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RESEARCH ARTICLE

Grounding a natural background level for fluoride in a potentially contaminated crystalline aquifer in south India

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Abstract Fluoride contamination is one of the most alarming issues for those countries that depend on groundwater drinking water supply. A careful examination of the hydrogeochemical conditions and routine monitoring of fluoride level are therefore quintessential. Estimation of natural background level (NBL) of fluoride becomes significant information for assessing the current and future contamination episodes. Vellore District in Tamil Nadu is a hard rock terrain known for its F-rich groundwater. In this study, we attempted to form a benchmark for fluoride using hydrochemical pre-selection (based on TDS and NO_3) and cumulative probability plots (CPP). Principle components analysis is (PCA) applied to evaluate the corresponding factor grouping of the total of 68 samples, which is later mapped using geostatistical tool in ArcGIS. From the CPP, we derived the NBL of F as 0.75 mg/L. This value is compared with the observed concentration in each sample and they were spatially plotted based on the NBL. Resultant plot suggests that W-NW part of the study area has exceeded and E-EW regions are below the NBL of F. Spatial variation of the factor scores also supported this observation. Grounding an NBL and extending it to other parts of the potential contaminated aquifers are highly recommended for better understanding and management of the water supply systems.

Keywords Groundwater · Fluoride natural background level (NBL) · Cumulative probability plots (CPP) · Multivariate analysis, crystalline aquifer · Tamil Nadu

Introduction

Fluoride contamination poses a serious concern on human health in regions were groundwater serves as the principal source of drinking water (Sajil Kumar 2014). Countries across the globe like Egypt, Libya, Syria Algeria, Jordan Sudan, Kenya, Turkey, Iraq, Iran, Afghanistan, India, Northern Thailand, America, and China are suffering from the ill effects of fluoride contamination in groundwater (Brindha and Elango 2011). It is clear that all these countries are largely depending on groundwater for drinking and domestic purposes. The permissible level of fluoride, in drinking water, recommended by the World Health Organization (WHO) is 1.5 mg/L. However, each and every country has its own standards set on the basis of regional climate and per capita water intake.

In India, groundwater is the major source of drinking water and this is the reason for its increased and adverse impacts on human health. India is well known for groundwater fluoride contamination and the associated health risks such as dental and skeletal fluorosis (Jolly et al. 1968). In India, most of the village people depend on their own dug/bore wells for daily water needs. The major issue is that there are no adequate water quality assessment programs in the rural areas. Moreover, the severity of the water-borne deceases will be high when identified in the last stages. In India, water quality standards are set and maintained by Indian standards and the recommended level of fluoride is 0.6 to 1.2 mg/L (BIS 1992). A certain amount of fluoride in drinking water is considered to be useful for dental health in some parts of the world. On the

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other hand, high intake of the same may cause serious health effects (WHO 2011).

Fluoride contamination in the groundwater is a natural hazard. The origin of fluoride is mostly from the geological formations like charnockites, granite, gneisses, etc. with substantial amount of fluoride-bearing minerals such as fluorite, apatite, mica, amphiboles, clay, and villiaumit (Apambire et al. 1997). Hadrochemical processes in the subsurface causes the mobilization of fluoride which results in an increase in F concentration in the groundwater. Consumption of water per day by the human being depends mostly on the loss of water through evaporation from the body. Tropical arid countries will have more water consumption than those of cold countries. This causes a notable difference in the intake of fluoride from case to case.

As the intake of fluoride varies in different geographical regions, it is very important to assess a background level of this ion in areas as a benchmark for future studies focusing on further contamination of the aquifer. In this context, estimation of fluoride levels in the groundwater and setting up of a background concentration are important for the water supply schemes depending mainly on groundwater. This can be done effectively by determining the natural background level (NBL). The estimation of NBL was carried out by many researchers in different parts of the world (Wendland et al. 2005; Walter 2008; Molinari et al. 2012). Most of the fluoride studies in India are focused on the normal estimation of the concentrations, geochemical evaluations, assessment of health impacts, potential of treatment, etc. (Sajil Kumar et al. 2014; Subba Rao 2011; Rafiquea et al. 2009; Kim et al. 2011; Gwala et al. 2014; Gogoi et al. 2015). However, there were no studies reported in literature for the estimation of a natural background level of fluoride contamination. With this aim, we employed hydrochemical and statistical methods for establishing the NBL of fluoride in Vellore District, Tamil Nadu. This must be a stepping stone for further research on fluoride contamination in the region.

Study area

Physiographical classification of Vellore District can be mainly identified as a hilly terrain in the E and SE parts and plain regions in the eastern part. The hilly terrain forms a part of the Eastern Ghats. Geology of the region comprises mainly of hard rocks of Archean age and sedimentary formations of recent age. Hard rock formations comprise mostly of charnockites, gneisses, and granites (Fig. 1). In these formations, groundwater occurs mainly in fractures and lineaments (CGWB 2009). Predominant trend of lineament is NE-SW, whereas in the central part, both NE-SW and NW-SE trending lineaments have been identified in the remotely sensed data. Schematic of the stratigraphic succession of study area is shown in Fig. 2.

Soils are mainly sandy soil, sandy loam, red loam, clay, clayey loam, and black cotton soil. The red loamy soil is generally observed at the highest elevations whereas the black cotton soil is present in the valleys. Other types of soils are found at intermediate elevations. Geomorphology of the study mainly shows structural hills, residual hills, plateaus, valley fills, pediments, buried pediments, pediplains, and alluvial plains. The major source of groundwater replenishment in the study is monsoon rain from southwest and northeast monsoons. The contribution of these two seasons is 45 to 52% and 30–43% respectively towards the total annual rainfall of 949.8 mm. Summer is very hot and the temperature rises up to 37 °C during May and June. The mean daily minimum and maximum temperature are 18.2 to 36.8 °C. The relative humidity ranges from 37 to 85%. Groundwater occurs in crystalline aquifers and abstraction method is dug wells of depth ranging from 8 to 19.5 mbgl (CGWB 2009).

Materials and methods

Sampling and analytical procedures

A total of 68 groundwater samples were collected from the study area during June 2010. A strict reconnaissance survey was carried out and representative samples were selected. Location of the samples was marked using a handheld GPS (HC Gramin). Wells were pumped out till the in situ parameters were alleviated. Electrical conductivity (EC) and pH were measured on site with digital meters. Alkalinity was measured by titration with 0.02 N H_2SO_4 prior to the groundwater sampling. Groundwater was collected in polyethylene bottles (1 L capacity); bottles were sealed and brought to the laboratory for analysis and stored properly (4 °C) before analysis. Laboratory analysis was carried out as per the standard methods suggested by APHA (1995). Major ions like Ca, Mg, Na, K, Cl, SO_4, NO_3, and F were analyzed. Ca and Mg were analyzed using titration with EDTA. Cl concentration was determined using argentometric titration. UV visible spectrophotometer was used for analysis of sulfate. Sodium and potassium were analyzed using flame photometer. Fluoride concentration of water samples was determined using SPADNS method (APHA, AWWA, WEF 1998). The minimum detectable level of the SPADNS method was 0.02 mg/L. Nitrate was measured using an ion chromatograph. The analytical precision of the measurements of cations and anions is indicated by the ionic balance error, which has been computed on the basis of ions expressed in milliequivalent per liter (meq/L). The values were observed to be within the standard limit of ± 5%.

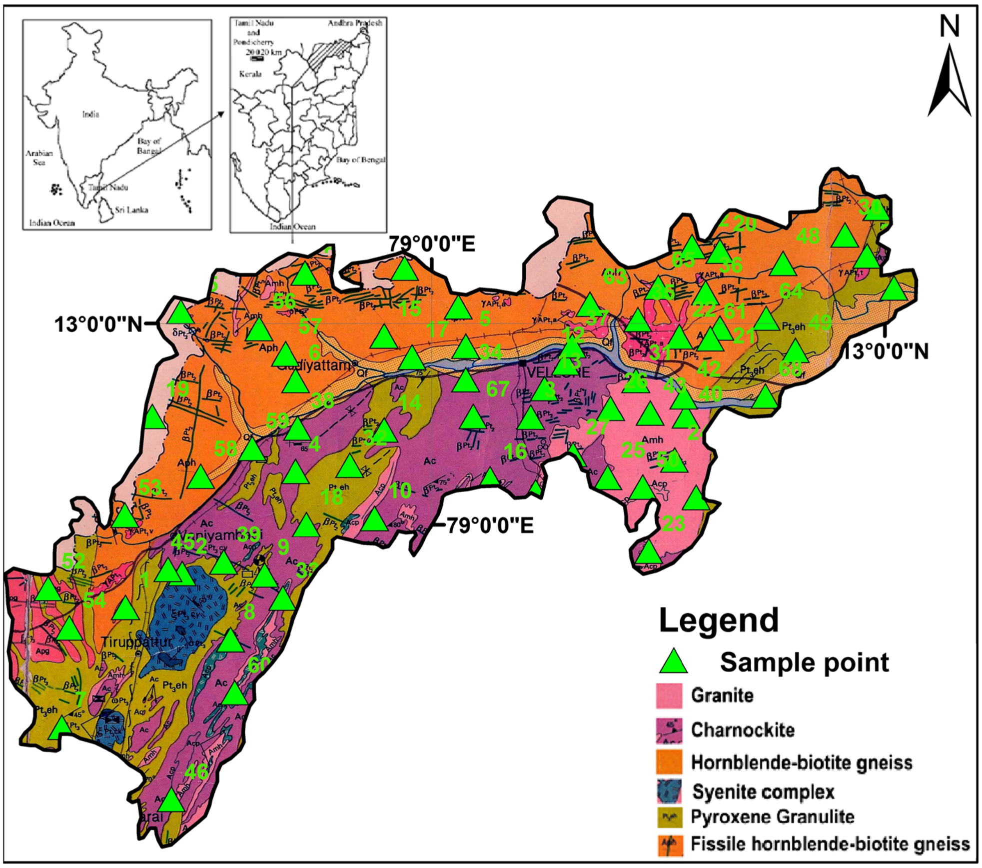
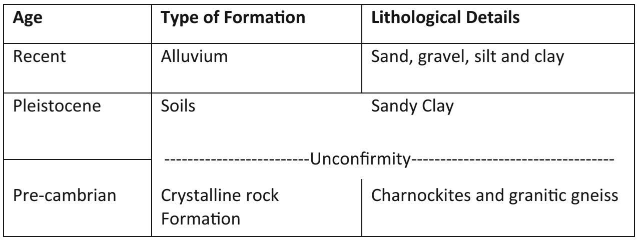


Fig. 1 Location map of the study are showing geology and sampling points

Multivariate analysis

Statistical analysis such as principal component analysis and geostatistical analysis were carried out using XLSTAT and Arc GIS 9.3, respectively. Principle component analysis was used to understand the correlation between each chemical parameter and to identify the factors responsible for the geochemical variations in groundwater. In the first step, data was standardized and correlation matrix was generated. In the next step, based on the correlation values, principal components were calculated. Among the total generated components, the significant complements (those with more variation in data) were selected based on the Eigenvalues (> 1). In the last step, by varimax rotation, factor loading of individual variable on one of the extracted factors was maximized and all remaining factors were minimized. With the rotated components, variables were grouped according to the hydrogeochemical condition of the study area.



Age	Type of Formation	Lithological Details
Recent	Alluvium	Sand, gravel, silt and clay
Pleistocene	Soils	Sandy Clay
	------------------------Unconfirmity----------------------------------	
Pre-cambrian	Crystalline rock Formation	Charnockites and granitic gneiss

Fig. 2 Stratigraphic succession of the study area

Pre-selection and cumulative probability plots

In order to evaluate the background level of ions, we adopted cumulative probability plots (CPP), which was developed for the geochemical exploration (Sinclair 1974) and then used by the researchers in water resources (Park et al. 2005; Panno et al. 2006). In this method, maximum curvature of any two lines indicates the inflection points of two populations. The assumption is that values of log- or normal distributed populations will form a straight line. Number of inflection points is decisive of single or mixed populations, i.e., natural or anthropogenic or both.

In this study, the major focus is on determining the natural background level estimation of fluoride. As the major origin of this ion is from natural sources, we wanted to omit anthropogenic-influenced samples. All the samples were preselected based on a modified criterion suggested by Wendland et al. (2005) with slight modification. We adopted a criterion to distinguish the natural groundwater as,

(i) *TDS > 1000 mg/L; TDS represent overall water quality and the permissible limit is 1000 mg/L.*

Table 1 Hydrogeochemical parameters and water types of individual groundwater samples in the study area with corresponding geographical coordinates

ID	Long.	Lati.	pH	EC	TDS	TH	Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4	NO_3	F	Water types
1	78.55	12.58	8.2	810	513	270	46	38	92	5	2	397	67	58	2	1.13	Na-Mg-Ca-HCO_3
2	78.63	12.63	7.9	3360	2153	940	72	185	460	4	12	567	808	221	27	1.62	Na-Mg-Cl-HCO_3
3	79.08	12.75	7.4	2640	1501	840	240	58	207	11	9	488	397	216	29	0.46	Ca-Na-Cl-HCO_3
4	78.80	12.78	8.1	810	533	225	40	30	115	4	5	366	71	86	1	1.51	Na-Mg-Ca-HCO_3-Cl
5	79.05	12.97	7.6	990	646	285	52	38	138	6	4	427	121	60	4	0.45	Na-Mg-Ca-HCO_3-Cl
6	78.80	12.92	8.2	1220	682	380	50	62	115	7	5	323	188	81	4	0.5	Na-Mg-Cl-HCO_3
7	78.46	12.41	7.8	1180	748	435	112	38	97	7	5	433	113	58	24	0.54	Ca-Na-Mg-HCO_3-Cl
8	78.70	12.54	8.1	2260	1573	430	36	83	437	4	0	848	284	230	17	3	Na-Mg-HCO_3-Cl
9	78.75	12.63	7.9	2000	1155	650	72	114	173	9	0	342	355	221	9	1.68	Mg-Na-Cl-HCO_3-SO_4
10	78.88	12.79	7.8	1000	688	375	58	56	115	5	1	421	121	91	7	0.93	Na-Mg-Ca-HCO_3-Cl
11	78.92	13.01	8.2	1210	876	440	44	80	173	4	8	616	110	104	12	2.17	Na-Mg-HCO_3
12	79.20	12.94	7.9	1170	751	330	76	34	150	5	7	268	220	123	2	0.37	Na-Ca-Mg-Cl-HCO_3
13	79.20	12.94	7.9	1170	751	330	76	34	150	5	9	268	220	123	2	0.37	Na-Ca-Mg-Cl-HCO_3
14	78.93	12.84	7.8	2520	1752	790	96	134	345	7	6	750	383	288	28	1.2	Na-Mg-HCO_3-Cl
15	78.93	12.98	7.8	2880	1912	660	76	114	472	12	2	756	503	326	7	0.96	Na-Mg-Cl-HCO_3-SO_4
16	79.09	12.77	8	1390	888	505	96	64	138	4	3	433	209	134	6	0.8	Na-Mg-Ca-HCO_3-Cl
17	79.05	12.92	7.6	2610	1711	720	164	75	322	74	6	756	503	173	5	0.1	Na-Ca-Mg-Cl-HCO_3
18	78.82	12.71	7.8	1150	705	345	74	39	127	7	0	299	195	96	4	0.45	Na-Ca-Mg-Cl-HCO_3
19	78.67	12.80	8	840	557	350	62	47	81	4	0	500	25	53	8	2.13	Na-Ca-Mg-HCO_3
20	79.42	13.11	7.7	1450	874	430	64	66	161	4	0	421	213	102	12	0.34	Na-Mg-Ca-Cl-HCO_3
21	79.42	12.99	7.5	3050	2127	700	120	97	414	149	17	616	624	247	38	0.12	Na-Mg-Cl-HCO_3
22	79.36	12.98	7.2	2310	1629	590	160	46	311	70	9	641	326	192	46	0.2	Na-Ca-HCO_3-Cl
23	79.39	12.65	7.2	1200	739	275	26	51	184	8	7	342	227	72	0	0.36	Na-Mg-Cl-HCO_3
24	79.36	12.80	7.9	1830	1169	310	44	49	322	2	10	415	319	163	14	0.58	Na-Mg-Cl-HCO_3
25	79.31	12.76	7.6	1560	988	360	84	36	230	4	1	488	234	94	14	0.21	Na-Ca-HCO_3-Cl
26	79.26	12.88	7.6	1340	676	510	40	100	69	3	2	390	142	87	9	0.44	Mg-Na-HCO_3-Cl
27	79.21	12.81	7.6	990	590	325	54	46	92	23	0	397	138	7	7	0.42	Na-Mg-Ca-HCO_3-Cl
28	79.72	13.08	8.5	1100	742	145	18	24	242	3	45	500	103	38	9	0.85	Na-HCO_3-Cl
29	79.69	13.14	8.1	2460	1681	520	56	92	322	196	6	946	340	175	6	0.09	Na-Mg-HCO_3-Cl
30	79.61	13.13	7.8	1520	939	370	56	56	219	7	0	378	291	112	2	0.71	Na-Mg-Cl-HCO_3
31	79.30	12.92	8.2	1060	659	300	70	30	127	5	8	238	213	82	3	0.49	Na-Ca-Mg-Cl-HCO_3
32	78.88	12.79	8.1	1160	733	430	88	51	115	4	1	549	113	61	6	1.11	Na-Ca-Mg-HCO_3-Cl
33	78.75	12.62	7.4	2280	1475	700	120	97	276	7	9	384	518	216	11	0.84	Na-Mg-Ca-Cl-HCO_3
34	79.05	12.92	7.7	2600	1669	710	160	75	322	72	3	769	518	120	4	0.07	Na-Ca-Mg-Cl-HCO_3
35	79.30	13.01	7.7	970	610	265	24	50	138	7	7	415	117	49	4	0.14	Na-Mg-HCO_3-Cl
36	79.40	13.05	7.3	1630	966	530	120	56	161	7	0	409	312	101	1	0.14	Na-Ca-Mg-Cl-HCO_3
37	79.21	12.97	7.5	1540	925	410	88	46	196	5	7	336	312	101	2	0.08	Na-Ca-Mg-Cl-HCO_3
38	78.80	12.85	7.5	860	562	370	44	63	81	3	9	512	25	50	9	1.96	Mg-Na-Ca-HCO_3
39	78.69	12.65	7.7	2100	1421	550	48	105	322	7	7	653	291	180	32	2.53	Na-Mg-HCO_3-Cl
40	79.37	12.87	7.3	4210	2686	1000	220	109	621	4	9	464	1170	264	15	0.08	Na-Ca-Cl
41	79.68	13.17	7.9	920	634	225	38	32	161	2	6	403	106	49	10	0.57	Na-Mg-HCO_3-Cl
42	79.37	12.89	7.3	2100	1308	510	72	80	230	72	7	451	326	134	38	0.05	Na-Mg-Cl-HCO_3
43	79.37	12.89	7.6	2010	1319	550	44	107	299	2	9	573	376	151	12	0.74	Na-Mg-Cl-HCO_3
44	78.87	13.03	7.6	1210	779	235	22	44	219	4	6	622	78	88	3	1.31	Na-Mg-HCO_3
45	78.61	12.64	7.9	3410	2136	1080	104	199	380	9	2	531	766	288	28	2.06	Na-Mg-Cl-HCO_3
46	78.48	12.42	8	1050	679	445	60	72	92	5	3	464	110	86	5	1.26	Mg-Na-Ca-HCO_3-Cl
47	79.15	12.75	7.7	1430	852	670	84	112	69	5	0	488	206	110	5	1.08	Mg-Ca-HCO_3-Cl
48	79.52	13.09	7.7	670	388	370	60	54	15	2	6	268	74	41	4	0.09	Mg-Ca-HCO_3-Cl
49	79.54	12.96	7.6	2300	1467	740	176	73	265	4	8	494	518	175	2	0.02	Na-Ca-Mg-Cl-HCO_3
50	79.31	12.76	7.4	1470	860	500	100	61	127	4	12	403	227	77	14	0.05	Na-Mg-Ca-Cl-HCO_3

Table 1 (continued)

ID	Long.	Lati.	pH	EC	TDS	TH	Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4	NO_3	F	Water types
51	79.04	13.03	8	1210	722	290	36	49	161	7	4	293	223	77	5	0.26	Na-Mg-Cl-HCO_3
52	78.44	12.61	7.6	1670	1021	670	68	122	127	7	27	555	206	120	21	2.24	Mg-Na-HCO_3-Cl
53	78.56	12.65	7.9	880	562	340	46	55	81	7	9	384	82	55	10	1.2	Mg-Na-Ca-HCO_3-Cl
54	78.47	12.55	7.7	1250	761	405	32	79	138	9	0	470	145	96	6	1.59	Na-Mg-HCO_3-Cl
55	78.63	13.04	7.9	1560	1009	270	38	43	184	125	3	427	213	104	20	0.02	Na-Mg-Cl-HCO_3
56	78.75	12.99	7.7	1050	654	305	22	61	138	6	9	488	78	87	4	1.24	Na-Mg-HCO_3
57	78.79	12.96	7.7	1310	813	330	38	57	173	6	0	415	142	65	28	1.26	Na-Mg-HCO_3-Cl
58	78.66	12.78	8.1	1140	685	285	36	47	150	7	4	299	206	72	4	0.2	Na-Mg-Cl-HCO_3
59	78.74	12.82	7.9	910	589	275	30	49	115	5	7	372	85	101	4	1.49	Na-Mg-HCO_3-Cl
60	78.65	12.51	8	1640	1106	640	116	85	138	8	3	317	184	394	5	2.29	Na-Mg-Ca-SO_4-Cl-HCO_3
61	79.41	12.98	7.4	880	549	280	42	43	108	7	5	482	50	58	0	0.4	Na-Mg-HCO_3
62	79.42	13.11	7.3	2560	1680	705	96	113	357	5	0	604	496	218	21	0.02	Na-Mg-Cl-HCO_3
63	79.23	13.03	7.9	1910	1240	370	56	56	299	33	8	592	248	132	27	0.02	Na-Mg-HCO_3-Cl
64	79.49	13.01	7.5	2120	1363	860	164	109	173	4	0	421	496	180	6	0.5	Ca-Mg-Na-Cl-HCO_3
65	79.33	13.05	7.6	1890	1202	530	104	66	219	32	0	586	255	127	24	0.08	Na-Ca-Mg-HCO_3-Cl
66	79.42	12.77	7.8	2720	1596	1020	152	156	219	4	54	378	752	106	4	0.08	Mg-Na-Ca-Cl-HCO_3
67	79.06	12.86	7.7	2220	1400	680	88	112	276	4	0	641	390	196	3	1.55	Na-Mg-Cl-HCO_3
68	79.40	12.87	7.8	1170	685	360	50	57	120	7	8	299	202	82	4	0.37	Na-Mg-Ca-Cl-HCO_3
Min.			7.2	670	388	145	18	24	15	2	0	238	25	7	0	0.02	
Max.			8.5	4210	2686	1080	240	199	621	196	54	946	1170	394	46	3	
Average			7.75	1663	1059	486	76.8	71.49	203.9	17.15	6.4	474.13	274.69	128.29	11.16	0.8	

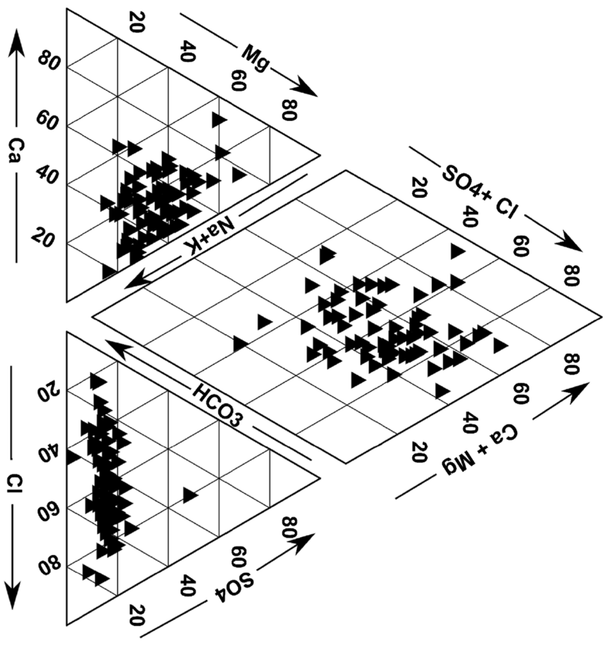


Fig. 3 Piper plot showing water types in the groundwater

(ii) *Cl and NO_3 > NBL (in this study)*; Cl and NO_3 are naturally unavailable in the study area and their presence in the groundwater is often indicative of direct or indirect human interventions

After the application of these two conditions, groundwater is expected to be free from anthropogenic inputs, which can rightly be considered as natural water for estimation of NBL of fluoride.

Results and discussion

Major ion chemical characteristics

General expressions of the hydrogeochemical data of 68 groundwater samples are presented in Table 1. Total dissolved solids (TDS) can give a holistic value that can directly represent water quality of the area. In this study, TDS values range

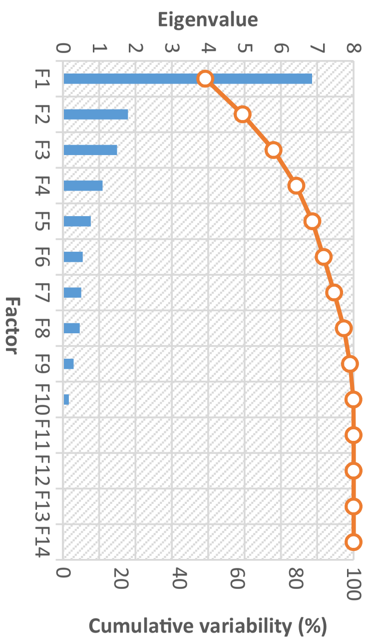


Fig. 4 Eigenvalues obtained from the factor analysis

Table 2 Correlation analysis of the groundwater chemical data (*n* = 68)

Variables	pH	EC	TDS	TH	Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4	NO_3	F
pH		− 0.31	− 0.28	− 0.33	− 0.42	− 0.14	− 0.18	− 0.06	− 0.06	0.34	− 0.31	− 0.14	− 0.27	0.35
EC	− 0.31		**0.99**	**0.86**	**0.66**	**0.73**	**0.89**	0.32	0.52	− 0.09	**0.94**	**0.79**	**0.50**	− 0.07
TDS	− 0.28	**0.99**		**0.83**	**0.62**	**0.71**	**0.92**	0.36	**0.58**	− 0.08	**0.92**	**0.80**	**0.51**	− 0.04
TH	− 0.33	**0.86**	**0.83**		**0.75**	**0.85**	**0.58**	0.10	0.36	− 0.20	**0.85**	**0.71**	0.36	0.04
Ca	− 0.42	**0.66**	**0.62**	**0.75**		0.30	0.39	0.13	0.16	− 0.15	**0.67**	**0.50**	0.25	− 0.30
Mg	− 0.14	**0.73**	**0.71**	**0.85**	0.30		**0.53**	0.04	0.39	− 0.16	**0.69**	**0.64**	0.32	0.30
Na	− 0.18	**0.89**	**0.92**	**0.58**	0.39	0.53		0.28	0.61	0.04	**0.81**	**0.71**	0.45	− 0.01
K	− 0.06	0.32	0.36	0.10	0.13	0.04	0.28		0.46	− 0.05	0.19	0.18	0.32	− 0.32
HCO_3	− 0.06	**0.52**	**0.58**	0.36	0.16	0.39	**0.61**	0.46		0.02	0.28	0.41	0.37	0.22
CO_3	0.34	− 0.09	−0.08	− 0.20	− 0.15	− 0.16	0.04	− 0.05	0.02		− 0.10	− 0.15	−0.03	0.01
Cl	− 0.31	**0.94**	**0.92**	**0.85**	**0.67**	**0.69**	**0.81**	0.19	0.28	− 0.10		**0.66**	0.31	− 0.18
SO_4	− 0.14	**0.79**	**0.80**	**0.71**	**0.50**	**0.64**	**0.71**	0.18	0.41	− 0.15	**0.66**		0.38	0.22
NO_3	− 0.27	**0.50**	**0.50**	0.36	0.25	0.32	0.45	0.32	0.37	− 0.03	0.31	0.38		0.06
F	0.35	− 0.07	− 0.04	0.04	− 0.30	0.30	− 0.01	− 0.32	0.22	0.01	− 0.18	0.22	0.06	

from 388 to 2686 mg/L (Avg. = 1059 mg/L). This shows that the groundwater in the study area is mostly contaminated with various ions. Among the major cations, sodium showed a range of 15 to 621 mg/L (Avg. = 204 mg/L). Considering the different origins of sodium in groundwater of Vellore District, natural and anthropogenic (predominantly tannery industries) can be found. Ions such as calcium and magnesium showed a range 18 to 240 mg/L (Avg. = 77 mg/L) and 24 to 199 mg/L (Avg. = 71.49 mg/L), respectively. Major anions bicarbonate, chloride, sulfate, and nitrate were in the range of 238 to 946 mg/L (Avg. = 474 mg/L), 25 to 1170 mg/L (Avg. = 274 mg/L), 7 to 394 mg/L, (Avg. = 251 mg/L), and 0 to 46 mg/L (Avg. = 11 mg/L). Very high concentration of Cl and SO_4 ions in the groundwater is an indication of pollution from the tannery effluents (Thangarajan 1999).

Table 3 Results of factor analysis of the groundwater samples

	F1	F2	F3	F4
pH	− 0.35	**0.65**	0.10	0.34
EC	**0.99**	− 0.01	0.02	0.10
TDS	**0.99**	0.04	0.09	0.07
TH	**0.89**	− 0.05	− 0.33	0.04
Ca	**0.68**	− 0.46	− 0.17	0.18
Mg	**0.76**	0.30	− 0.34	− 0.08
Na	**0.85**	0.16	0.22	0.14
K	0.32	− 0.14	**0.77**	− 0.20
HCO_3	**0.56**	**0.37**	0.46	− 0.25
CO_3	− 0.15	0.32	0.35	0.73
Cl	**0.91**	− 0.15	− 0.13	0.26
SO_4	**0.82**	0.23	− 0.14	− 0.02
NO_3	**0.53**	0.07	0.31	− 0.33
F	− 0.02	**0.84**	− 0.33	− 0.29
Variability (%)	46.382	13.088	13.012	7.823
Cumulative %	46.382	59.470	72.482	80.305

Fluoride geochemistry

This study which primarily focuses on fluoride, its concentrations, and the background levels will be discussed in detail. Groundwater has a concentration of F ranging from 0.2 to 3 mg/L with an average of 0.8 mg/L. In total, 35% of the samples have exceeded the permissible limit of 1.2 mg/L (BIS 1992). Certain amount of fluoride is good for dental and skeletal health. Thus, the acceptable limit is between 0.6 and 1.2 mg/L. Origin of fluoride in groundwater is mostly from geogenic sources, though some exceptional anthropogenic sources were reported in the literature. Mostly minerals like fluorite, apatite, mica, amphiboles, clay, and villuamite are rich in fluoride. Geology of the study area shows that

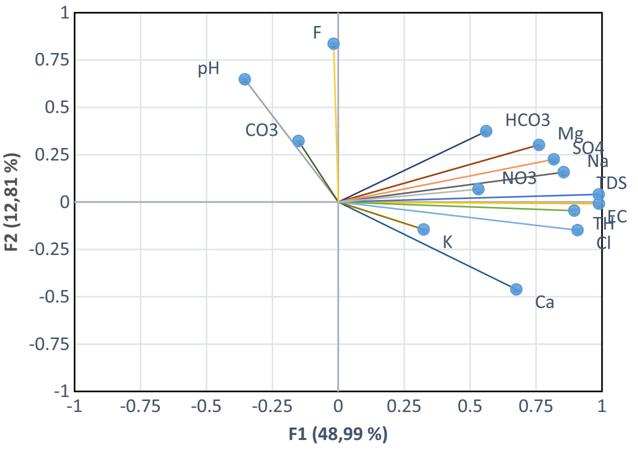


Fig. 5 Vector plot showing the factor loadings for factor 1 vs factor 2

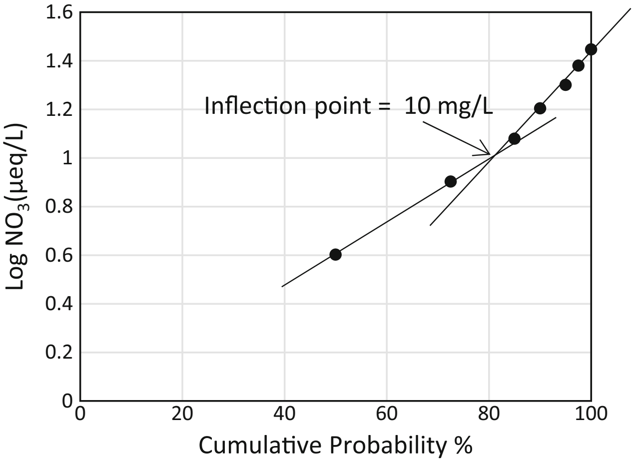


Fig. 6 Cumulative probability plots showing the NBL of Cl

crystalline rocks such as charnockite and gneisses are acting as the source for fluoride. The major controlling factors of fluoride geochemical dynamics in groundwater are solubility of F minerals, pH, temperature, anion exchange capacity of aquifer materials, type of geological materials and residence time, porosity, structures, groundwater age depth, concentration of carbonates, and bicarbonates in water (Chandra et al. 1981; Apambire et al. 1997; Sajil Kumar et al. 2014). Application of fertilizers and industrial activities can also increase the fluoride concentration in groundwater (Brindha and Elango 2011).

Geochemical facies

Geochemical facies are important indicators of the hydrogeochemical conditions of an aquifer and also playing a vital role in the mobilization of fluoride in groundwater. Two distinct water types were observed, i.e., Na-Ca-Mg-HCO_3-Cl types and Ca-Na-Mg-Cl-HCO_3 types (Fig. 3). The first type is favorable for fluoride enrichment in groundwater. It is frequently reported that high Na/Ca with elevated HCO_3 concentration is determining factor of the groundwater fluoride concentration in F-rich aquifers (Reddy et al. 2010; Grützmacher et al. 2013). In case of Na-rich Ca-poor groundwater, precipitation of fluoride as calcium fluoride (CaF_2), which is the most important controlling factor of the fluoride concentration in groundwater, will not occur. Moreover, Na-rich water will mobilize fluoride from the aquifer materials. Majority of the samples corresponding to the first group will be favoring this kind of hydrogeochemical conditions.

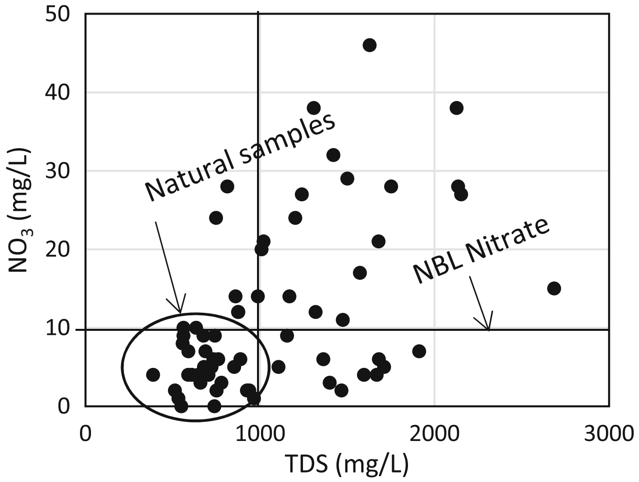


Fig. 8 Bivariate plot showing the relation between TDS and nitrate

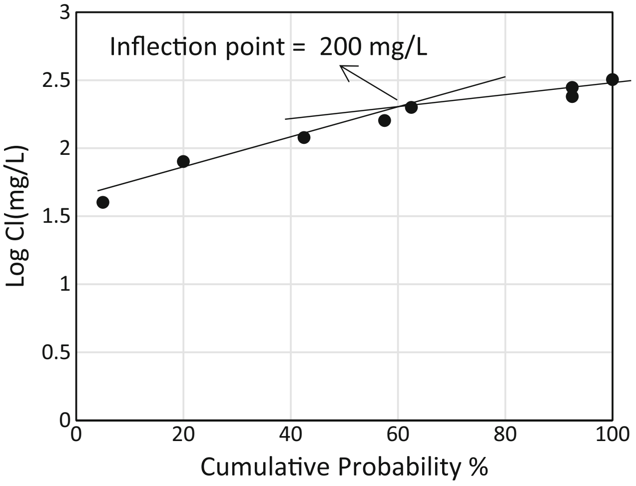


Fig. 7 Cumulative probability plots showing the NBL of NO_3

Multivariate analysis of groundwater chemical data

All groundwater samples (*n* = 68) were analyzed and correlation coefficient among each parameter was obtained (see Table 2). Electrical conductivity showed very good positive correlation with TDS, TH, Ca, Mg, Na, Cl, SO_4, and NO_3, indicating that all these parameters are strongly contributing

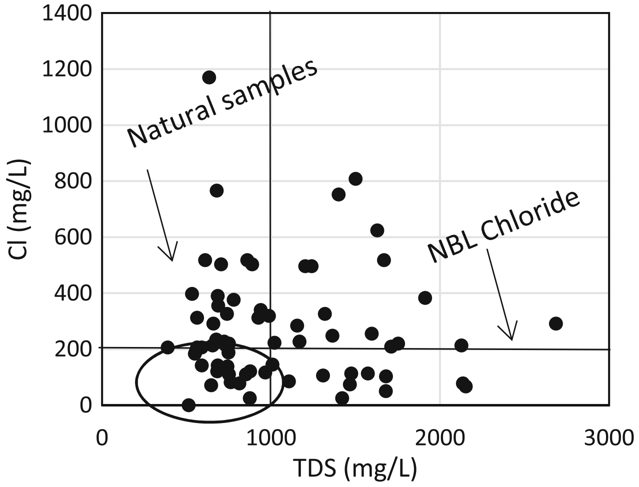


Fig. 9 Bivariate plot showing the relation between TDS and chloride

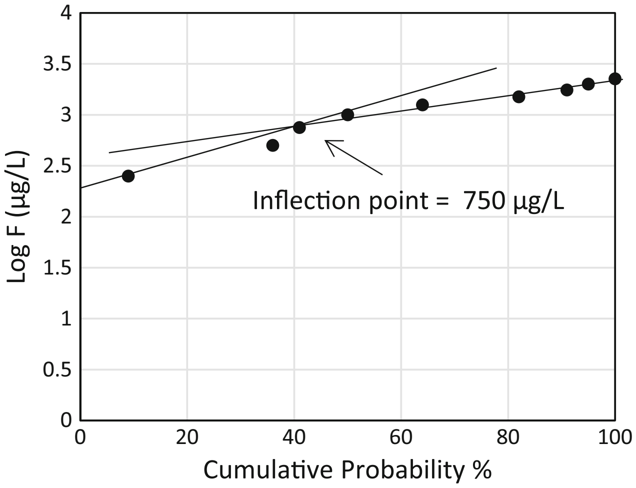


Fig. 10 Cumulative probability plot showing the NBL of fluoride

towards the total hydrochemistry of groundwater. Very high correlation for TH (total hardness), Ca ($r2$ = 0.75), and Mg ($r2$ = 0.85) clearly shows that temporary hardness in groundwater is mainly due to the increase of these ions. Significant positive correlation is observed from Na with Cl ($r2$ = 0.81) and SO_4 ($r2$ = 0.75) showing the salinity origin from tannery effluents. Correlation of F with the other parameters was not so significant with any other parameters than pH ($r2$ = 0.35) and Mg ($r2$ = 0.30). This result shows that groundwater is considerably biased to the anthropogenic influences, like tannery pollution, agricultural activities and municipal sewage etc. Hence, we have done a more detailed study with the factor analysis.

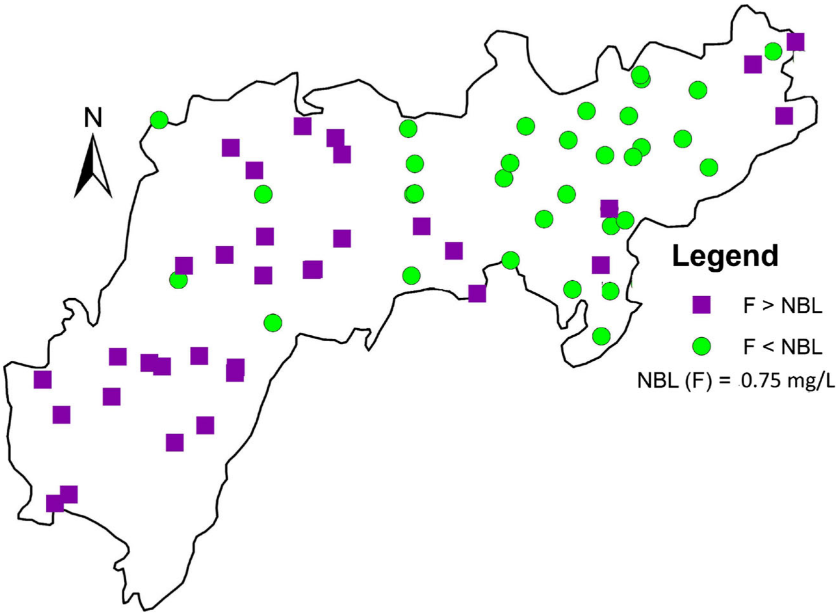
Factor analysis was performed and the principal components were derived for the entire population. Though there are several components reported, significant components were chosen based on the eigenvalues (see Fig. 4). Four factors were found to have an Eigenvalue more than 1, and they were considered for the further analysis.

All the four components were critically analyzed based on the individual factor loadings of the parameters. These four components effectively explained 80.30% of the total variance in the population and individually PCA1 = 42.38%, PCA2 = 13.08%, PCA3 = 13.01%, and 7.82%, respectively. Table 3 shows the results of PCA of groundwater samples.

Factor shows a strong loading for EC (0.99), TDS (0.99), TH (0.89) Ca (0.68), Mg, (0.76) Na (0.85), HCO_3 (0.56), Cl (0.91), SO_4 (0.82), and NO_3 (0.53). High factor loading for the parameters like Cl, SO_4, Na, EC, TDS, etc. shows that the samples are affected by the anthropogenic influences like tannery industries (Sajil Kumar 2014). Additionally, presence of NO_3, the first factor shows the agricultural and sewage pollution in groundwater. However, this factor has high loading for calcium and hardness, showing an impact of groundwater-aquifer interaction as well. Thus, this factor can be considered as affected by the anthropogenic as well as geogenic sources.

In factor 2, high loading was found for pH (0.65) and F (0.84), and a slightly significant loading for HCO_3. Influence of pH and bicarbonate on the fluoride mobilization is well documented in the literature (Handa 1975; Jacks et al. 1993; Saxena and Ahmed 2001). All the three parameters listed in factor 2 have natural origin and represent natural processes that control the water chemistry. Factor 3 has high loading for K (0.77). This can be related to the K-feldspars in the gneissic formations in the study regions and also to the fertilizer usage in agricultural fields. Factor 4 could not show any significant factor loading that can be accounted to any specific

Fig. 11 Spatial distribution of fluoride concentration in groundwater based on the NBL analysis



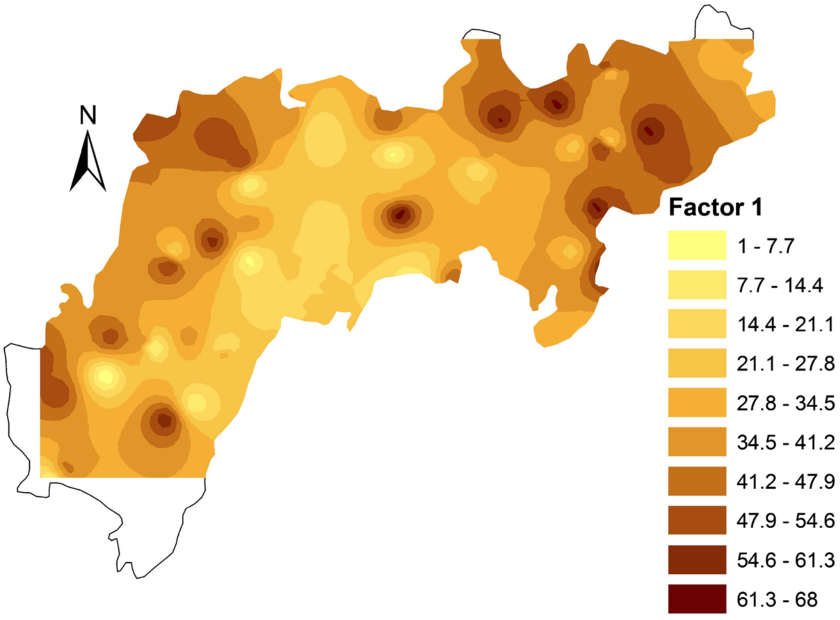


Fig. 12 Spatial distribution of factor 1 scores

geochemical process. The factor loading for the most prominent factors (1 and 2) is further presented in vector plot (Fig. 5).

Natural background level estimation

Methodology for the pre-selection is presented in "Pre-selection and cumulative probability plots" section. With the criterion 1, groundwater samples were separated base on the TDS values, and 28 samples found to be exceeding the limit 1000 mg/L (fresh drinking water standard based on WHO 2011). Remaining 40 samples were used in the further analysis. TDS is representing the mixture of natural and human impacted groundwaters. By separating highly impacted samples, further analysis will give more reliable results.

NBL values were estimated for Cl and NO_3 based on the remaining 40 samples. Frequency distribution for Cl concentrations was created and the values were converted into logarithmic scales. Log converted values were plotted against the cumulative probability percentages and the probability plots (CPP) were generated. Same methodology followed in the case of nitrates. In the CPP, inflection point indicated the threshold values. Calculated intersection points were 200 and 10 mg/L, for Cl and NO_3, respectively. Chloride and

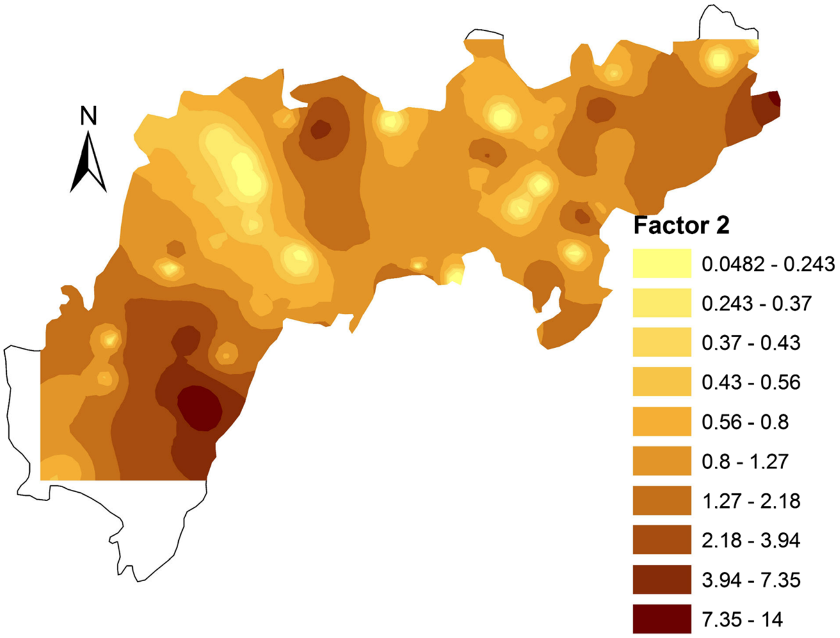


Fig. 13 Spatial distribution of factor 2 scores

nitrate were not available in natural groundwater of the study area and found to be sourced from tanneries and agricultural/sewage sources, respectively. We omitted those samples that crossed NBL values of these ions and the remaining 24 samples were used in the NBL estimation of fluoride. Figures 6 and 7 show the probability plots used in the estimation of NBL (Cl) and NBL (NO_3), respectively.

After the NBL values were fixed for Cl and nitrate, we have plotted TDS vs Cl (Fig. 8), and TDS vs NO_3 (Fig. 9) graphs. NBL values derived in the previous step was marked in the plot so that the natural samples can be selected as those below 1000 mg/L (TDS), 10 mg/L (NO_3), and 200 mg/L (Cl). By combining the results of Figs. 9 and 10, a total of 22 groundwater samples, with concentrations TDS < 1000 mg/L, Cl < 200 mg/L, and NO_3 (10 mg/L), were derived for the NBL estimation of fluoride. In case of NO_3, similar values (10 mg/L) were reported by European Environmental Agency (EUROWATERNET-Groundwater 2002). In their classic work in Midwestern Unites states, Panno et al. (2006) reported 0 to 2.5 mg/L of nitrate (as nitrogen), which is comparably a small value. In case of chloride, a threshold value of 167 mg/L was reported by Wendland et al. (2008) from Upper Rhine Valley. (Kelly 2000) reported a background concentration of 10 to 20 mg/L, from northeastern Illinois.

For the better visualization of samples, milligram per liter is converted to microgram per liter. After the preselection process, 22 groundwater samples were used in the analysis which showed a range of fluoride as 0.09 to 2.17 with an average of 0.78 mg/L. Based on this data, NBL was generated by CPP. As we have selected only fresh samples, no anthropogenic inputs were expected, and hence, only one inflection point (threshold value) was expected. From the inflection point, NBL was estimated as 0.75 mg/L (750 μg/L). This means that the normal expected concentration of F in the original groundwater in study area is ranging from 0.02 to 0.75 mg/L.

To understand the NBL of fluoride in the study area, total data set was classified into two categories, i.e., > NBL and ≤ NBL. Spatial distribution maps were created based on this classification (Fig. 11). It shows that majority of the samples in the western part of the study area exceeded NBL of fluoride, i.e., 0.75 mg/L. A cross check with aquifer chemistry of rocks suggested that the presence of F-rich minerals were present in the granitic-gneissic rocks in the study area. As it was already identified through multivariate analysis, a better visualization of the influencing processes was possible by spatial mapping of the factor scores (Figs. 12 and 13). It revealed that F1 was distributed in the eastern and northeastern parts, where F concentration was below the natural NBL. On the other hand, in the southern and southwestern parts, F2 has high loadings. This confirms the distribution of fluoride concentration within the study area and its correlative behavior with the natural/anthropogenic geochemical interventions.

Conclusions

Hydrogeochemical data from Vellore District is analyzed and a NBL of fluoride concentration in the groundwater is estimated. Geochemical methods, multivariate analysis, pre-selection method, and cumulative probability plots were employed in the study and found to be very effective in grounding the NBL of fluoride for this region. Component 1 of the factor analysis indicated the natural and anthropogenic influences, whereas factor 2 showed natural process with very high factor loadings for pH and F. This result goes well in line with the two major water types Na-Ca-Mg-HCO_3-Cl types and Ca-Na-Mg-Cl-HCO_3. Mobility of fluoride is found to be increased with the increase in Na, HCO_3, pH and decrease in Ca values. For the NBL estimation, groundwater samples were preselected initially with TDS values and then with Cl and NO_3 to eliminate the human affected samples. In total, 22 natural groundwater samples were selected from 68 samples and the cumulative probability plot showed that natural threshold value for fluoride in the study are is 0.75 mg/L. Based on the NBL values, 29 groundwater samples were found to be exceeding this limit. Spatial variation mapping of NBL and factor scores showed that the Southern and Southwestern regions of the study area were more impacted with fluoride contamination. This observation is supported by fluoride-rich minerals in the hard rocks of this region. This study established the present natural background level of fluoride for the first time in the study area, which will be of great use in the future management of fluoride contamination, especially with human health perspectives. We suggest to use the research methodology in other regions of the country to make a benchmark for the contamination status. This will be helpful in the future water management strategies.

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