Chemometric and GIS Based Analysis of Geogenic Augmentation of Fluoride in Groundwater of Arid Region of India

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Abstract- **Groundwater is the only available potable source of water for drinking, sanitation and other uses in this region of Thar Desert of India. The intention of this study was to assess the toxicity of fluoride in groundwater and to identify major factors controlling its occurrence. A total of 66 water samples were collected and analyzed from the study area. The analyzed water quality parameters formed the attribute database for statistical and GIS analysis. Chemometric analysis of the water quality parameters was done using factor analysis and principal component analysis to identify the major factors controlling the fluoride enrichment. Piper diagram was used to identify geochemical facies of groundwater samples and to determine the role of water facies for fluoride enrichment in the region. The principal component analysis of the water quality parameters resulted in three major factors which explained 73.65% of the total variance. The factors suggest that mineral dissolution, evaporation, reducing environment and ion exchange are the major processes controlling fluoride hydro-geochemistry. The study concludes that the water is not potable in most of the locations due to high fluoride concentration exceeding the limits as recommended by World Health Organization (WHO) for drinking water.**

Keywords- Groundwater; Fluoride, Rajasthan; Principal Component Analysis; Evaporation

I.   INTRODUCTION

It is estimated that fluoride constitutes about 0.032% of the earth's crust. India shares 14.1% of total fluoride deposits present in the earth's crust and 17 states of India is endemic in fluorosis [30]. The geochemical pathways of fluoride involve human populations of the tropics more directly than those of the temperate regions where food and water may be obtained from distant sources [9]. Fluoride occurrence is very common in semi-arid climate with crystalline igneous rocks and alkaline soils [3]. Higher concentration of fluoride (>1.5 ppm) in drinking water is considered as health hazard and it causes chronic endemic fluorosis [7]. Fluorosis at more severe stage causes bilateral lameness and stiffness of gait [22]. The fluoride occurrence in groundwater in an area, where anthropogenic input is almost trifling, can be attributed to the dissolution of calcite, weathering and leaching of amphiboles, fluorite, apatite and mica [8]. Thus the areas where such rock types are dominant high fluoride concentration can be suspected [2]. Some of the natural sources of fluoride include fluorite, apatite, amphiboles, cryolite, muscovite, hornblende etc. [11],[18], [19], [3], [32] from different rocks types, while anthropogenic point and non-point sources include industrial activity and agriculture. Fluorite, the only principal mineral of fluorine in nature occurs mostly as an accessory mineral in granitic rocks. The granite rocks contain fluoride concentrations of 20-3600

ppm [15], [24]. In Rajasthan granites, minerals like sepiolite and palygorskite, acid volcanic and basic dykes [23], [13] are identified as rock sources. High concentration of fluoride in water is common in pegmatite rich fractured hard rock terrains, which contain minerals like fluorite, topaz, fluorite, fluorapatite, villuamite, cryolite and fluoride-replaceable hydroxyl ions in ferromagnesium silicates. Fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations. Fluoride content in groundwater usually depends on rock type, contact period with host rock, in addition to the chemical kinetics of fluoride containing minerals. In India much of the fluoride input into human body is through drinking water; an understanding of the geochemistry of its presence in groundwater is relevant in the etiology of fluorosis. The present study is a result of a preliminary investigation done in this region [8] wherein it was found that it had occurrences of fluoride in the groundwater and thus the study was further extended in this region covering an area of 6000km^2 to study spatial variation of fluoride, its occurrences and geochemistry.

II.   STUDY AREA

The study area consists of one of the three blocks of Jaisalmer district. The Pokharan block is located between 71.39-72.09°E longitudes and 26.32-27.54°W latitudes covering an area of approximately 6000km2. The study area along with landuse/landcover is shown in Fig. 1. The district is situated in the extreme western side of the Rajasthan state, in the heart of Thar Desert, hence it possesses typical arid climate. The air is extremely dry throughout the year, except for a very brief monsoon period. It experiences very large extremes of temperatures and a very erratic and scanty rainfall. The district on an average receives 148.3 mm of the rainfall annually. However, the average normal rainfall of the district, based on the data for the period 1901-2008, is 158.60 mm.
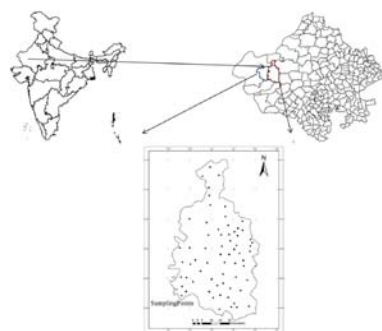
Fig.1 Study area along with sampling locations

Exposed rocks are not much prominent except in northern part of the area. The area is covered by eroded hills in northern part (granite, red sandstone, limestone in association with other igneous rocks) and the southern part is covered by sand dunes. Sparse vegetation in found in the region. There is no major river or perennial stream in the district; only small seasonal streams form the entire drainage features of the district. Most of these drainages have no well-defined channels, but only slight topographic depressions mark their course. These drainage courses also go on shifting with the shifting of the sand-dunes. Natural depressions called Rann are also present which often get filled during the rainy season. The topographic highs, viz., the domes, inselbergs, small plateaus and Aravalli hills are made up of rocks like shales, quartzites, phyllites, grits, conglomerates, granites, calc-slates, and calc-gneisses. The domes and inselbergs comprise mostly granites and rhyolites. The small plateaus are made up of sedimentary rocks like sandstone, limestone and shale. The pediments that are observed around the topographic highs are made of eroded rocky surfaces covered with thin veneer of colluvial materials and at places with windblown sands. The relict alluvial fans found close to the topographic highs are limited in areal extent [28]. They consist of stratified deposits of diverse sizes. Sandy plains cover comparatively a larger area of the region [29]. The geological and geochemical observations in the region indicate the presence of metamorphic rocks of with intrusions of pegmatites, volcanics and sedimentary rocks under the thick cover of Quaternary sand [10]. The Archaean granites, gneisses, amphibolites and pegmatites are overlain by the metamorphic rocks of the Aravalli supergroup and Delhi supergroup. The highly folded metamorphosed rocks of the Delhi supergroup form the main part of the mountains and consist of quartzite, mica schist and gneiss [25]. A wide spread volcanic event at the end of the Proterozoic is marked by the isolated exposures of the Malani igneous suite. This igneous suite consisting of basalt and rhyolite is overlain by the sandstone and limestone of the Marwar supergroup. The Palaeozoic Bap boulder bed along with dolomite and minor shale overlie the Marwar rocks. Both the Malani and Marwar rocks are exposed in western Rajasthan [4].

III. METHODOLOGY

The study was carried out with the help of topographic sheets, Garmin GPSMAP76, ArcGIS 9.2, and fieldwork. Water samples were collected from 66 bore wells/dug wells and hand pumps present in the study area (Fig. 1) and their location was recorded using Garmin global positioning system (GPS). The physical parameters [pH, total dissolved solid (TDS) and electrical conductivity (EC)] of the water samples were measured onsite using respective portable (HANNA) electrodes. The samples were acidified using HNO3 (Ultrapure Merck) for cation analysis. Immediately after the water samples were transported to the laboratory major cations were (Mg2+, Ca2+, Na+, K+) analyzed using atomic absorption spectrometer and major anions (F-, Cl-, SO42-, NO3-) were analyzed using Ion Chromatograph. Bicarbonate (HCO3-) was determined by titration method using the protocol as mentioned in standard methods for the examination of water and wastewater [1]. The sampling points were brought into GIS environment and the attribute database

was updated using the analyzed water quality parameters as the variables. The analytical precision of the ions analyzed was determined by calculating the normalized ionic charge balance error which varied in between ±5%.

A. Statistical Methods

Chemometric analysis of the data was performed using principal component analysis (PCA), factor analysis (FA) [26]. Data standardization is essential in multivariate cluster analysis because in the computation the parameter with higher variances tend to have a greater influence over those with lower variances [6]. The data were standardized before performing statistical analysis as per criterion by Davis [14]. Thus the z-scale transformation renders the data normalized with mean and variance of zero and one, respectively. Standardization tends to increase the influence of variables whose variance is small and reduce the influence of variables whose variance is large. Correlation matrix was studied to point out any relationship between the observed parameters so as to explain factor loadings during PCA. When the value of correlation coefficient value is 1, it shows a good relation between two variables and correlation coefficient value around zero means no relationship between them at a significant level of p value <0.05. Spearman rank coefficient was used to study the relation between the observed parameters.

B. Principal Component Analysis

Principal component analysis (PCA) is a multivariate statistical technique used for data reduction and deciphering patterns within large datasets. This method forms, from a set of existing variables, a set of new variable that contain maximum variability of the original dataset. It allows finding out association between variables, thus reducing the dimensionality of the data set. The principal components (PCs) are the uncorrelated (orthogonal) variables, obtained by multiplying the original correlated variables with the eigenvector. PCA reduces a large dataset into two smaller ones that consist of principal component scores and loadings. PCs are calculated so that they take into account the correlations present in the original data. The first PC explains maximum of the variance in the original dataset and subsequent PCs explains relatively less. Principal component analysis was performed using varimax rotation method with Kaiser Normalization. PCs with eigenvalue greater than 1 were taken into consideration to explain the dataset [27]. The largest component loading (which measure the degree of closeness between the variables and the PC) either positive or negative, suggests the meaning of the dimensions. Positive loading indicates that the contribution of the variables increases with the increasing loading in dimension; and negative loading indicates a decrease [12]. In general, component's loading greater than 0.6 may be taken into consideration for the interpretation. In other words, the most significant variables in the components represented by high loadings have been taken into consideration while evaluating the components [21]. The PCA was performed using an add-on of MS-Excel, XL-STAT, which provides a very friendly user interface for performing all sorts of statistical calculations.

IV. RESULTS AND DISCUSSION

The statistical parameters for all the water quality parameters are described in Table 1. The concentration of fluoride varied between 0.56-6.60mg/l with a mean value of

2.56mg/l. It was observed that 89.39% of the samples exceeded the maximum desirable limit (1mg/l) as per the criteria of Bureau of Indian Standards [5] whereas 71.12% of the samples of Pokharan were above permissible limit compared to WHO standards, (1.5mg/l). It was very critical to observe that approximately 31.81% of the samples were found to have concentration of fluoride above 3mg/l. Higher fluoride concentration is mostly observed in central, south eastern and south-western part of the study area (Fig. 2). At higher pH

ionic-exchange takes place between fluoride and hydroxyl ions (mica and amphiboles) resulting in increase of fluoride concentration in groundwater. The presence of high HCO3, Na and pH favours the release of fluoride from aquifer matrix into groundwater. The pH of groundwater in the region varied from 7.5-8.6 with a mean value of 8.01, which is mainly alkaline in nature. The alkaline groundwater favours the solubility of fluoride bearing minerals thereby increasing its concentration.

TABLE 1 STATISTICAL SUMMARY OF WATER QUALITY PARAMETERS

|	pH	EC	TDS	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	NO$_3$	F
Mean	8.01	3009.39	1920.64	442.36	20.16	88.73	53.49	560.36	184.45	438.48	176.17	2.56
Minimum	7.50	890.00	520.00	98.00	2.89	30.00	12.16	106.00	25.00	170.00	9.92	0.56
Maximum	8.60	12000.00	5296.00	1400.00	117.39	228.00	170.24	1601.00	852.00	1220.00	1050.28	6.60
Range	1.10	11110.00	4776.00	1302.00	114.50	198.00	158.08	1495.00	827.00	1050.00	1040.36	6.04
Std. Deviation	0.25	2057.15	980.78	317.65	17.27	32.03	28.46	365.11	153.12	192.84	177.34	1.43
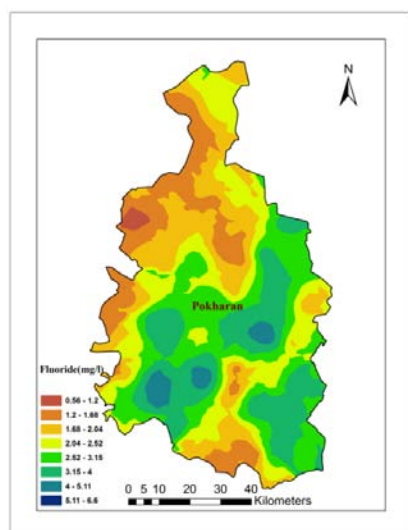
Fig. 2 Spatial distribution of fluoride in study area

A. Factor Analysis

The correlation matrix for all the parameters is shown in table 2. Strong correlation was observed between EC-TDS, EC-Na, EC-Cl, EC-SO$_4$ while EC-HCO$_3$ showed moderate correlation. TDS also showed strong correlation with several parameters (Na, Mg, Cl, SO$_4$, HCO$_3$ and NO$_3$) while moderate correlation was observed with Ca and NO$_3$. Sodium showed good correlation with Cl, SO$_4$ while moderate correlation with HCO$_3$. Calcium showed correlation with nitrate while magnesium showed good correlation with Cl, SO$_4$. A strong correlation was observed between Cl-SO$_4$ (Table 2).

The correlation of the parameters suggests that the ions have resulted mainly due to soil mineralization, evaporation and ion-exchange processes which are predominant in the study area. Water with high F- concentration can form in the areas where alkaline (carbonate rocks) waters are in contact with fluoride bearing minerals. Fluoride concentration is generally independent of other water soluble components but a noticeable correlation exits between F and pH.

TABLE 2 CORRELATION MATRIX OF WATER QUALITY PARAMETERS

Variables	pH	EC	TDS	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	NO$_3$	F
pH	1.000	-.128	.020	-.090	.135	.104	-.044	-.069	-.048	-.014	.049	.380
EC		1.000	**.689**	**.799**	.055	.286	.391	**.884**	**.723**	**.505**	.358	.183
TDS			1.000	**.693**	.265	**.590**	**.637**	**.785**	**.890**	**.629**	**.566**	.320
Na				1.000	-.020	.136	.336	**.795**	**.751**	**.594**	.441	.106
K					1.000	.620	.181	.030	.051	.019	.349	.255
Ca						1.000	.558	.312	.378	.253	**.523**	.248
Mg							1.000	**.526**	**.636**	.151	.450	-.045
Cl								1.000	**.801**	.436	.263	.193
SO$_4$									1.000	.571	.512	.208
HCO$_3$										1.000	.447	.366
NO$_3$											1.000	.165
F												1.000

TABLE 3 PRINCIPAL COMPONENT ANALYSIS OF WATER QUALITY PARAMETERS

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	*% of Variance*	*Cumulative %*	*Total*	*% of Variance*	*Cumulative %*	*Total*	*% of Variance*	*Cumulative %*
1	5.555	46.292	46.292	5.555	46.292	46.292	4.766	39.713	39.713
2	1.918	15.985	62.278	1.918	15.985	62.278	2.543	21.189	60.902
3	1.365	11.375	73.652	1.365	11.375	73.652	1.530	12.751	73.652
4	.850	7.082	80.734						
5	.719	5.991	86.725						
6	.544	4.534	91.258						
7	.355	2.962	94.220						
8	.271	2.261	96.481						
9	.172	1.431	97.912						
10	.129	1.072	98.983						
11	.076	.634	99.617						
12	.046	.383	100.000						

B. Principal Component Analysis

Factor 1 which explains 46.29% of the total variance shows higher loading for EC, TDS, Na^+, Cl^-, SO_4^{2-} and HCO_3^- (Fig. 3). High loading variables for Factor 1 shows higher mineralization from geological components of soil i.e. mineral dissolution, salinity enhancement (Table 3).
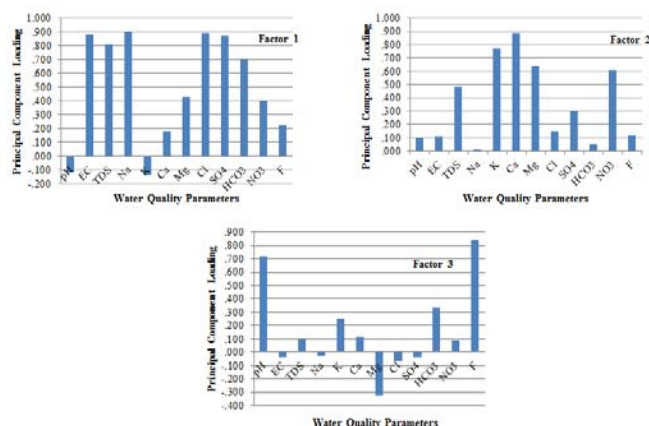

Fig. 3 Factor loading plot for obtained 3 factors after PCA

Factor 2 which contributes 15.98% of total variance shows higher loading for K^+, Ca^{2+}, Mg^{2+}, and NO_3^- which might be a result of ion exchange process. Certain minerals such as montmorillonite have high capacity for base-exchange like subsurface limestone; calcite may enrich water by calcium. Higher loading of NO_3^- which at first instance appears to be due to anthropogenic inputs, however misleading in the study area as it is a part of Thar Desert where agricultural activities are very less and habitations are very few. The high nitrate may be due to its accumulation through millions of years. The sustained absence of downward water movement below subsoil reservoir has enabled nitrate to accumulate for thousands of years [17]. The Factor 3 shows significant loading

for pH and fluoride with 11.37% contribution in total variance. The alkaline pH increases the fluoride concentration in groundwater; dissolution of calcite in the area enriches fluoride in groundwater. Lower pH favours the adsorption of fluoride on the surface of clay. A higher value of pH favours the enrichment of fluoride in groundwater [7]. The arid to semiarid climatic conditions are quite favourable for chemical weathering, which results in enhanced salinity and fluoride abundances in phreatic water system. It has been observed that waters with relatively high pH have a tendency to displace fluoride ions from the mineral surface. From the above, it is evident that relatively high alkalinity has played an important role in the enrichment of fluoride in groundwater of the study area.

The hydroxyl ions in groundwater (basic/alkaline pH) can replace the fluoride from fluoride containing minerals (biotite/muscovite) thus enriching fluoride concentration in groundwater.

The hydroxyl ions replace fluoride from clay minerals as:

Muscovite

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^-$$
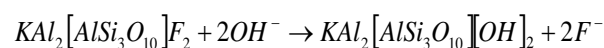
The adsorption strength of clay to fluoride is high enough to inhibit release of fluoride in groundwater. It was observed by Madhavan and Subramanian (2002) in Ajmer, Rajasthan that clay contained a high amount of fluoride whereas sand and silt fractions contain less amount of fluoride. The anomalous distribution of fluoride can be ascribed to assortment in landuse, soil texture and relative abundance of fluoride bearing minerals.

C. Ionic Mobility of Fluoride

Fluorine is most electronegative element with small ionic radii and fairly high mobility. It can remain soluble in both oxidizing and reducing environments at variable pH [31]. An

approximation of the mobility can be made by comparing the composition of water and the rocks in contact. The mobility of an element can be quantitatively estimated by Perel'man [16].

Coefficient of aqueous migration (K) = 100*W/T.R

Where W is the concentration of the element in water (mg/l), T is total dissolved solids (mg/l) and R is the concentration of the element in rock (%).

Taking the average values (Table1) of the of fluoride and TDS and R = 0.1939 for average concentration of fluoride in granite rock in the above equation, the coefficient of aqueous migration (K) is calculated as 0.539 for Jaisalmer block and 0.687 for Pokharan block, thus the K value suggest moderate mobility of element (K 0.1–1) group [30].

D. Hydrochemical facies

The hydrochemical facies of the groundwater was studied and it was found that Na-Cl-HCO$_3$ (16 samples), Na-Ca-Cl-HCO$_3$ (13 samples), Na-Ca-Mg-Cl-HCO$_3$ (11 samples) and Na-Cl (9 samples) type of water facies are dominant in the study area (Fig. 4). Bicarbonate is predominant in almost all the type water facies. Sodium bicarbonate type water facies are capable of releasing fluoride from fluorite mineral [3]. In granitic or sandstone dominant aquifers dissolution of fluoride can be possible reason for presence of fluoride in groundwater. The hydrolysis of alumino-silicate minerals in the hard rock aquifers produces bicarbonate ion, which can enhance fluorite dissolution as below.
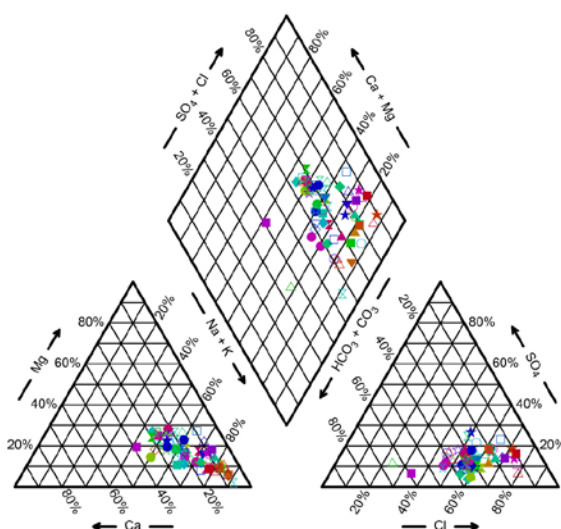

Fig. 4 Diagram illustrating water facies in study area

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

V.   CONCLUSION

An arid climate with low rainfall and high evapotranspiration and insignificant natural recharge cumulatively lead to salinization of groundwater and precipitation of calcite. Soils become more alkaline with a very high pH that affects the solubility of calcite. These conditions lower the activity of calcium and increase the Na-Ca ratios, thus allowing fluoride to distillate in the groundwater. Bedrock containing fluoride minerals is generally responsible for the high concentration of this ion in groundwater.

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