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Assessment of Fluoride Contamination in Groundwater as Precursor for Electrocoagulation

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Abstract The Present study was conducted in January 2010, in order to assess the fluoride contamination in the Thirupathur Taluk. The major objective of this study was to locate the vulnerable areas in terms of fluoride contamination. The range of fluoride concentration varied between .26 and 2.75 mg/L. 60 % of the samples were above the permissible limit. Good correlation was observed between pH, Na, HCO_3, CO_3 TDS and NO_3. A negative correlation showed by Ca and K. The results show that Geochemistry of these ions controls the Fluoride concentration in the study area. All the samples exceeded the permissible limit of F was characterized by Na-HCO_3 type of water. A fairly good correlation between F and NO_3 suggest an anthropogenic input of F, mainly from the agricultural fields. Spatial distribution map of Fluoride shows very high concentration in the SW part of the study area.

Keywords Groundwater · Fluoride · Hydrochemistry · Thirupathur

Accessibility to good quality drinking water is a primary right of all the human beings. However in many locations of the developing world the quality of water has deteriorated due to pollution. Assessment of water quality is essential to understand its suitability for different purposes. Groundwater in the Vellore district is mostly contaminated with industrial wastes and natural processes. According to CGWB (2009), many parts of the district are overexploited. High saline effluents from the tanneries are the common water quality problem. On the other hand, elevated concentration of fluoride is the major natural water quality problem. According to WHO (2004), the permissible limit of fluoride in drinking water is 1.5 mg/L. An optimum level of fluoride in drinking water is good for teeth and bones. However, the lowest permissible limit is not exactly known. Consumption of fluoride in high concentration leads to fluorosis. Fluorosis is one of the major groundwater pollutant originates from the natural processes. High fluoride concentration in water is reported from many locations in India, particularly in the arid to semi-arid western states of Rajasthan, Gujarat and in the southern states of Andhra Pradesh, Karnataka and Tamil Nadu (Indu et al. 2007). Numerous studies were done by various researchers in order to evaluate the groundwater quality problems due to high fluoride concentration (Jacks et al. 1993; Dhiman and Keshari 2006; Reddy et al. 2010; Padhi and Muralidharan 2011). The present study aims to assess the groundwater quality of Thirupathur Taluk with a special reference to fluoride, as a preliminary step to choose the locations for electrocoagulation.

Thirupathur is located in Vellore district of Tamil Nadu, India. Detailed map of the study area with groundwater sample points is shown in Fig. 1. The mean minimum and maximum temperature are 18.2–36.8°C. Relative humidity ranges from 37 % to 85 %. Annual normal rainfall of the district is 949.8 mm. Though both hard rock and sedimentary formations are existing, hard-rock formation constitutes 90 % of total geographical area. Most common hard-rock formations are gneisses and charnockite of Achaean age. Groundwater occurs under phreatic conditions in the weathered zone and under semi-confined conditions in the fractures (CGWB 2009). Thickness of the weathered zone varies from less than a meter to about 15 m in the area depending on the topography. Potential aquifer zones are also developed in these rocks by fractures persisting to depths, particularly along lineaments and their

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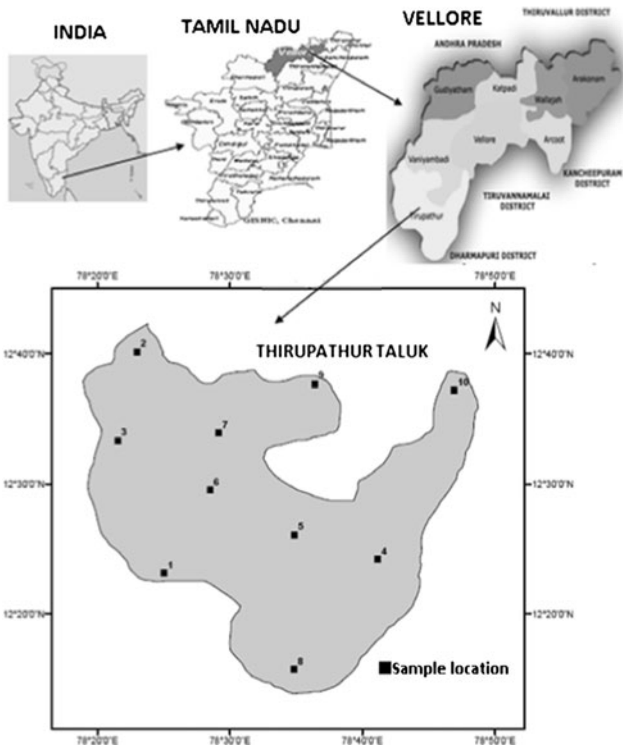

Fig. 1 Location map of the study area

intersections. The thickness of alluvium along the course of Palar River ranges from 8 to 12 m. In Gondwana formations; groundwater abstraction is through dug wells and dug cum bore wells.

Materials and Methods

Extensive geological and hydrogeological survey was conducted prior to the sampling process. A special care has been given to those areas where the fluoride contamination was expected. Based on this study, representative wells were selected and the samples were collected during January 2010. Sampling was carried out using a stainless steel container tightened with a fiber rope. Samples are immediately transferred to pre-cleaned polythene bottles with 500 mL capacity. Collected samples were preserved at 4°C and taken to the laboratory for analysis. Electrical conductivity (EC) and pH were measured in situ. Chemical parameters were determined by following standard and recommended methods of American Public Health Association (APHA 1995). HCO_3, Cl, Ca and Mg were determined by titration. SO_4 was determined by UV–visible spectrophotometer. Flame photometer was employed in the analysis of Na and K. Fluoride concentration of water samples was determined Using SPADNS method according to instruction of Standard Methods (APHA/AWWA/WEF 1998). The minimum detectable level of the SPADNS method was .02 mg/L. Extreme precision was maintained throughout the analysis. The ion balance error was calculated and all the samples show an error of ±5 %. Microsoft Excel and SPSS software were used in the data analysis.

Results and Discussion

Hydrochemistry of individual water samples is given in the Table 1. In general, the abundance of major cations and anions were in the order of Na>Mg<Ca<K and HCO_3<Cl<SO_4<CO_3 respectively. Major water type identified as NaCl and $NaHCO_3$, which is confirmed by the piper diagram in Fig. 2 (after Piper 1953). Fluoride rich minerals are fluorite, apatite, Mica, amphiboles, clay and villiaumite. In the study area the major source of F are gneissic and charnockitic rocks, which has high concentration of F (.5–4 mg/L). Important factors that determine

Table 1 Results of hydrochemical parameters

S. no	pH	EC	TDS	Ca	Mg	Na	K	Cl	SO4	CO3	HCO_3	NO_3	F
1	8.6	1,300	875	12	46	248	4	163	173	65	258	8	1.75
2	8.1	1,350	869	28	36	242	5	162	154	0	414	8	1.69
3	8.3	1,300	783	28	63	163	10	199	152	28	226	6	1.15
4	8.3	1,250	724	26	51	196	9	142	76	54	305	4	.26
5	8.4	1,250	787	22	55	198	9	158	69	62	348	9	2.15
6	8.7	1,720	1,027	24	62	276	4	241	175	53	367	2	2.45
7	8.6	1,220	718	18	31	194	30	216	73	36	214	3	.53
8	8.8	1,960	1,231	16	51	396	5	164	127	135	595	9	2.75
9	8.4	770	484	38	54	53	5	85	56	22	191	17	1.41
10	8.0	1,690	1,000	98	81	124	9	197	346	0	245	5	1.6
Min.	8.0	770	484	12	31	53	4	85	56	0	191	2	.26
Max.	8.8	1,960	1,231	98	81	396	30	241	346	135	595	17	2.75
Avg.	8.4	1,378	851	35	54	212	10	171	150	49	329	7.5	1.56

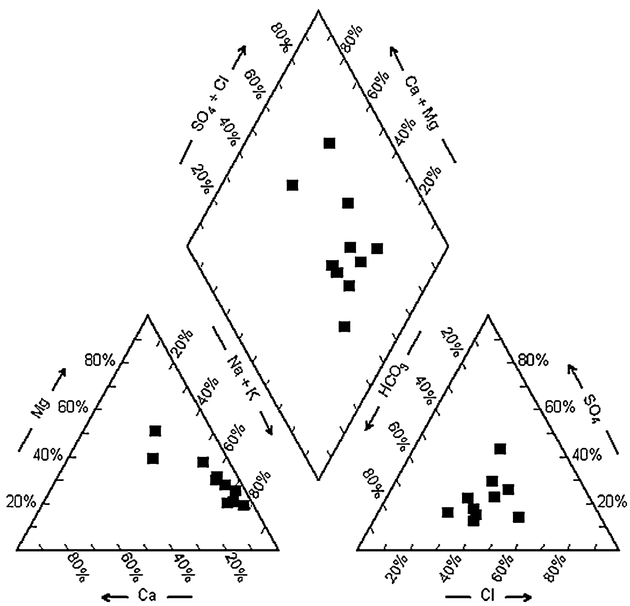

Fig. 2 Piper plot

concentration of fluoride in groundwater is availability and solubility of F minerals, pH, temperature, anion exchange capacity of aquifer materials, type of geological materials and residence time, porosity, structures, depth, groundwater age, concentration of carbonates and bicarbonates in water (Apambire et al. 1997). The concentration of fluoride is ranged between, .26 and 2.75 mg/L with an average of 1.56 mg/L. 60 % of the samples showed a concentration is above the maximum permissible limit of 1.5 mg/L (WHO 2004). All the samples exceeded the maximum permissible limit and have Na and HCO_3 as dominant cation and anion, with comparatively less concentration of Ca.

Correlation matrix for the study is given in Table 2. A good correlation is displayed between pH, TDS, Na, CO_3 and HCO_3 and a negative correlation is shown by Ca and K. The value of pH ranged between 8 and 8.5, suggests alkaline nature of water. A positive correlation was observed between fluoride and pH. This indicates that the increase in concentration of alkalinity (carbonate and bicarbonate) resulted from rock-water interactions, which has enhanced the fluoride concentration. The acidic water leads the absorption of fluoride to clay layers; whereas the increase of pH to alkaline nature desorbs the fluoride (Saxena and Ahamed 2001). The possible reaction which shows the alkaline influence on fluoride concentration is given in Eq. (1) (Salve et al. 2008)

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2. \quad (1)$$

Calcium showed a negative correlation with F. When calcium and fluoride combine to form fluorite, the solubility is reduced and it gets precipitated. This decreases concentration of Fluoride with high concentration of calcium. The relation of ($HCO_3 + CO_3$) and (Ca + Mg) with F is be explained in Fig. 3. Samples having F concentration greater than 1 mg/L were selected for this purpose. As the ($HCO_3 + CO_3$)/(Ca + Mg) ratio increases, there is a subsequent increase in fluoride concentration was observed. The resulting reaction is shown in Eqs. (2) and (3)

$$CaF_2 = Ca^{2+} + 2F^- \quad (2)$$

$$CaCO_3(s) + H^+ + 2F^- = CaF_2(s) + HCO_3^-. \quad (3)$$

A positive correlation between Na and F were observed from the study area. The possible origins for the sodium are silicate weathering and the tannery effluents. High Na/Ca ratio along with high pH and HCO_3 can mobilize the

Table 2 Correlation matrix for the different hydrochemical parameters

	pH	EC	TDS	Ca	Mg	Na	K	Cl	SO_4	CO_3	$HC0_3$	NO_3	F
pH	1.000												
EC	.249	1.000											
TDS	.291	.981	1.000										
Ca	−.694	.152	.069	1.000									
Mg	−.330	.325	.251	.728	1.000								
Na	.608	.745	.806	−.510	−.279	1.000							
K	.067	−.194	−.280	−.059	−.396	−.179	1.000						
Cl	.176	.595	.519	.055	.148	.349	.354	1.000					
SO_4	−.418	.562	.537	.753	.655	−.010	−.235	.443	1.000				
CO_3	.800	.461	.514	−.558	−.144	.759	−.159	−.025	−.317	1.000			
$HC0_3$	.368	.702	.757	−.296	−.132	.867	−.377	.061	−.025	.671	1.000		
NO_3	−.042	−.510	−.406	−.031	−.057	−.326	−.392	−.862	−.334	.023	−.036	1.000	
F	**.378**	**.582**	**.671**	**−.061**	**.254**	**.551**	**−.587**	**.121**	**.248**	**.462**	**.662**	**.207**	**1.000**

Bold values indicate the correlation between F and other water quality parameters

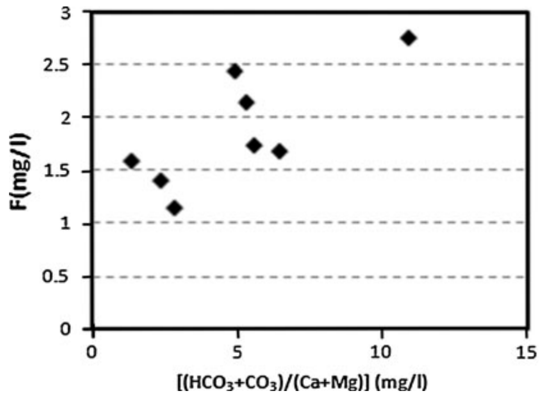

Fig. 3 Plot of [(HCO_3 +CO_3)/(Ca + Mg)] vs. F

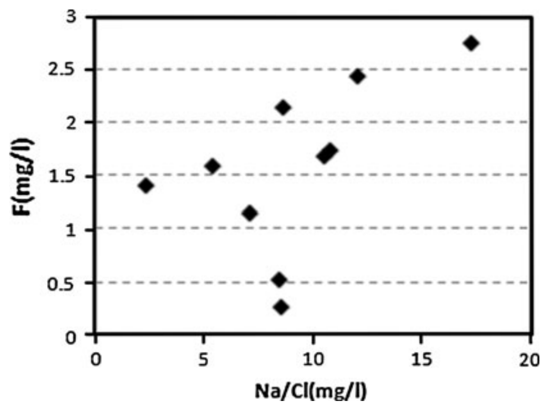

Fig. 4 Plot of Na/Cl versus F

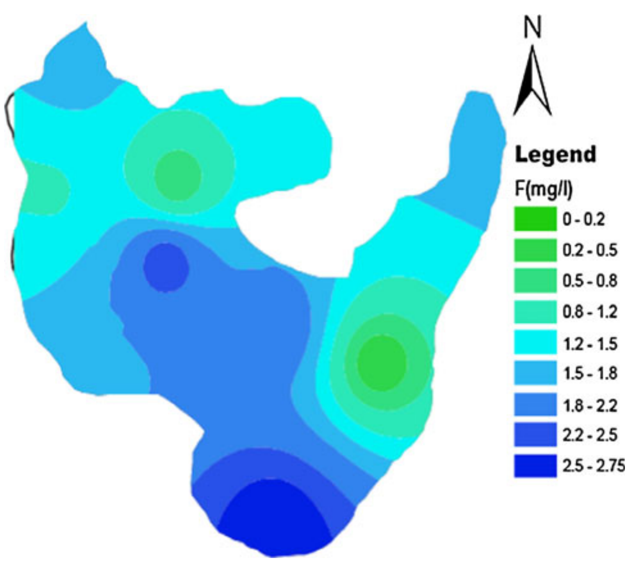

Fig. 5 Spatial variation of Fluoride

fluoride in groundwater (Currell et al. 2011). The relation between Na, Ca and F can be better explained by a plot between Na/Ca versus F (Fig. 4). This ratio between Na and Ca is greatly influenced by the cation exchange. Results show that Na rich aquifer matrix released high fluoride to the groundwater.

A spatial variation map of fluoride concentration was plotted in Fig. 5. A high concentration was observed in the southern and SW part of the study area. The high concentration can be attributed to release of fluoride from the hard rocks. A relatively lesser concentration was observed in the SE parts. However most part of the study area is polluted by high concentration of fluoride. Sufficient treatment facilities are necessary to control the groundwater contamination. Majority of the samples need to be treated for fluoride, using modern technology like electrocoagulation.

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