A Study on the Geochemistry of Fluoride in Groundwater for the Delineation of Fluoride Zones

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Author's contribution

The only author performed the whole research work. Author AOA wrote the first draft of the paper. Author AOA read and approved the final manuscript.

ABSTRACT

In view of the reports of fluorosis, a geochemical exploration of groundwaters along the coast of Bay of Bengal of Srikakulam was carried out for the delineation of fluoride zones. The correlative interpretation of the 50 groundwater sample's geophysical and chemical data of two seasons with computed arguments revealed mechanisms controlling its genesis. Geochemical ratios and base index patterns revealed the groundwater chemistry. Fluoride spatial distribution and its mineral species were also delineated. It was understood that the local topographic nature and sporadic presence of the apatite traces is the source. Also the geochemistry of the mineral in its dissemination is of high curiosity in its leaching behavior due to geological formations and needs in depth study in the area. Data disseminated to groundwater board and civil societies evoked for necessary actions in avoiding further menace.

Keywords: Fluoride; geochemical; genesis; spatial distribution; Bay of Bengal.

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1. INTRODUCTION

Fluoride is the most electronegative of all chemical elements and is therefore never encountered in nature in the elemental form. It is seventeenth in the order of frequency of occurrence of the elements, and represents about 0.06 to 0.09% of the earth's crust [1]. Fluoride is a typical lithophile element under terrestrial conditions. The bulk of the element is found in the constituents of silicate rocks, where the complex fluorophosphates like apatite $(Ca_{10}(PO_4)_6F_2)$, seems to be one of the major fluoride minerals [2,3]. Omueti [4] observed that, with regard to fixation of the bulk of fluoride as complex hydroxy-silicates and hydroxyalumino-silicates, in which the hydroxyl ions (OH) may be largely replaced by fluoride, as observed in amphiboles and minerals of the mica family (biotite and muscovite). In many rocks, especially in those of late magmatic stages of evolution, the fluoride in such silicates may even greatly exceed the amount fixed in apatite. Not uncommonly one encounters CaF_2 as a constitution of magmatic rocks; much more rarely one finds villiaumite (NaF), in a few nephaline syenites [5]. Fluoride in the ground/surface water derives from the weathering and subsequent leaching of fluoride-bearing minerals in rocks and soils like Fluorspar, Cryolite and Fluorapatite. A substantial amount of this fluoride is retained in subsoil horizons, where it complexes with Aluminium that is most likely associated with phyllosilicates [6].

Larsen and Widdowson [7] observed that the solubility of fluoride in soils is highly variable and has the tendency to be higher at pH <5 and >6 values. It appears that the predominant retention mechanism is that of fluoride exchange with the OH group of amorphous materials, such as Al-hydroxides [8,9]. In this case, fluoride resulting in a simultaneous release of Al and Fe replaces the crystal lattice OH- of clay minerals. Other fluoride retention mechanisms include the binding of fluoride to soil cations (e.g., Ca^{2+}, Al^{3+}), or fluoride precipitation as CaF_2, as in calcareous soils [10].

Fluoride has dual significance. It helps in the normal mineralisation of bones and formation of dental enamel. Fluoride when consumed in inadequate quantities (less than 0.5ppm) causes health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children. On the contrary, when fluoride consumed in excess (more than 1.0ppm), it leads to several health complications observed in all ages [11].

Being a cumulative bone seeking mineral, the resultant skeletal changes are progressive. Higher fluoride concentration exerts a negative effect on the course of metabolic processes and an individual may suffer from skeletal fluorosis, dental fluorosis, nonskeletal manifestation or a combination of the above [12]. The incidence and severity of fluorosis is related to the fluoride content in various components of environment, viz. air, soil and water and Chen et al. [13] stated that, out of these, groundwater is the major contributor to the problem. If dental caries is affected in the front row (Canines) of the teeth it becomes a cosmetic feeling to the individual as they expose while talking or smiling, which may cause Psychological effect like inferiority complex before others thus leading in decrease of self-esteem according to Susheela [14].

UNICEF estimates that "fluorosis" is endemic in at least 25 countries across the world, whereas in India, certain parts of 17, out of 32 states have been identified as "endemic" areas, with an estimated 66 million people seriously afflicted [15,16]. The difficulties in diagnosing the early stages of fluorosis those from the arthritic symptoms is always leading to occur damage before detectable bone changes are evident. The early symptoms may be

misdiagnosed as rheumatoid or osteoarthritis as the symptoms in all these cases is similar in nature. Bassin et al. [17] stated that the misdiagnosis of possible skeletal fluorosis, often leads to severe disability while closely mimicking a wide variety of other disorders including damage to developing brain and its intelligent quotient will be low.

In Srikakulam district, factors controlling groundwater quality was studied by V. Rao et al. [18]. Fluoride occurrence and behavior in some parts of the district was earlier reported by S. Rao [19] and also groundwater potential zones using GIS thermic maps in the district were reported by Murthy et al. [20]. In view of the above observations and reports of fluorosis the present study area was selected, where stations which were neither monitored by groundwater board nor by the private were chosen. Fundamental knowledge of processes that control natural water composition is required for rational management of water quality. As the chemical composition of natural water is controlled by many interrelated processes, it follows that some understanding of these processes is needed before one can speak or act intelligently towards the sole aim of water-quality control and its improvement. Following the fact, more samples give more accuracy; the present study covering entire district will reveal the present status.

2. STUDY AREA

Srikakulam district is the extreme northeastern district of Andhra Pradesh situated within the geographic co-ordinates of 18°-20′ and 19°-10′ of Northern latitude and 83°-50′ and 84°-50′ of Eastern longitude. A portion of Srikakulam district is a plain terrain with intense agriculture and another portion of the district is rocky and hilly terrain covered with forests. The district is skirted by Kandivalasagedda, Vamsadhara and Bahuda at certain stretches of their courses while a line of heights of the great Eastern Ghats run from North East. Vizianagaram District flanks in the south and west while Orissa bounds it on the north and Bay of Bengal on the East. Some extent of Mahendragiri hills also covers the district. The total area of the district is 5837 Sq. km. with a population over forty two thousand according to the 2001 census. Most of the forest area of the plain terrain has been damaged by intense agriculture. Kotthuru, Hiramandalam, Pathapatnam, Kalingadal reservoir and some other areas are still covered with dense forests. The sampling stations in the study area are given in Fig. 1.

3. METHODOLOGY

All the analytical assessments were carried following standard methods for examination of groundwater [21]. The geographical parameters (Latitude and Longitude) for the exact location of the sampling station noted at the site were referred with the help of the district topo sheets obtained with a special permission from Deputy Director, Groundwater Board, Visakhapatnam. The term parts per million is a weight-to-weight ratio. Its use was more or less universal and unquestioned when analysis was principally concerned with water, because a liter of water weighs approximately 1000gm or 1,000,000mg, and hence 1 mg/L was considered to be equal to 1ppm. Hence in the present study the results have been expressed in parts per million (ppm). These units were prescribed by Indian Standard Institutions (IS 3025/1964) [22], International Standards for Drinking Water, WHO [21]. The statistical summary of the analytical results is summarized in Table 1. Fluoride concentration was determined using 'Omega' fluoride ion selective electrode in combination with a double junction reference electrode (with inner junction made of 4M KCl and outer junction 1M KNO_3) and Consort P602 ion meter. 25 mL of each sample and standard solution (0.1ppm - 10ppm, from NaF) were mixed with equal volumes of TISAB buffer [23]. The instrument was

calibrated with standards, after compensation for temperature had been done. The instrument directly records the concentration of fluoride in the water samples. With the help of Surfer 8.0 programmer, the base map of the district with its limits was drawn and later the sampling stations coordinates were incorporated by drawing a new post map in the base map. The contour (spatial distribution) map was drawn by taking the latitude and longitude of respective stations along with the parameter's concentration.
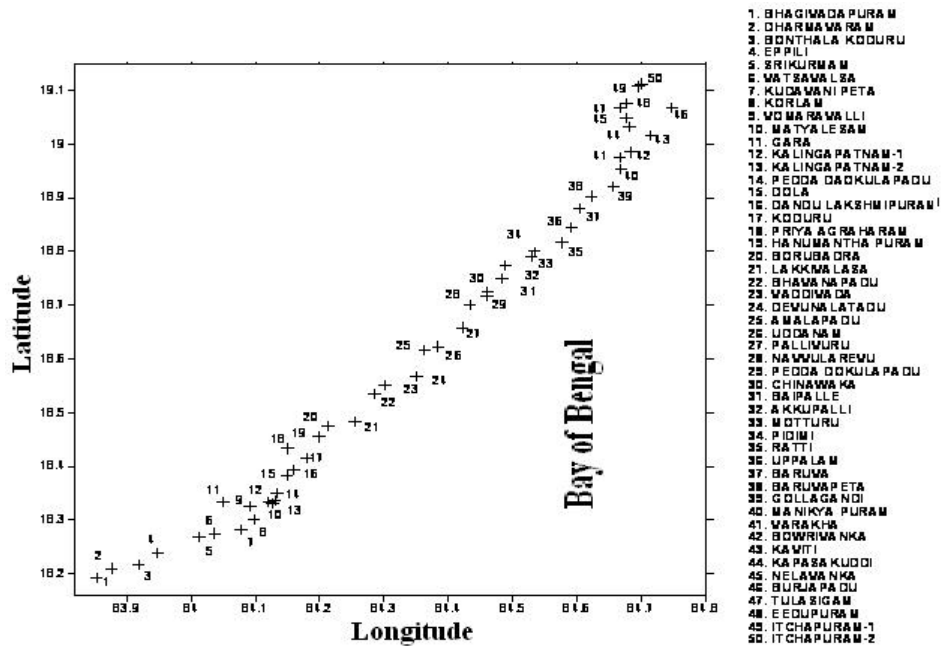

Fig. 1. Map of the study area

**Table 1. Statistical summary of the analytical results**

Parameter*	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation
pH	7.22	8.35	7.70	0.26	3.40
E.C.	847.00	2446.00	1413.10	413.02	29.22
TDS	524.00	1674.00	942.22	257.58	27.33
Ca^{2+}	37.00	146.00	63.70	18.91	29.69
Mg^{2+}	21.00	115.00	52.56	16.52	31.43
Na^+	85.00	386.00	172.40	59.25	34.36
K^+	2.00	80.00	8.78	12.40	141.27
CO_3^-	0.00	40.00	3.60	9.63	267.73
HCO_3^-	220.00	522.00	341.80	69.35	20.28
Cl^-	134.00	508.00	264.80	91.88	34.69
SO_4^{2-}	19.00	124.00	42.82	21.08	48.81
F^-	0.10	2.04	0.86	0.41	48.21
NO_3^-	2.00	52.00	14.24	11.21	78.78
PO_4^{2-}	0.00	2.55	0.43	0.58	133.92

*All parameters are expressed in mg/L, except pH and E.C.;
TDS = Total Dissolved Solids, E.C. = Electrical Conductivity (µSiemens/cm^2).

4. RESULTS AND DISCUSSION

Assessment of the chemical quality of drinking water relies on comparison of the results of the water analysis with guideline values. As the term quality is relative, its standardization is always complicated and debatable. One such standard, always in the limelight is fluoride. Some countries have fixed its minimum value as 1.5ppm, while India along with some others has fixed it as 1ppm. The tropical nature, dietary habits, physiological formation etc, are the reasons for this deviation of fluoride standard from others. Likewise many of the constituents for Indian Standards of potable waters like chloride, nitrate, sulphate etc. differ from those of other countries in the world.

High concentrations of fluoride (>1.5ppm) are observed in stations (16, 23, 34, 39 and 7). The samples (5, 10, 13, 17, 20, 27, 30, 36, 37, 40, 41, 43, 45, 48 and 49) show concentrations more than 1ppm. The former set of groundwater samples come under the non-potable type as fluoride concentration crossed the permissible limit of 1.5ppm prescribed for safe drinking by World Health Organization and Indian Standards. In these areas the vulnerability towards dental and skeletal fluorosis will be at its high. The delineation of fluoride zones in the study area is given in Fig. 2.
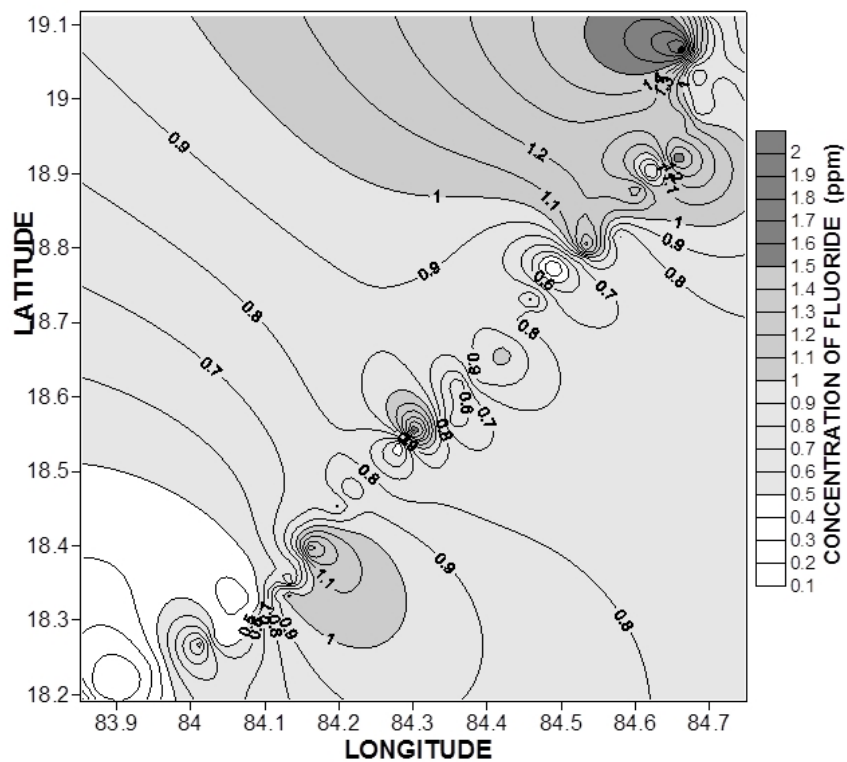
Fig. 2. Delineation of fluoride zones along Bay of Bengal

As far as the second set of samples which had fluoride concentration more than 1ppm, fall under the non-reliable source for safe drinking, as concentrations at this rate taken as a daily dose for considerable amount of time will show its effects, especially the dental fluorosis. Especially the young with developmental stages of teeth are more vulnerable. As the onset

of fluorosis is not instantaneous, its effects need time to take toll on the body and by then it would be too late neither to cure nor to prevent from further damage.

The origin of high fluoride concentrations in these samples in interpreted with the help of WATEQ4F programmer [24]. It correlates an input data of the parameters given to predict the possible mineral source responsible for its existence in that particular area. The concentrations of parameters determined (Physical Characteristics, Cations, Anions, Geophysical etc.) in the present study were recorded in the tabular form of the input data file was the first step of the programme. Then, with a specific input file name with simultaneous output file, the programme will be executed.

The WATEQ4F programmer correlates the concentrations of the parameters in their cationic and anionic ratios with that of the existed mineral forms. Here, as all the available mineral species cationic and anionic ratios are pre-recorded, the best possible correlation will be displayed in the form of Saturation Indices (S.I.). Theses S.I. of the mineral species of an area signify the ease with which the ions are able to leach into the groundwaters. The ionic strength of the elements constituting the mineral determines the ionic exchange on contact with the groundwaters. The difference in these strengths will initiate the process; likewise the resident time is also a key factor in leaching to the mineral species into the groundwaters. Here comes the role of other ions in the vicinity, like Calcium, Phosphate etc. where the role of pH being critical. Positive S.I. values indicate a possible existence of an anion or cation in that form (mineral), whereas the negative values signify an under saturation of the form (mineral) or non-likely existence. These signify the leaching of the ions into the groundwaters of the study area.

In case of fluoride, as its main combinations includes the concentrations of Ca^{2+}, Cl^-, PO_4^{3-} were given along with all other parameters given as input, as in general, its principle mineral forms are Apatite $Ca_5 (OH, F, Cl) (PO_4^{-3})$, Fluorapatite $Ca_5(OH, F, Cl)(PO_4^{-3})$ and Fluorite CaF_2. Then the WATEQ 4F programme was executed and an output file showing different Saturation Indexes (S.I.) values of the possible combinations of fluoride existence mineral forms such as Apatite, Fluorapatite and Fluorite in the area were obtained (Table 2).

For the present study area the Wateq-4F programmer had given the positive Saturation Index values of Apatite and negative values of Fluorite minerals. Higher the positive value, indicate the higher possibility for existence of that mineral species in the given area. These establish the fact that the origin of high fluoride is courtesy of former than that of the later. The correlation coefficient values of Fluoride with Calcium (0.07) and Phosphate (0.08) are far more correlated than any other ions of the data strengthen the arguments and signify their integration of availability. The correlation of fluoride with its mineral species is given in the Figs. 3, 4 and 5 also signifies the above trend. The concept of hydro geochemical facies is widely used to explain the distribution and genesis of principal groups or types of groundwaters in a selected area according to Back [25], as it reflects the dominant type of chemical processes in a lithological framework and pattern of water flow in it.

Table 2. Saturation index values of fluoride minerals in srikakulam district

| Sampling station	Apatite	Fluorapatite	Fluorite	Sampling station	Apatite	Fluorapatite	Fluorite
1 BHAGIVADAPURAM	8.759	-1.405	-1.757	26 UDDANAM	17.15	3.576	-1.203
2 DHARMAVARAM	0	0	-3.264	27 PALLIVURU	16.197	2.956	-1.155
3 B. KODURU	9.24	-0.609	-3.264	28 NAUVVLAREVU	15.964	3.086	-1.497
4 EPPILI	12.33	1.03	-2.294	29 P DOKULAPADU	16.793	3.831	-1.667
5 SRIKURAMAM	5.329	-3.497	-1.22	30 CHINAWAKA	17.681	3.734	-0.942
6 VATSAVALASA	13.258	1.618	-2.094	31 BAIPILLE	0	0	-1.616
7 KUNDAVANI PETA	16.31	2.857	-1.674	32 AKKUPALLI	9.763	-0.704	-2.433
8 KORLAM	16.535	2.973	-1.408	33 MOTTURU	15.438	2.74	-1.408
9 VOMARAVALLI	11.592	0.516	-2.07	34 PIDIMI	12.278	0.655	-0.806
10 MATYALESAM	9.507	-1.274	-1.223	35 RATTI	19.891	5.317	-1.521
11 GARA	17.851	4.037	-2.027	36 UPPALAM	11.192	-0.058	-1.137
12 KALINGAPATNAM-1	19.442	4.767	-1.158	37 BARUVA	12.912	0.962	-1.834
13 KALINGAPATNAM-2	18.529	4.462	-1.046	38 BARUVAPETA	10.915	0.204	-1.857
14 PEDDA PALIPETA	0	0	-1.791	39 GOLLAGANDI	18.9	4.5	-0.836
15 DOLA	14.543	1.721	-1.344	40 MANIKYAPURAM	17.947	4.153	-1.234
16 D.LAKSHMIPURAM	14.964	2.064	-0.766	41 VARAKHA	18.188	3.876	-1.177
17 KODURU	0	0	-1.099	42 BOWRIVANKA	9.571	-0.937	-1.378
18 PRIYA AGRAHARAM	10.102	-0.277	-1.585	43 KAVITI	19.18	4.756	-1.07
19 HANUMNTHAPURAM	15.378	3.048	-1.679	44 KAPASAKUDDI	16.401	3.334	-1.5
20 BORUBADRA	13.397	1.148	-1.143	45 NELAVANKA	14.348	2.066	-1.23
21 LAKKIVALASA	17.67	3.643	-1.275	46 BURJAPADU	18.609	4.644	-1.607
22 BHAVANAPADU	15.034	2.613	-2.183	47 TULASIGAM	21.185	5.682	-0.574
23 VADDIVADA	16.395	2.9	-0.746	48 EEDUPURAM	17.705	3.742	-1.009
24 DEVUNALATADU	10.687	-0.624	-1.418	49 ITCHAPURAM	13.578	1.408	-1.075
25 AMALAPADU	11.002	-0.011	-1.799	50 ITCHAPURAM	16.4	3.11	-1.435
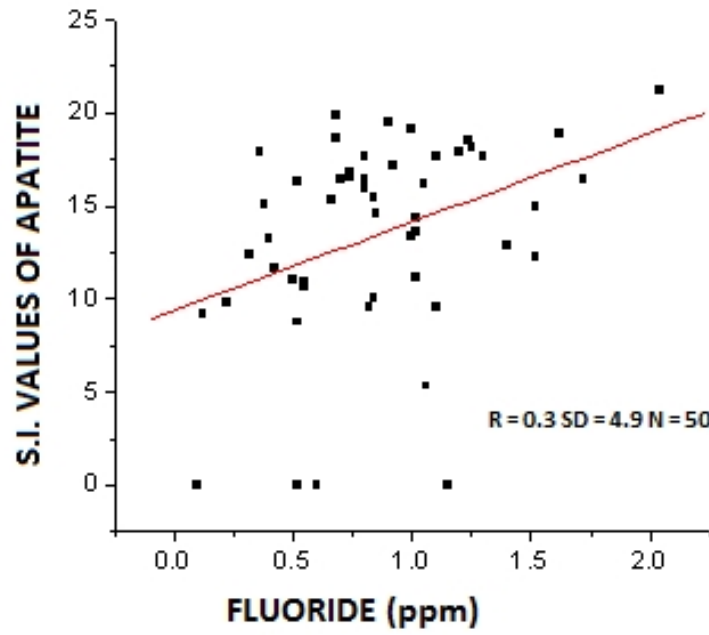
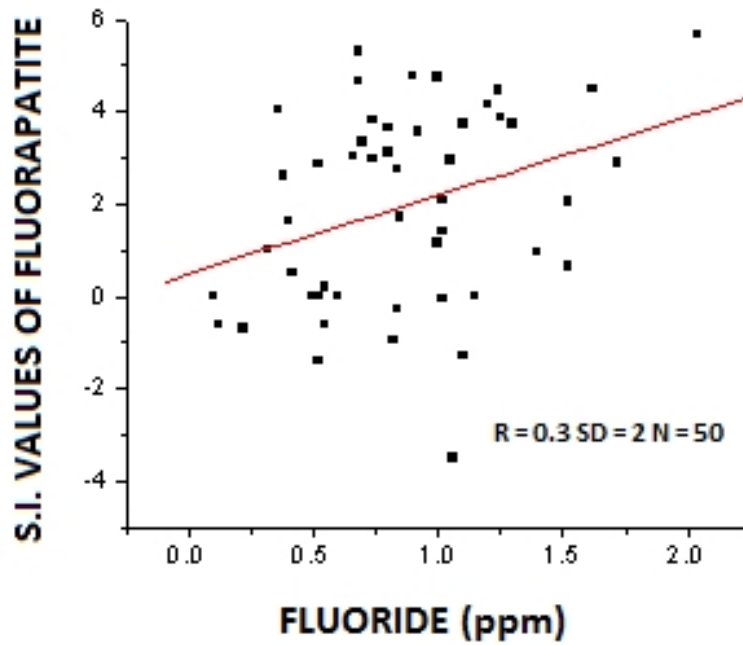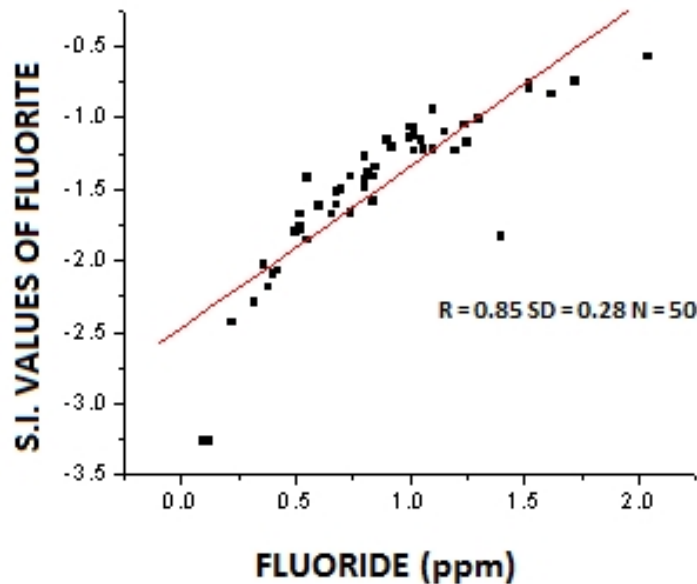**Fig. 3. Fluoride Vs S.I. values of apatite mineral**

Fig. 4. Fluoride Vs S.I. values of fluorapatite mineral

Fig. 5. Fluoride Vs S.I. values of fluorite mineral

In the study area, the hydrogeochemical facies is classified into two types. They are (a) Na^+ > Ca^{2+} > Mg^{2+} : HCO_3^- > Cl^- > SO_4^{2-} and (b) Na^+ > Mg^{2+} > Ca^{2+} : HCO_3^- > Cl^- > SO_4^{2-} and Cl^- > HCO_3^- > SO_4^{2-}. As per the hydrogeochemical facies, 68% (2, 3, 6, 7, 8, 10, 11, 14, 15, 16, 17, 18, 20, 21, 23, 24, 25, 26, 27, 29, 30, 34, 35, 36, 37, 39, 40, 41, 43, 44, 46, 48, 49 and 50) of the total samples belong to the Na^+:HCO_3^- type, indicating the presence of similar sources for the origin and hence they are responsible for the similar environmental hydro geological conditions. The occurrence of Na^+ : Cl^- type in the remaining 32% (1, 4, 5, 9, 12, 13, 19, 22, 28, 31, 32, 33, 38, 42, 45 and 47) samples can be attributed to their local variations of the geological conditions like clay horizons, low lying areas and backwater zones.

Geochemical ratios are widely applied to establish the facts about the chemical similarities among the waters, which are used for deciding the origin of the water chemistry. According to Sarin et al. [26], source for the ions in the groundwaters can be predicted using the HCO_3^- : Cl^- ratio along with Ca^{2+} + Mg^{2+} : TC (Total Cations) and Na^+ + K^+ : TC ratios. They further stated that, the cationic and anionic ratio of sodium and chloride also has to be included with the above in cases where their percentage of contribution in the total numbers is as significant as others.

In the study area, the mean HCO_3^- : Cl^- ratio in all the district is more than unity with value of 1.41. The Ca^{2+} + Mg^{2+} : TC (Total Cations) and Na^+ + K^+ : TC ratios mean values are less than unity, which are - 0.40 and 0.59 respectively. With the above conditions in the study area the major source for the chemical ions would be the rock weathering (i.e. from the mineral sources of the fluoride). As the sampling sources have coastal origin, it is obvious that the sodium and chloride ratio would contribute significant information for the assessment of the source of ions in these groundwaters, where effects of the elevated and the plain are often carried over and settles in the coast with time and time and space.

In general, with the ratios of alkaline earths and alkalies with their total concentrations showing values less than unity, their values should be more than unity in order to support the above prediction. But, the mean of sodium and chloride ratios (0.60, 0.73 and 0.66) are less than unity in the study areas in the area. Even though there are cases which validate the criteria, the overall scenario looks quite opposite, supporting the view that rock weathering is not the only source but also other factors play their part in the genesis of the chemical ions. These include from anthropogenic, seasonal or effects carried from the elevated and the plain.

Dominance of the local variations from place to place makes groundwater chemistry change quite appreciably. This can be understood by the study of two Base Exchange Index patterns of the particular area [27]. These indexes are, $CA_1 = Cl^- - (Na^+ + K^+) : Cl^-$ and $CA_2 = Cl^- - (Na^+ + K^+) : (SO_4^{2-} + HCO_3^- + CO_3^- + NO_3^-)$. Where CA_1 and CA_2 are cation and anion ratios. When there is an exchange of Na^+ and K^+ in the groundwaters with Mg^{2+} or Ca^{2+} in the rock/weathered products (clays), both the indices will be positive. If there is a reverse exchange, then both the indexes will be negative. In the study area, mean values of the two indices are 0.3 and 0.21. In general, groundwaters with negative values of both the indices signify that the host rocks are the primary source for dissolved ions (fluoride, Calcium, etc.) in the area, but as in the above cases where the values obtained are positive.

5. CONCLUSIONS

The positive values observed in some stations of the Fluorapatite mineral signify the isomorphous nature of Apatite form of Fluoride in saturation form in the study area. The dominance of Apatite over Fluorapatite (irrespective of its lower standard deviation than Apatite in their plots with fluoride) values conform its presence of the mineral in those areas of high fluoride. The hydrogeochemical facies and the geochemical ratios strengthen the evidence of this observation. By the Base Exchange index it gives the reason would be the highest electronegativity of fluoride than chloride enabling it to quickly leach upon the contact of groundwater with time and space attributes its presence. Added to these are the local geological conditions where there are topographically low lying areas are more vulnerable as groundwater fluctuations might be higher. The stations thus identified were being informed to groundwater board and local civic bodies for immediate closer as onset of fluorosis is evident in these areas in avoiding further health effects.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1.	Wedepohl. Hand book of geochemistry. Springer-Verlage. New York. 1974;2.

2.	Subramanian V. A geochemical model for phosphate mineralization in marine environment. Geological survey of India. 1980;44:308-313.
3.	Rutherford PM, Dudas MJ, Arocena JM. Trace elements and fluoride in phosphor-gypsum leachates. Environmental Technology. 1995;16343-354.
4.	Omueti JAI, Jones RL. Fluoride adsorption by Illinois soils. Journal of Soil Science. 1977;28:564-572.
5.	Deshmukh AN, Wadaskar PM, Malpe DB. Fluorine in environment: A review. Geology Magazine. 1995;9:1-20.
6.	Huang MP, Jackson ML. Mechanism of reaction of neutral fluoride solution with layer silicates and oxides of soils. Soil Science Proceedings. 1965;2:661-665.
7.	Larsen S, Widdowson AE. Soil fluorine. *Journal of Soil Sci*ence. 1971;22:210-221.
8.	Flühler H, Polomski J, Blaser P. Retention and movement of fluoride in soils. Journal of Environmental Quality. 1982;11:461-468.
9.	Barrow NJ, Ellis AS. Testing a mechanistic model- III, the effects of pH on fluoride retention by a soil. Journal of Soil Science. 1986;37:287-293.
10.	Gupta RK, Chhabra R, Abrol IP. Fluorine adsorption behavior in alkali soils: Relative roles of pH and sodicity. Soil Science. 1982;133:364-368.
11.	Vaish AK, Vaish P. A case study of fluorosis mitigation in Dugnarpur district, Rajasthan, India. 3rd International Workshop on Fluorosis Prevention and Defluoridation of Water. 2002;97-104.
12.	Wagner BM, Burt BA, Cantor KP, Krewski D, Levy MS, Mcconnell EE, Whiteford FM. Heath effects of ingested fluoride. Fluoride. 1993;26:278-281.
13.	Chen HS, Huang ST. Effect of fluoride on deciduous teeth resorption of young rabbits. Bulletin of Environmental Contaminant Toxicology. 1994;52:212-219.
14.	Susheela AK. Fluorosis Management Programme in India. Current Science. 1999;77(10):1250-1256.
15.	Chidambaram S, Ramnathan AL, Vasudevan S. Fluoride removal studies in water using natural materilas. Water SA. 2003;29(3):339-343.
16.	Abdel-Ghani NT, Hefny M, El-Chagbaby GAF. Removal of lead from aqueous solution using low cost abundantly available adsorbents. International Journal of Environmental Technology. 2007;4(1):67-73.
17.	Bassin EB, Wypij D, Mittleman MA. Age-specific fluoride exposure in drinking water and osteosarcoma. Cancer Causes and Control. 2006;17:421-8.
18.	Venkateswara Rao S, Krishna Rao G, Subba Rao N. Factors controlling groundwater quality in parts of Srikakulam District, Andhra Pradesh, India. Journal of Indian Academic Geosciences. 1996;39:33–39.
19.	Rao NVR, Rao KSP, Schuiling RD. Fluorine distribution in waters of Nalgonda district, Andhra Pradesh, India. Environmental Geology. 1993;21:84-89.
20.	Murthy KSR, Amminedu E, Rao VV. Integration of thematic maps through GIS for identification of groundwater zones. Journal of Indian Society of Remote Sensing. 2003;31 (3):197-210.
21.	WHO Guidelines for drinking water quality Recommendations. WHO. Geneva. 1995;1:188,.
22.	I.S.I. Indian Standard Specification for drinking water (15: 10500); 1983.
23.	Corning's Fluoride selective electrode. Operating instructions and technical specification. Corning medical, Massachusetts. 1979;7.
24.	Plummer LN, Jones, BF, Truesdell AH. WATEQ 4F- a FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. USGS Water Resource Invest. 1976;13:61-76.

25. Back W. Origin of hydrochemical facies of groundwater in the Atlantic coastal plain. Report Pt. I, Geochemical Cycles, XXI Session, Norden, International Geological Congress, Copenhagen. 1960;87-95.
26. Sarin MM, Swamy SK, Dilip K, Moore WS. Major ion chemistry of the Ganga-Brahmaputra river system-weathering processes and fluxes to the Bay of Bengal. Geochimica Cosmochim Acta. 1989;53:997-1109.
27. Schoeller H. Hydrodynamique lans le karst. Actes. Du. Colloque. Dubrovnik. IAHS/UNESCO, Wallingford, UK and Paris, France. 1965;(I):3-20.

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