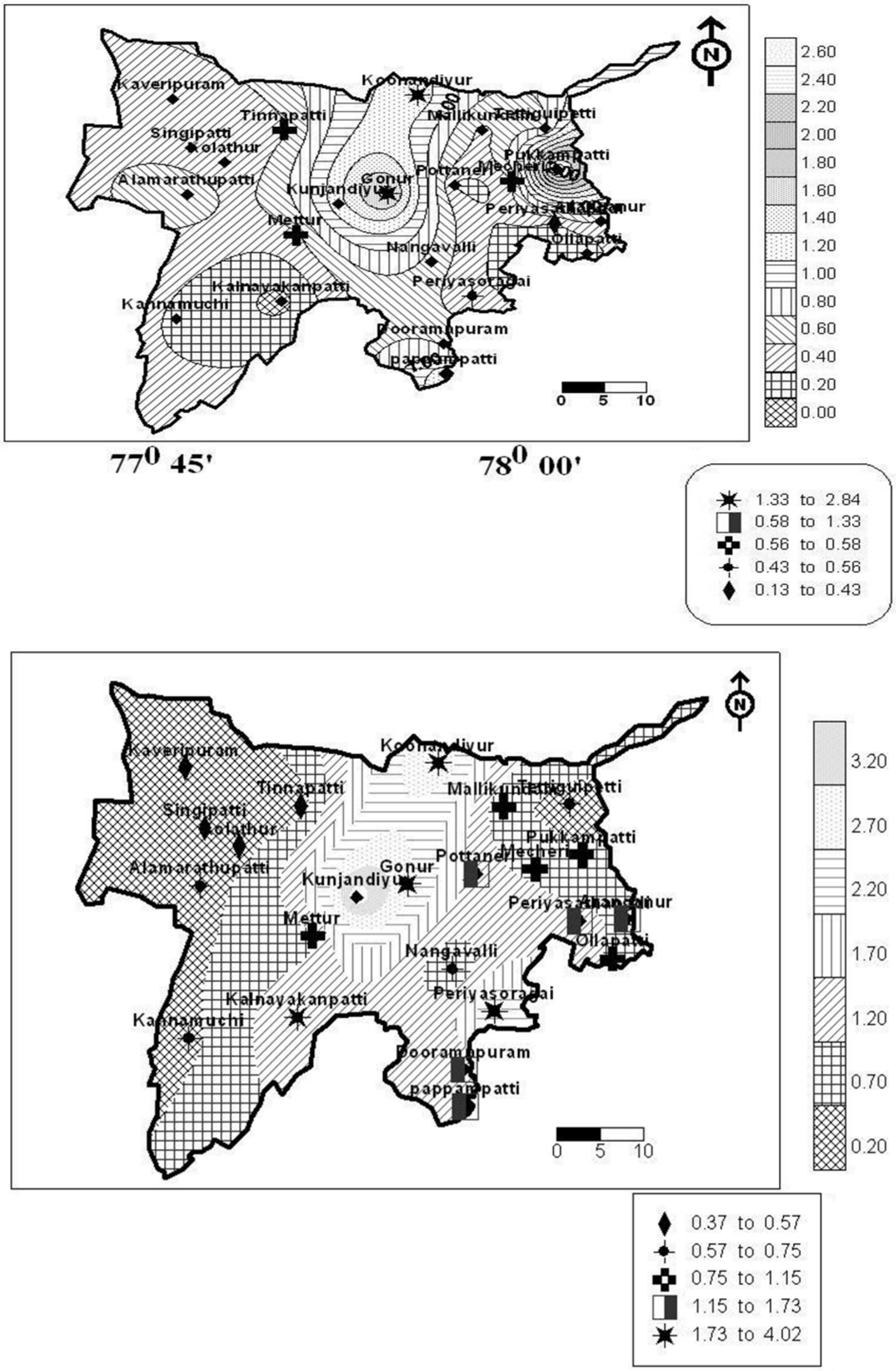

Figure 3. Spatial distribution of fluoride during pre- and post-monsoon.

The correlation coefficient was used as a measure of interrelationship for all pairs of constituents. The first principal component accounts for variance of observed variants. The second principal component accounts for residual variances not accounted for by the first principal component. Factor I is represented by Cl, Mg, Na and K indicating anthropogenic and lithological influence on water chemistry. Factor II is represented by F indicating weathering from fluoride rich minerals. In the post-monsoon season Factor I is influenced by Cl, Ca, Na and HCO3 once

Table 3. Correlation matrix for pre-monsoon season.

Ions	F	pH	EC	Cl	Ca	Mg	Na	K	H_4SIO_4	HCO_3	SO_4
F	1.00										
pH	0.41	1.00									
EC	0.39	0.23	1.00								
Cl	-0.28	0.09	-0.09	1.00							
Ca	0.00	-0.25	-0.19	0.35	1.00						
Mg	-0.35	0.16	-0.03	0.73	-0.13	1.00					
Na	-0.15	0.04	0.06	0.68	0.07	0.34	1.00				
K	-0.33	-0.10	-0.18	0.77	0.50	0.47	0.44	1.00			
H_4SIO_4	-0.20	0.13	-0.11	0.22	0.26	0.18	0.01	0.01	1.00		
HCO_3	-0.19	-0.41	-0.04	0.04	0.25	0.17	-0.03	0.34	0.02	1.00	
SO_4	0.11	0.32	-0.06	0.13	0.15	0.11	0.32	-0.14	0.16	-0.22	1.00

Table 4. Correlation matrix for post-monsoon season.

Ions	F	pH	EC	Cl	HCO_3	SO_4	H_4SIO_4	Ca	Mg	Na	K
F	1.00										
pH	0.04	1.00									
EC	-0.17	0.24	1.00								
Cl	-0.26	-0.08	0.79	1.00							
HCO_3	0.04	-0.06	0.54	0.38	1.00						
SO_4	-0.07	-0.09	0.30	0.32	0.26	1.00					
H_4SIO_4	0.02	-0.29	-0.11	-0.06	-0.03	0.26	1.00				
Ca	-0.31	-0.08	0.78	0.97	0.44	0.32	-0.09	1.00			
Mg	0.30	0.05	0.09	0.07	0.36	0.38	0.21	0.03	1.00		
Na	-0.12	0.06	0.64	0.69	0.38	0.36	0.06	0.63	-0.13	1.00	
K	-0.11	-0.26	0.25	0.23	0.06	0.18	0.11	0.19	-0.22	0.11	1.00

again indicating the influence of anthropogenic and lithological activities (Figure 4 A and B). Factor II is represented by F and Mg ions indicating the dissociation of fluoride and other minerals. Factor III is represented by H_4SIO_4 which indicates the resistance of weatherability of silicate bearing minerals in the study area.

Equilibrium State

Disequilibrium indices log (IAP/KT) were calculated by the WATEQ4F geochemical model for fluoride minerals like FCO_3 apatite, flourapatite, fluorite and hydroxyapatite to determine if water is in thermodynamic equilibrium log (IAP/KT)=0, oversaturated log (IAP/KT)>0 or undersaturated log (IAP/KT)<0 with respect to certain solid phases. In the pre-monsoon season FCO_3 apatite was over saturated, fluorapatite was in equilibrium and fluorite was undersaturated. In the post-monsoon effect of dilution is well noted in all the fluoride minerals where fluorite still shows undersaturation. The statistics also show that fluoride is represented as the second factor in the factor analysis. Hence it plays a significant role in water chemistry of the study area. Fluoride chemistry of the region is highly influenced by dissolution and precipitation along with mixing, apart from anthropogenic activities (Figure 5 A and B).

SUMMARY AND CONCLUSION

A high degree of weathering and easy accessibility of circulating water to the weathered rocks due to intensive and long time irrigation are responsible for the leaching of fluoride minerals present in the study area. Higher concentration of fluoride was noted in charnockite due to the higher weathered zone thickness compared to Peninsular gneiss. Correlation study shows

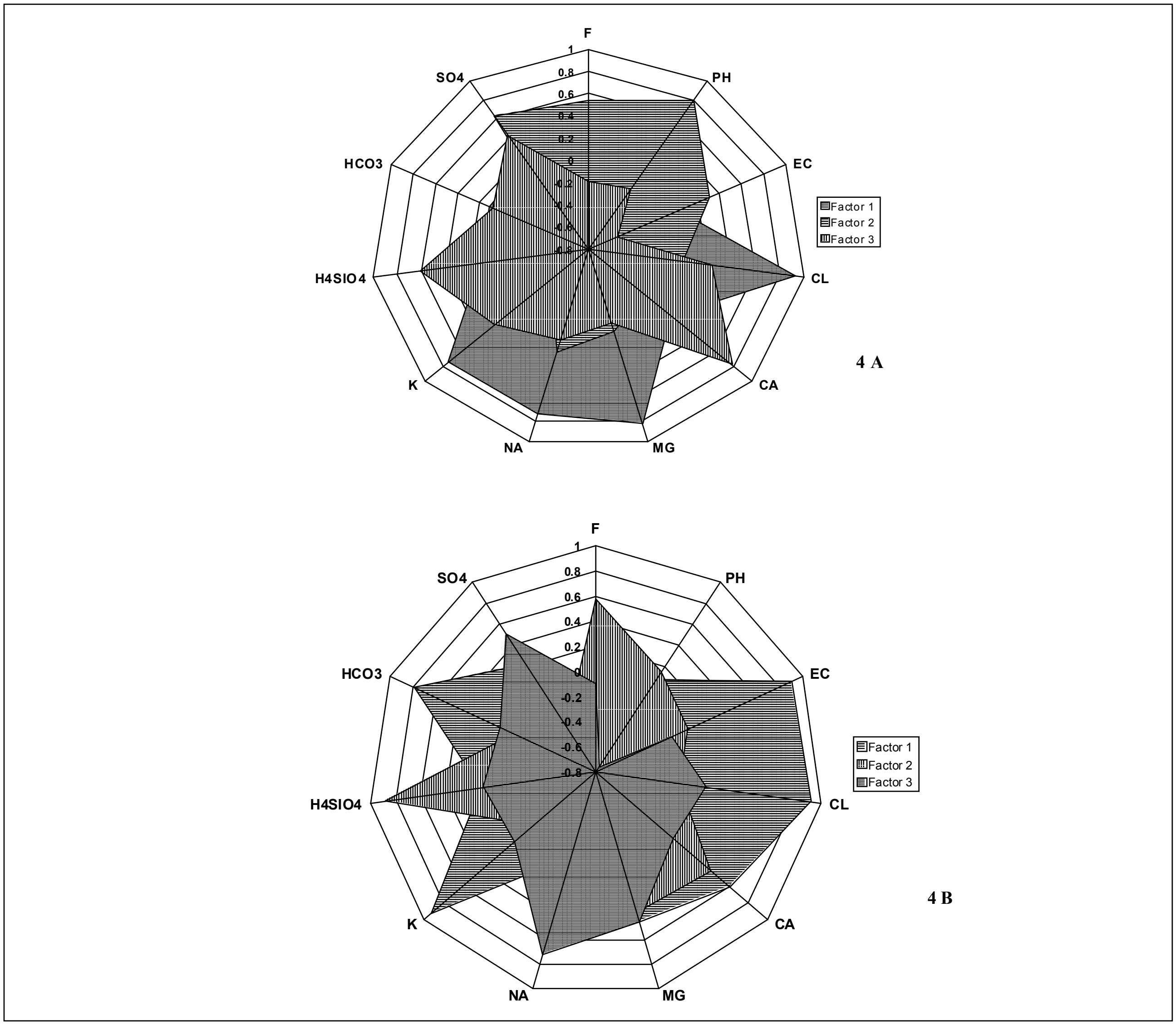

Figure 4. A and B. Factor score plots for pre- and post-monsoon.

correlation between pH and fluoride concentration indicating higher alkalinity of water promotes the leaching of fluoride ions to the groundwater. Factor analysis reveals the influence of anthropogenic and lithological activities. Disequilibrium indices show fluorides in groundwater are mainly due to dissolution of apatite and fluoride bearing minerals from the major rock types prevailing in the study area.

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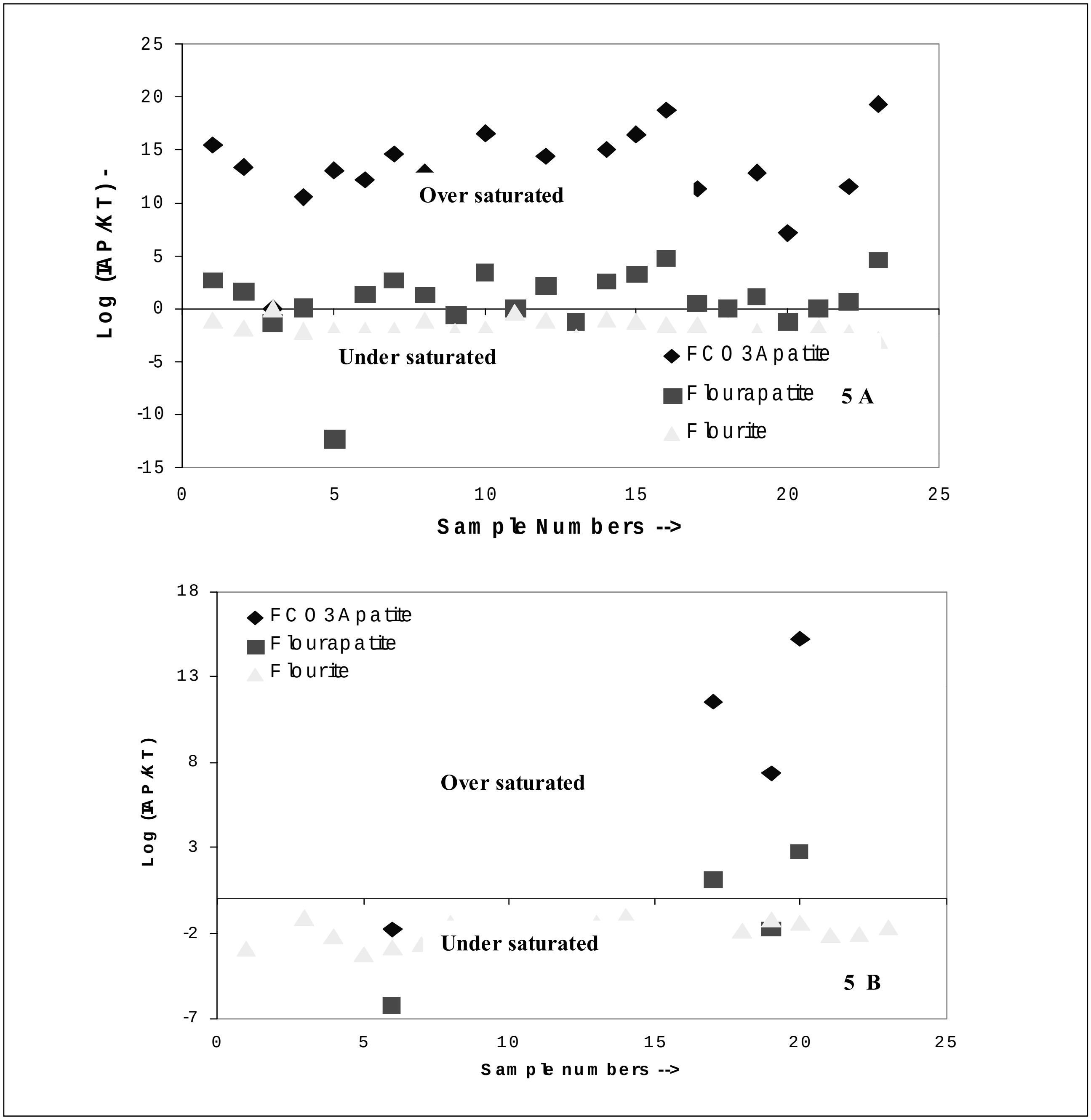

Figure 5. A and B. Equilibrium indices for fluoride minerals during pre- and post-monsoon seasons.

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