



## **Geochemistry of Fluoride bearing Groundwater from Nuzendla Mandal, Guntur District, Andhra Pradesh, India**

**G BABU RAO AND P V NAGESWARA RAO**

*Department of Geology, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur-522 510, Andhra Pradesh, INDIA*

*Email: gudipudi.br@gmail.com*

**Abstract:** *The continuous consumption of groundwater carrying high amount of fluoride causes dental and skeletal fluorosis to humans. Excessive fluoride concentrations in groundwater have been reported in 25 nations including India where 14 states are facing fluoride problem. In view of this, an attempt has been made to find out the fluoride content in the groundwater and impact on the people. Nuzendla mandal, Guntur district is the present study area which is identified as one of the drought prone and fluoride incidence mandals of Andhra Pradesh. Groundwater samples from different hydro-geological set-up have been collected during pre- and post-monsoon seasons and determined for various physico-chemical parameters. About 62 % and 68% of the samples collected respectively during pre-and post-monsoon seasons are exceeding the safe limit of 1.5 Mg/L of Fluoride. The chemical data of the groundwater shows positive correlation between F<sup>-</sup> & pH; F<sup>-</sup> & Na<sup>+</sup>; F<sup>-</sup> & HCO<sub>3</sub><sup>-</sup> whereas negative correlation is observed between F<sup>-</sup> & Mg<sup>2+</sup>; F<sup>-</sup> & Ca<sup>2+</sup>. Probable sources of fluoride are weathering and leaching of fluoride bearing minerals under the alkaline environment along with high rate of evaporation and longer residence time of water. Correlation matrix also supports the above observations.*

**Keywords:** *groundwater, geochemistry, ionic ratio, fluoride, Nuzendla*

### **Introduction**

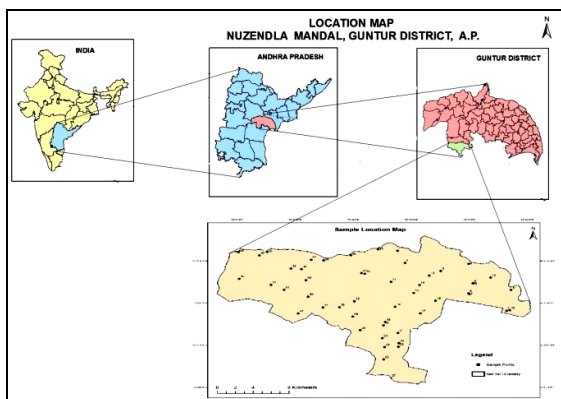
Groundwater comes into contact with various minerals which are soluble in water to varying degrees. The dissolved solutes determine the utility of water for various purposes. Ground and surface water attain their characteristics by chemical reactions with solids, i.e., soil sediments and rocks [1]. The chemical composition of water is mainly due to dissolved inorganic constituents from the source rocks and also due to anthropogenic activities. Excess of these constituents causes water to be marked as unsafe for drinking purposes. The notable constituents include heavy metals like Fe, Mn, Cu and Zn along with fluoride, chloride and nitrates. Fluoride is a major inorganic pollutant which is found to be associated with in groundwater. Fluorite (CaF<sub>2</sub>) has generally been considered a dominant source of groundwater fluoride, especially in granitic terrains [2]. However, its solubility in fresh water is low and its dissolution rate is remarkably slow [3].

Sources of fluoride is also due to dissolution of biotite, which may contain fluorine at the OH<sup>-</sup> sites of the octahedral sheet [4,5,6]. Fluorosis is caused by ingestion of excess fluoride through drinking water, food, drugs and industrial wastes. Clinically the fluorosis appears in three forms –dental fluorosis, skeletal fluorosis and non-skeletal (soft-tissue) fluorosis of which former two types are irreversible. Rural populations that are dependents on ground water for drinking water supply are worst affected. According to W.H.O, 2006 guidelines for drinking water quality, the limit for fluoride is 1.5 mg/L

Fluorosis is a considerable health problem worldwide, which is affecting millions of people in many areas of the world, for example East Africa [7,8,9], Turkey [10], India [11,12,13], southeastern Korea [14], northern China [15] and in Yemen [16]. Dental fluorosis is endemic in about 1,50,000 villages located in 14 states [17]. In Andhra Pradesh-the districts of Guntur, Nalgonda, Cuddapah, Hyderabad, Krishna, Medak, Anantapur, Warangal, Karimnagar, Chittoor, Prakasam, Khammam, Mahabubnagar, Nellore, Rangareddy and Kurnool were identified as fluoride sensitized areas [18,19]. The present study area has no exception in having affected zone in the district of Guntur, Andhra Pradesh.

### **Study area**

The study area is Nuzendla mandal of Narasaraopet Revenue Division of Guntur District in the Andhra Pradesh state, India (Fig.1). It is geographically located between the co-ordinates; lat; 79°33'28" - 79°52'51" E and long; 15°49'26"-16°01'42" N falls in the Survey of India toposheet nos. 56P/12, 56P/16, 57M/9 and 56M/13. The total areal extent of the study area is 350 Sq.Km. About 82% of the total study area is occupied by agricultural land, 5% by forest area and 4 % by water bodies like river, stream, canals and tanks. Waste land covers 7% and built up land occupies 4% of the study area.



**Fig.1:** Location map with Geology and sample locations

The study area is covered by various lithological units like sandstone, alkali granite, gabbro/norite, quartz mica schist and banded biotite- hornblende gneiss with migmatite patches. Major part of the study area (86%) of the area is occupied by quartz-mica schist with minor portions of hornblende gneiss (6%), sandstone (5%), Alkali granite and gabbro (3%). Gundlakamma River is the main source for surface water which is flowing from northern to western periphery of the area with dendritic to sub-dendritic drainage pattern. The climate of the area is semi-arid and hot throughout the year. Average annual rainfall (2000-2015) is 717.1mm. The percent of negative deviation ranges from -3.40 to -52.55% which indicates drought conditions in the study area [20]. Most of the study area has nearly level slope (0-1%). The soil type is reddish brown loamy to clayey skeletal deep reddish skeletal deep reddish brown soils. Majority of the study area is covered by Pedi plain. The maximum and minimum altitudes are 334m and 48.5m above mean sea level respectively. Agriculture is the main occupation.

### Materials and Methods

Fifty groundwater samples were collected during pre-monsoon (May) and post-monsoon (December) seasons during the year 2013. About 38 samples were collected from Quartz-mica schist, 5 from gneiss and 7 from sandstone formations respectively. The samples were collected in 500 ml clean plastic containers, following the procedures of APHA [21]. The sampling bottles were soaked in 1:1 HCl for 24 hours and were rinsed with distilled water, followed by deionized water. They were washed again prior to each sampling of the filtrates. The samples were analyzed to assess various physico-chemical parameters like pH and electrical conductivity (EC) of the groundwater samples were measured using pH meter (Systronics 335). Total alkalinity and total hardness are found out by titrimetric using sulphuric acid and EDTA respectively and Phosphate by Gravimetric method. The cations sodium and potassium were analyzed by flame photo meter (Systronics 130), Calcium by titrimetric, chloride by

argentometric method and Fluoride using SPADNS method by spectrophotometer. Analytical grade chemicals were used for the analysis and all reagents and calibration standards were prepared using double distilled water. Total cation ( $TZ^+$ ) and total anions ( $TZ^-$ ) balance [22] were between +1% to +5% with few exceptions as certain ions show abnormally higher concentrations occurring in different seasons. The correlation coefficient between  $TZ^+$  and  $TZ^-$  is around 0.6 to 0.9. TDS/EC ratio was ranging from 0.5 to 0.9.

### Results & Discussion

The pH of the groundwater ranges from 7.3 to 8.8 with a mean of 8.2 during pre-monsoon season (PRM), while during post-monsoon (POM) season it is between 7.30 and 8.92, with an average value of 8.16 indicating alkaline condition. Total Dissolved Solids, a salinity indicator for the classification of groundwater varies from 690 to 2036 during PRM and 965 to 2399 mg/L. The mean value of TDS is 1334.61 and 1541.39 during PRM and POM seasons respectively. EC values ranges from 1078.18 mg/L to 3182.11 mg/L and 1507.81 mg/L to 3748.91 mg/L during PRM and POM periods respectively. The variation in the average EC values during POM (2408.42 mg/L) and PRM (2106.40 mg/L) is due to wide range of geochemical process operating in the study area. The calcium concentration in the study area varies from 32 to 193  $mgL^{-1}$  and 16 to 197 mg/L with average values of 96.53 mg/L and 95.49 mg/L during PRM and POM respectively. Mg ranges from 19 to 98 mg/L with a mean of 45.48 mg/L during PRM, while in the POM it is between 5.0 to 112 mg/L, with a mean of 43.20 mg/L. The  $Mg^{2+}$  concentration was higher during PRM indicating the weathering from primary mineral sources. The Na concentrations ranges from 72 to 544 mg/L and 86 to 776 mg/L with mean values of 288.53 mg/L and 361.86 mg/L during PRM and POM respectively. The contribution of  $Na^+$  is high during both the seasons indicate the weathering and or dissolution of soil salts stored by the influences of evaporation and anthropogenic activities [23]. The  $K^+$  concentration ranges from 9 to 107, 5 to 221 mg/L with a mean of 26.61 and 44.61 mg/L during PRM and POM respectively.  $K^+$  concentration was lower in both the seasons, indicating its lower geochemical mobility. Among the cations,  $Na^+$  is higher in both seasons (PRM-288.53 mg/L, POM-361.86 mg/L) indicating weathering from plagioclase bearing rocks and also due to over exploitation [24]. The concentration of  $Cl^-$  ranges from 59 to 398 mg/L and 86 to 488 mg/L during PRM and POM respectively.  $Cl^-$  is higher during POM (265.94 mg/L) compared to PRM (226.89 mg/L) due to leaching from upper soil layers due to industrial, domestic activities and dry climates [25]. The bi-carbonate content varies from 220 to 587 mg/L with a mean of 396.14 mg/L during PRM and varies from 264 to 777 with a mean of

424.80 during POM seasons respectively. The higher concentration was noted during POM compared to PRM due to weathering of silicates present in the granitic rocks.  $\text{SO}_4^{2-}$  ranges from 32 to 288 mg/L during PRM and during POM it ranges from 12 to 356 mg/L.  $\text{SO}_4^{2-}$  was higher in POM (151.61) compared to PRM (137.16mg/L) indicating breaking of organic substances from topsoil/water, leachable sulfate present in fertilizer, and other human influences [26,27,28]. This was supported by the primary occupation the people in the study area (Agriculture) and poor drainage conditions. The  $\text{NO}_3^-$  concentration ranges from 5 to 174 PRM and 16 to 187 mg/L with a mean values of 60.63 and 68.40 mg/L during PRM and POM respectively. (Table.1). The general dominance of ions are  $\text{HCO}_3^- > \text{Na}^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+$ . Fluoride concentration ranges from 0.5 to 12.4 and 0.14 to 16 mg/L with mean value of 2.54 mg/L and 2.97 mg/L during PRM and POM seasons respectively. Only 2 % of the samples during PRM and 6 % of the samples during POM are below the limit of 0.6 which may cause dental caries in children. About 62 % and 68 % of the total samples during PRM and POM seasons exceed the safe limit of 1.5 mg/L prescribed by WHO [29] which may cause dental, skeletal and crippling fluorosis. The

semi-arid climatic condition (mean average temperature 29.2°C and average rainfall of 717.1 mm) promotes high degree of weathering, easy accessibility of circulating water to the weathered rocks and long residence time of groundwater in the aquifer are responsible for leaching of fluoride from rocks and soils [18]. When compared to BIS [30] standard, 78 % of the samples during PRM and 86 % of the samples during POM are exceeding 1 mg/L (Fig.2). In order to identify possible combinations, ratio values of important variables were selected.

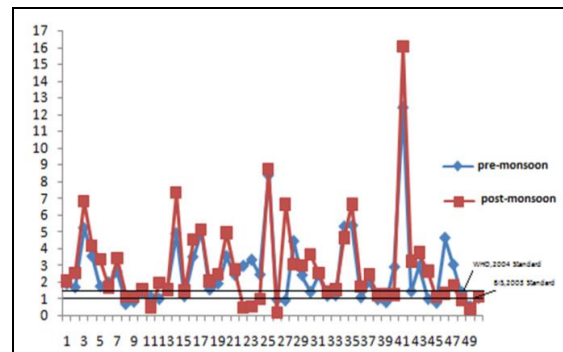


Fig.2: Comparison of Fluoride with WHO and BIS standards

Table.1: Statistical summary of groundwater samples during pre-and post-monsoon periods of the study area

| parameter                         | pre-monsoon |       |         |         |         | post-monsoon |         |         |         |        |
|-----------------------------------|-------------|-------|---------|---------|---------|--------------|---------|---------|---------|--------|
|                                   | min         | max   | aver    | med     | std dev | min          | max     | avg     | media   | std    |
| pH                                | 7.33        | 8.87  | 8.20    | 8.25    | 0.31    | 7.30         | 8.92    | 8.16    | 8.24    | 0.38   |
| TDS                               | 690         | 2036  | 1348.10 | 1334.61 | 312.17  | 965.00       | 2399.30 | 1541.39 | 1547.00 | 314.89 |
| EC                                | 1078        | 3182  | 2106.40 | 2085.33 | 487.76  | 1507.81      | 3748.91 | 2408.42 | 2417.19 | 492.01 |
| TA                                | 180         | 481   | 324.84  | 326.36  | 79.83   | 216.48       | 637.14  | 345.58  | 337.84  | 75.40  |
| TH                                | 157         | 884   | 426.55  | 392.47  | 150.63  | 60.50        | 872.56  | 411.83  | 432.67  | 197.74 |
| $\text{Ca}^{2+}$                  | 32          | 193   | 96.53   | 89.00   | 40.73   | 16.00        | 197.00  | 95.49   | 86.00   | 52.36  |
| $\text{Mg}^{2+}$                  | 19          | 98    | 45.18   | 43.00   | 17.35   | 5.00         | 112.00  | 42.18   | 42.00   | 21.70  |
| $\text{Na}^+$                     | 72          | 544   | 288.53  | 278.00  | 120.92  | 86.00        | 776.00  | 361.86  | 351.00  | 172.09 |
| $\text{K}^+$                      | 9           | 107   | 26.61   | 21.00   | 17.38   | 5.00         | 221.00  | 44.61   | 32.00   | 38.19  |
| $\text{CO}_3^{2-}$                | 0           | 220   | 67.88   | 65.00   | 42.82   | 28.00        | 135.00  | 84.80   | 87.00   | 30.30  |
| $\text{HCO}_3^-$                  | 220         | 587   | 396.14  | 398.00  | 97.35   | 264.00       | 777.00  | 424.80  | 412.00  | 88.79  |
| $\text{Cl}^-$                     | 59          | 398   | 226.90  | 212.00  | 90.39   | 66.00        | 488.00  | 265.94  | 287.00  | 104.33 |
| $\text{NO}_3^-$                   | 5           | 174   | 60.63   | 56.00   | 33.58   | 16.00        | 187.00  | 68.49   | 65.00   | 37.05  |
| $\text{SO}_4^{2-}$                | 32          | 288   | 137.16  | 134.00  | 63.01   | 12.00        | 356.00  | 151.61  | 143.00  | 67.38  |
| $\text{SiO}_4$                    | 11          | 42    | 26.57   | 28.00   | 8.05    | 10.00        | 39.00   | 23.53   | 24.00   | 7.79   |
| $\text{F}^-$                      | 0.50        | 12.40 | 2.57    | 1.86    | 2.18    | 0.14         | 16.00   | 3.01    | 2.40    | 2.66   |
| $\text{HCO}_3^- / \text{Cl}^-$    | 0.83        | 6.20  | 2.06    | 1.63    | 1.06    | 0.88         | 4.36    | 1.91    | 1.60    | 0.89   |
| $\text{Na}^+ / \text{Cl}^-$       | 1.02        | 2.96  | 1.28    | 1.18    | 0.31    | 1.01         | 2.20    | 1.34    | 1.23    | 0.31   |
| $\text{Na}^+ / \text{Ca}^{2+}$    | 0.40        | 16.00 | 3.89    | 3.11    | 3.11    | 0.47         | 38.80   | 7.65    | 4.08    | 8.98   |
| $\text{HCO}_3^- / \text{Ca}^{2+}$ | 1.41        | 17.72 | 5.05    | 3.93    | 3.20    | 1.46         | 48.56   | 7.99    | 4.79    | 9.13   |

### Ionic ratios

During rock weathering,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{SiO}_2$  are added to water. The amount of each ion in water is dependent on the rock mineralogy. However, the use of major ions chemistry to identify rock mineralogy can be useful but must be applied carefully. Mineral precipitation, ion exchange and evaporation can modify chemical composition. In many cases, the source rock minerals may be deduced from the water composition. Using ionic ratios in

groundwater, it is possible to indicate the minerals of source rock types [31].

The ratio of  $\text{HCO}_3^- / \text{Cl}^-$  during PRM and POM were in the ranges of 0.82-6.20 and 0.88- 4.36 respectively (Table 1). The average ratio 2.06 and 1.91 indicates dominance of carbonate ions from silicate weathering, whereas values less than one indicate the predominance of Bi-carbonates in the study area. The  $\text{Na}^+ / \text{Cl}^-$  ratio ranges between 1.01 and 2.96, 1.01 and 2.19 during PRM and POM seasons respectively. The lower average ratio 1.28 and 1.34 indicates

modification of sodium carbonate water by dissolution or mixing with sodium chloride, whereas increase in chloride may be due to local recharge [32]. The ratio value of  $\text{Na}^+/\text{Ca}^{2+}$  was observed in the range of 0.40 – 16 and 0.47 – 38.8 during PRM and POM seasons respectively. The increase in average 3.89 and 7.65 ratios may be due to lowering calcium activity whereby high sodium activates the dissolution of fluoride-bearing minerals at higher pH in groundwater system [33, 28]. The  $\text{HCO}_3^-/\text{Ca}^{2+}$  ratio was observed in the range of 1.40 to 17.7 and 1.46– 48.56, with an average of 5.05 and 7.89, which indicate favorable chemical condition for fluoride dissolution [34].

### Fluoride concentrations in different Litho units

The fluoride concentration in Quartz mica schist ranges from 0.65 to 12.40 mg/L during PRM with an average of 2.75 while during POM period it is in between 0.45 and 16 mg/L with an average of 3.3. The F-values in sandstone formation varies from 0.5 to 1.85, 0.14 to 2 with an average of 1.12 and 1.07 during PRM and POM seasons respectively. The Fluoride values in Gneiss ranges from 2.92 to 5.86 during PRM and 2.27 to 6.6 during POM. The mean values are 3.93 and 3.90 during both seasons respectively. The increase of these values from PRM to POM periods is due to leaching action. Sources of F- in natural waters are apatite and fluoride besides the replacement of OH- by F- ion in mica, hornblende and soil consisting of clay minerals [35,36]. Fluoride shows contrasting seasonal fluctuations. The mixed seasonal variation and uneven distribution of fluoride in space and time are primarily due to the relative abundance of, and variation in, fluoride-bearing mineral assemblages in the rock formations, the differential fracture system, and associated hydrochemical processes [37,38]. Granitic Gneissic rocks, which contain considerable amounts of fluorite minerals, especially fluor-apatite and biotite mica, are the source of fluoride ions to the percolating groundwater. Fluorite ( $\text{CaF}_2$ ) has been generally considered as a dominant source of groundwater fluoride, especially in granitic terrains [39].

### Comparison of fluoride with other ions

A perfect negative relation in the pre-monsoon and post-monsoon periods between Calcium and fluoride is observed (Fig.3).

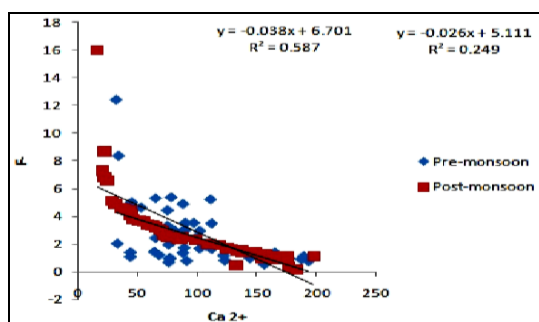
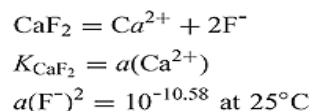


Fig.3:  $\text{Ca}^{2+}$  VS F- plot

This is due to the process of chemical weathering, dissolution of fluoride species in natural water is controlled by thermodynamic principles. Minerals rich in Calcite ( $\text{CaCO}_3$ ) also favour the dissolution of fluoride from fluoride rich minerals. Decreasing  $\text{Ca}^{2+}$  concentrations are found under alkaline conditions with corresponding rise in  $\text{Na}^+$ . Therefore fluoride can accumulate in water if soils and groundwater are low in calcium [40].



Where, K represents the solubility product constant and denotes the activities of the corresponding ions. Thus the activities of calcium and fluoride are negatively correlated. Minerals rich in calcite ( $\text{CaCO}_3$ ) also favour the dissolution of fluoride from fluoride-rich minerals.

A negative correlation between Magnesium and Fluoride (Fig.4) is observed during pre- and post monsoon periods. High fluoride and low Ca and Mg in water may be due to the prior precipitation of  $\text{CaCO}_3$  from water and only limited incorporation of F- in the  $\text{CaCO}_3$  structure [41], so that there is always a net balance of fluoride in solution. The fluoride in groundwater appears to be controlled by the distribution of  $\text{Ca}^{2+}$  [42]. A higher value of Fluoride with alkalinity indicates the carbonate rocks are in contact with the fluoride bearing minerals in these locations. The ground water in the area is brackish and highly contaminated by fluoride.

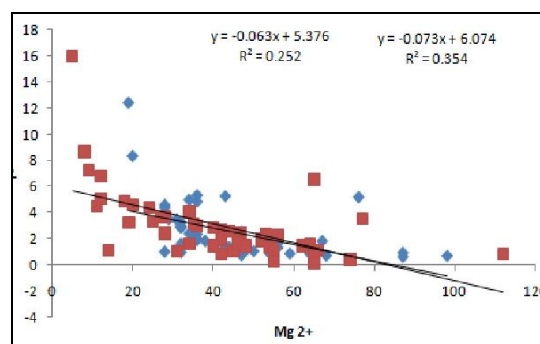


Fig.4:  $\text{Mg}^{2+}$  VS F- plot

The granitic rocks are present in this area contain large amount of fluoride bearing minerals and it leached out and dissolve in ground water. F-concentrations decreased with increasing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. This observation suggested that the solubility of fluorite and calcite controls the groundwater compositions of components such as F-,  $\text{Ca}^{2+}$  and carbonate [43].

A significant positive correlation is observed between  $\text{Na}^+$  and  $\text{F}^-$  during PRM and POM periods (Fig.5), which may be due to leaching of F- from the minerals in the soils and rock, which is more active in the semi-arid climate due to alternative wet and dry conditions

In addition to this, intensive and long term irrigation contributes leachable F<sup>-</sup> to the groundwater's [44,45]. The thick soil cover in the study area facilitates an interaction of the soils with groundwaters and environmental factors [46,47]. During weathering, the clay minerals promote ion exchange among the elements present in the soils and also among those present in the circulating waters [33,34].

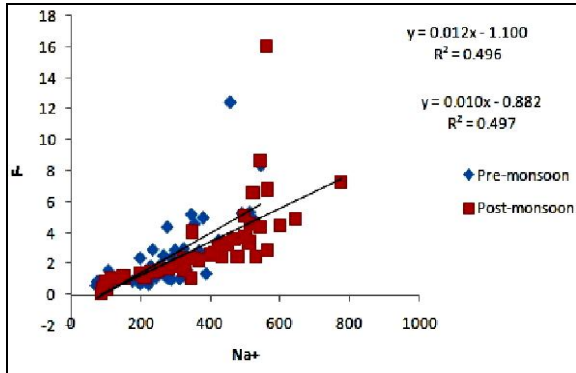


Fig.5: Na+ VS F- plot

A positive relation is observed between HCO<sub>3</sub><sup>-</sup> and F<sup>-</sup> during pre- and post-monsoon periods (Fig.6), which can be explained by the following mass law equation relating calcite and fluorite when both the minerals are in contact with water [48].

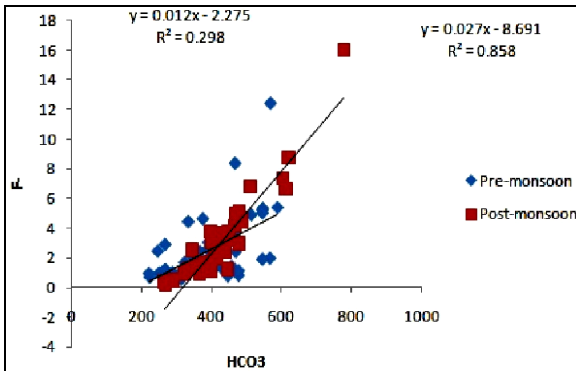
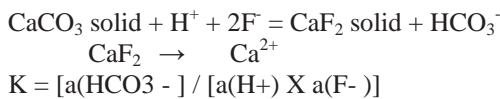


Fig.6: HCO3- VS F- plot



Where, K is equilibrium constant and is the activity. It is evident that if the pH is constant, the activity of fluoride is directly proportional to bicarbonate.

**Piper Trilinear Plot**

The dominant cations and anions present in water are generally reflected in the water type [49]. Hence, major ion chemistry of groundwater is examined by using Piper trilinear diagram to identify chemical alteration in groundwater. The Piper diagram consists of two lower triangular fields and a central diamond-shaped field. All the three fields have incorporation of major ions only. The triangular fields are plotted separately with epm values of cations (Ca<sup>2+</sup>+Mg<sup>2+</sup>) alkali earth, (Na<sup>+</sup>+K<sup>+</sup>) alkali, HCO<sub>3</sub><sup>-</sup> weak acid, and

(SO<sub>4</sub><sup>2-</sup>+Cl<sup>-</sup>) strong acid. Water facies can be identified by projection of plots in the central diamond shaped field as per the classifications made by Karanth [50]. Majority of the samples during the both seasons fall in the mixed type (Na-Cl type) about 68% during pre-monsoon and 70% during post-monsoon. The rest of the samples during pre-monsoon fall in mixed CaMgCl Type (10%), CaHCO<sub>3</sub> type (12%) and Mixed CaNaHCO<sub>3</sub> (10%) (Fig.7). The rest of the samples during post-monsoon fall in Mixed CaMgCl type (16%), mixed CaNaHCO<sub>3</sub> (6%), CaHCO<sub>3</sub> type (6%) and NaHCO<sub>3</sub> type (2%) (Fig.7). From the plots, it is observed that alkalinity (Na and K) exceeds alkaline earth (Ca and Mg) and strong acids exceed weak acids, in general water chemistry of the study area is dominated by alkali and strong acids.

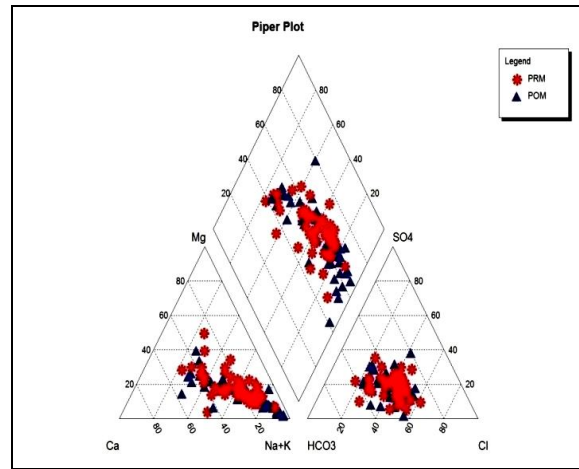


Fig.7: Piper Trilinear plot

The predominant facies during pre-monsoon and post-monsoon periods are Sodium-Calcium Facies among cations and Chloride and Chloride-Sulphate-Bicarbonate facies among anions. During post-monsoon the predominant cation facies are sodium calcium and sodium calcium facies. This indicates the predominance of base ion exchange between Na<sup>+</sup> and K<sup>+</sup> in rock with Mg<sup>2+</sup> or Ca<sup>2+</sup> in groundwater and Na<sup>+</sup> and K<sup>+</sup> in groundwater with Mg or Ca in rock during the both seasons. The Na<sup>+</sup>-HCO<sub>3</sub><sup>-</sup> type of water represents partly flushed remains of an ancient, confined saline water body or as exchange waters which imply that there is more HCO<sub>3</sub><sup>-</sup> than the available alkaline earth cations (Ca<sup>2+</sup> + Mg<sup>2+</sup>) in equal concentrations [51]. These excess HCO<sub>3</sub><sup>-</sup> ions then cause a release of the alkali ions (usually Na<sup>+</sup>) into the groundwater by ion exchange [52]. The high Na<sup>+</sup> and Cl<sup>-</sup> contents detected, suggest the dissolution of chloride salts or concentration processes by evaporation [52]. The annual rainfall and groundwater recharge of the area are insignificant; the process of evaporation might have incorporated some components of sodium and chlorine ions.

**Gibbs Plot**

Gibbs' ratio [55] for major cations (Na<sup>+</sup>+K<sup>+</sup>/Na<sup>+</sup>+K<sup>+</sup>+Ca<sup>2+</sup>) and major anions (Cl<sup>-</sup> / Cl<sup>-</sup>+HCO<sub>3</sub><sup>-</sup>) of

the water samples were plotted separately against respective values of total dissolved solids (Fig. 8 & 9). A simple plot could provide more information on the relative importance of three major natural mechanisms controlling surface water chemistry: (1) atmospheric precipitation; (2) rock weathering, and (3) evaporation and fractional crystallization.

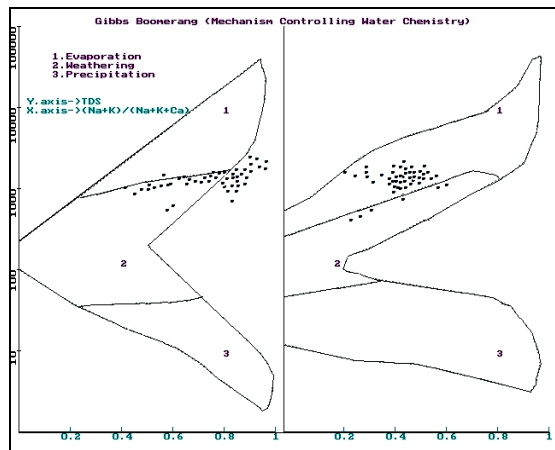


Fig.8: Gibbs plot during pre-monsoon

Therefore, the concentrations of major ions in groundwater and the mineralogy of different rocks have been used to determine the source of these major ions to the groundwater and their relation to regional geology and weathering processes. Majority of the samples during both the seasons fall under weathering zone during with reference to cations. Most of the samples during pre-and post-monsoon periods fall in evaporation zone with respect to anion ratios. The dominant control of rock weathering in the major ion chemistry of the study area indicates weathering of different source rocks (e.g., carbonate, silicate) yields different combinations of dissolved cations and anions in solution [56]. Minor number of samples fall in evaporation zone also. Since the study region experiences dry and semiarid climatic condition, evaporation may also contribute to changes in water chemistry of the groundwater chemistry in the study region to some extent.

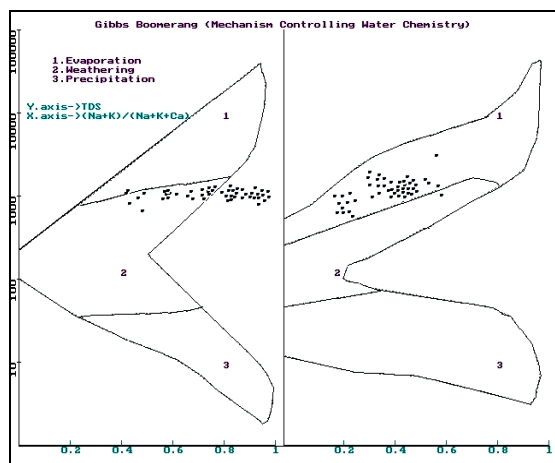


Fig.9: Gibbs plot during post-monsoon

### Interrelation of Chemical Parameters

The correlation coefficient expresses numerically the extent to which two variables are statistically associated. Correlation coefficient of 1 or nearly 1 indicates considered as high correlation between two hydro chemical parameters where as correlation coefficient of 0 indicates no correlation between two variables. The correlation values less than 0.5 indicate poor correlation, 0.5 indicates good correlation and greater than 0.5 represent strong or excellent correlation between two chemical parameters. During PRM period excellent correlation is observed between TDS-pH, pH-EC, pH-TA, pH-Na, pH-HCO<sub>3</sub><sup>-</sup>, pH-Cl<sup>-</sup>, pH-F<sup>-</sup>, TDS-TA, TDS-Na<sup>+</sup>, TDS-HCO<sub>3</sub><sup>-</sup>, TDS-Cl<sup>-</sup>, TDS-SO<sub>4</sub><sup>2-</sup>, TDS-F<sup>-</sup>, EC-TA, EC-Na, EC-HCO<sub>3</sub><sup>-</sup>, EC-Cl<sup>-</sup>, EC-SO<sub>4</sub><sup>2-</sup>, TA-Na<sup>+</sup>, TA-HCO<sub>3</sub><sup>-</sup>, TH-Ca<sup>2+</sup>, TH-Mg, TH-NO<sub>3</sub><sup>-</sup>, Ca-K, Ca-NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>-HCO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>-Cl<sup>-</sup>, Na<sup>+</sup>-SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>-F<sup>-</sup>, K<sup>+</sup>-NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>-F<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>-F<sup>-</sup> (Table.2). The positive correlation exhibits between Cl<sup>-</sup> and Na<sup>+</sup>, Ca<sup>2+</sup> and K<sup>+</sup>, Na<sup>+</sup> and EC, indicates chemical weathering and leaching of secondary salts dominating the geochemistry of water in the study area. High positive correlation between Na<sup>+</sup> with Cl<sup>-</sup> indicates that the dissolution of halite was important in regulating the concentration between Na<sup>+</sup> and Cl<sup>-</sup> in water samples during PRM and POM [57, 58, and 59]. During PRM good correlation is observed between TDS and EC, Na<sup>+</sup> and Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> indicating Na<sup>+</sup>, Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> derived from plagioclase weathering, anthropogenic activities and weathering of carbonate minerals.

In the post-monsoon positive correlation is observed between pH-TDS, EC-pH, pH-Na<sup>+</sup>, pH-HCO<sub>3</sub><sup>-</sup>, pH-F<sup>-</sup>, TA-TDS, TDS-Na<sup>+</sup>, TDS-HCO<sub>3</sub><sup>-</sup>, TDS-F<sup>-</sup>, TA-EC, EC-Na<sup>+</sup>, EC-HCO<sub>3</sub><sup>-</sup>, EC-F<sup>-</sup>, TA-Na, TH-Ca, TH-Mg<sup>2+</sup>, Ca<sup>2+</sup>-Mg<sup>2+</sup>, Na<sup>+</sup>-HCO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>-Cl<sup>-</sup>, Na<sup>+</sup>-F<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>-Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>-F<sup>-</sup> (Table.3). A positive correlation exhibits between Cl<sup>-</sup> and Na<sup>+</sup>, Cl<sup>-</sup> and K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> and Na<sup>+</sup>, indicates leaching of secondary salts with anthropogenic impact. EC showed a good correlation with major ions during both seasons due to the linear correlation between the dissolved ions and conductivity [54]. By this correlation matrix we can assume that chemical weathering is the dominant process controlling the groundwater chemistry along with the anthropogenic source. It reveals that Ca<sup>2+</sup> and Mg<sup>2+</sup> derived from carbonate weathering [60, 61]. EC and TDS showed a good correlation during both seasons due to the linear correlation between the dissolved ions and conductivity [62]. EC is positively correlated with almost all the major cations and anions. The parameters F-EC and F-TDS were positively correlated. In both the seasons, pre-monsoon and post-monsoon, the values indicate the association of calcium with bicarbonate, carbonate and fluoride. The correlations of F with TDS in study area indicated that groundwater F- could be attributed mainly to the dissolution of F- bearing minerals [43]. A positive correlation between pH and fluoride

indicates, high alkaline nature of water promotes leaching of fluoride and thus, increases fluoride in ground water. The ionic radius of fluoride (0.136 nm)

was same as that of hydroxyl ion which can be easily substituted for one another from water at high pH [62, 63].

**Table.2:** Correlation matrix-pre-monsoon

|       | pH          | TDS         | EC          | TA          | TH          | Ca2+        | Mg2+  | Na+         | K+          | CO32-       | HCO3-       | Cl-  | NO3-  | SO42- | Sio4 | F-   |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|-------|-------------|-------------|-------------|-------------|------|-------|-------|------|------|
| pH    | 1.00        |             |             |             |             |             |       |             |             |             |             |      |       |       |      |      |
| TDS   | <b>0.65</b> | 1.00        |             |             |             |             |       |             |             |             |             |      |       |       |      |      |
| EC    | <b>0.65</b> | 1.00        | 1.00        |             |             |             |       |             |             |             |             |      |       |       |      |      |
| TA    | <b>0.57</b> | <b>0.72</b> | <b>0.72</b> | 1.00        |             |             |       |             |             |             |             |      |       |       |      |      |
| TH    | -0.69       | -0.19       | -0.19       | -0.20       | 1.00        |             |       |             |             |             |             |      |       |       |      |      |
| Ca2+  | -0.54       | -0.03       | -0.03       | -0.10       | <b>0.91</b> | 1.00        |       |             |             |             |             |      |       |       |      |      |
| Mg2+  | -0.50       | -0.43       | -0.43       | -0.35       | <b>0.50</b> | 0.24        | 1.00  |             |             |             |             |      |       |       |      |      |
| Na+   | <b>0.80</b> | <b>0.89</b> | <b>0.89</b> | <b>0.59</b> | -0.56       | -0.42       | -0.55 | 1.00        |             |             |             |      |       |       |      |      |
| K+    | -0.15       | 0.25        | 0.25        | 0.06        | 0.37        | <b>0.45</b> | 0.17  | -0.01       | 1.00        |             |             |      |       |       |      |      |
| CO32- | 0.34        | 0.34        | 0.34        | 0.14        | -0.21       | -0.13       | -0.16 | 0.34        | 0.04        | 1.00        |             |      |       |       |      |      |
| HCO3- | <b>0.57</b> | <b>0.72</b> | <b>0.72</b> | <b>1.00</b> | -0.20       | -0.10       | -0.35 | <b>0.59</b> | 0.06        | 0.14        | 1.00        |      |       |       |      |      |
| Cl-   | <b>0.59</b> | <b>0.79</b> | <b>0.79</b> | 0.38        | -0.42       | -0.30       | -0.46 | <b>0.88</b> | 0.05        | 0.15        | 0.38        | 1.00 |       |       |      |      |
| NO3-  | -0.18       | 0.18        | 0.18        | -0.06       | <b>0.53</b> | <b>0.49</b> | 0.20  | -0.01       | <b>0.46</b> | -0.29       | -0.06       | 0.01 | 1.00  |       |      |      |
| SO42- | 0.36        | <b>0.66</b> | <b>0.66</b> | 0.35        | 0.01        | 0.19        | -0.25 | <b>0.49</b> | 0.20        | 0.15        | 0.35        | 0.35 | 0.12  | 1.00  |      |      |
| Sio4  | 0.26        | 0.24        | 0.24        | 0.19        | -0.27       | -0.19       | -0.17 | 0.31        | -0.08       | 0.08        | 0.19        | 0.34 | -0.31 | 0.16  | 1.00 |      |
| F-    | <b>0.80</b> | <b>0.59</b> | <b>0.59</b> | <b>0.55</b> | -0.58       | -0.50       | -0.44 | <b>0.70</b> | -0.14       | <b>0.49</b> | <b>0.55</b> | 0.38 | -0.18 | 0.37  | 0.15 | 1.00 |

**Table.3:** Correlation matrix-post-monsoon

|       | pH          | TDS         | EC          | TA          | TH          | Ca2+        | Mg2+  | Na+         | K+    | CO32- | HCO3-       | Cl-  | NO3-  | SO42- | Sio4 | F- |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|-------|-------------|-------|-------|-------------|------|-------|-------|------|----|
| pH    | 1           |             |             |             |             |             |       |             |       |       |             |      |       |       |      |    |
| TDS   | <b>0.84</b> | 1           |             |             |             |             |       |             |       |       |             |      |       |       |      |    |
| EC    | <b>0.84</b> | 1           | 1           |             |             |             |       |             |       |       |             |      |       |       |      |    |
| TA    | <b>0.59</b> | <b>0.49</b> | <b>0.49</b> | 1           |             |             |       |             |       |       |             |      |       |       |      |    |
| TH    | -0.92       | -0.74       | -0.74       | -0.53       | 1           |             |       |             |       |       |             |      |       |       |      |    |
| Ca2+  | -0.94       | -0.82       | -0.82       | -0.53       | <b>0.93</b> | 1           |       |             |       |       |             |      |       |       |      |    |
| Mg2+  | -0.66       | -0.45       | -0.45       | -0.40       | <b>0.85</b> | <b>0.61</b> | 1     |             |       |       |             |      |       |       |      |    |
| Na+   | <b>0.91</b> | <b>0.94</b> | <b>0.94</b> | <b>0.51</b> | -0.90       | -0.92       | -0.64 | 1           |       |       |             |      |       |       |      |    |
| K+    | -0.18       | 0.13        | 0.13        | -0.11       | 0.20        | 0.12        | 0.28  | -0.10       | 1     |       |             |      |       |       |      |    |
| CO32- | 0.05        | 0.09        | 0.09        | 0.13        | -0.05       | -0.04       | -0.04 | 0.06        | 0.06  | 1     |             |      |       |       |      |    |
| HCO3- | <b>0.78</b> | <b>0.71</b> | <b>0.71</b> | 0.35        | -0.70       | -0.72       | -0.49 | <b>0.70</b> | -0.08 | -0.25 | 1           |      |       |       |      |    |
| Cl-   | <b>0.75</b> | 0.86        | <b>0.86</b> | 0.45        | -0.69       | -0.72       | -0.47 | <b>0.86</b> | 0.01  | 0.02  | <b>0.48</b> | 1    |       |       |      |    |
| NO3-  | -0.04       | 0.10        | 0.10        | -0.15       | 0.03        | -0.07       | 0.17  | 0.15        | 0.19  | -0.24 | -0.06       | 0.06 | 1     |       |      |    |
| SO42- | 0.23        | 0.43        | 0.43        | 0.30        | -0.12       | -0.20       | 0.04  | 0.26        | 0.09  | 0.04  | 0.22        | 0.20 | -0.37 | 1     |      |    |
| Sio4  | 0.27        | 0.18        | 0.18        | 0.16        | -0.30       | -0.31       | -0.21 | 0.24        | -0.03 | 0.17  | 0.08        | 0.24 | -0.04 | -0.06 | 1    |    |
| F-    | <b>0.79</b> | <b>0.64</b> | <b>0.64</b> | 0.34        | -0.77       | -0.77       | -0.60 | <b>0.71</b> | -0.12 | 0.04  | <b>0.87</b> | 0.40 | -0.07 | 0.12  | 0.17 | 1  |

## Conclusions

The F- concentrations in the samples ranges from 0.5 to 12.4 and 14 to 16 during pre-and post-monsoon periods respectively. About 62% and 68% of the total samples during the both seasons are exceeding the safe limit of 1.5 mg/l respectively. The influence of local rock type and soil aided by other factors like very low fresh water exchange due to semi-arid climate of the region are responsible for higher concentrations of the fluoride in the groundwater of the study area. The increase of these values from pre- to post-monsoon periods is due to leaching action. The ionic plots indicate the chemical weathering, dissolution of fluoride bearing minerals; precipitation and alkaline conditions are responsible for higher fluoride contents in the granitic rocks of the study area. The piper trilinear plot indicates the predominance of base ion exchange between the various cations further this is supported by the low rainfall and insignificant groundwater recharge of the

area. Gibbs plot suggest that majority of the samples fall in weathering zone and with small percentage of samples in evaporation zone. This was also supported by correlation matrix.

## Acknowledgements

The first author wants to acknowledge Prof.P.Sankara Pitchaiah, Head Department of Geology for his constant encouragement throughout this research work.

## References

- [1] Chandrawat, M.P., Ojha, T.N., Yadav, R.N., "Hydrofluoroid problems in and around Ramgarh Town", Indian Journal of Environmental Sciences., Vol.5, pp.103, 2001.
- [2] Deshmukh, A.N., Valadaskar, P.M., Malpe, D.B., "Fluoride in environment: a review", Gondwana Geological Magazine, Vol.9, pp.1-20, 1995. doi: 10.12691/jgg-2-5-1.

- [3] Nordstrom, D.K., and Jenne, E.A., Fluoride solubility in selected geothermal waters". *Geochim Cosmo chim Acta*, Vol. 41, pp. 175–188, 1977. [https://doi.org/10.1016/0016-7037\(77\)90224-1](https://doi.org/10.1016/0016-7037(77)90224-1)
- [4] Nordstrom, D.K., Ball, J.W., Donahoe, R.J., and Whittemore. D., "Groundwater chemistry and water-rock interactions at Stripa", *Geochim Cosmo chim Acta*, 53, 1727–1740, 1989. DOI: 10.1016/0016-7037(89)90294-9
- [5] Li, Z., Tainosho Y., Shiraishi. K., and Owada. M., "Chemical characteristics of fluorine-bearing biotite of early Paleozoic plutonic rocks from the Rondane Mountains East Antarctica", *Geochemical Journal*, Vol.1, Issue No.37, pp. 1456, 2003. DOI:10.2343/geochemj.37.145
- [6] Chae, G.T., Yun, S.T., Kwon, M.J., Kim, S.Y., and Mayer. B., "Batch dissolution of granite and biotite in water: implication for fluorine geochemistry in groundwater". *Geochemical Journal*, Vol.40, pp.95-102, 2006. DOI:10.2343/geochemj.40.95
- [7] Nanyaro, J.T., Aswathanarayana, U., Mungere, J.S. and Lahermo, P., "A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania", *Journal of African Earth Sciences*, Vol No.2, pp.129–140, 1984. DOI:10.1016/S0731-7247(84)80007-5
- [8] Gaciri, S.J. and Davis, T.C., "The occurrence and geochemistry of fluoride in some natural waters of Kenya". *Journal of Hydrology*, Vol.143, pp.395–412, 1993. DOI: 10.1016/0022-1694(93)90201-J
- [9] Gizaw, B., "The origin of high bicarbonate and fluoride concentrations in waters of the main Ethiopian Rift Valley". *Journal of African Earth Sciences*, Vol.22, pp.391-402, 1996. DOI:10.1016/08995362(96)00029-2
- [10] Oruc, N., "Problems of high fluoride waters in Turkey" (hydrogeology and health aspects). The short course on medical geology-health and environment. Canberra, Australia, 2003.
- [11] Subba Rao, N., and Devadas. D.J., "Fluoride incidence in groundwater in a area of Peninsula India", *Environmental Geology*, Vol.45, pp.243–251, 2003 DOI: 10.1007/s00254-003-0873-3
- [12] Gupta, S.K., Deshpande, R.D., Meetu, Agarwal and Raval, B. R., "Origin of high fluoride in groundwater in the North Gujarat-Cambay region, India", *Hydrogeology Journal*, Vol.13, pp.596–605, 2005. DOI: 10.1007/s10040-004-0389-2
- [13] Jacks, G., Bhattacharya, P., Chaudhary, V., and Singh K.P., "Controls on the genesis of some high-fluoride groundwaters in India", *Applied Geochemistry*, vol.20, pp.221–228, 2005. DOI:10.1016/j.apgeochem.2004.07.002
- [14] Kim, K., and Jeong, G.Y., "Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the south eastern part of the Korean Peninsula", *Chemosphere*, Vol.58, pp.1399–1408, 2005. DOI:10.1016/j.chemosphere.2004.10.002
- [15] Guo, Q., Xang, Y., Ma, T. and Ma, R., "Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China". *Journal of Geochemical Exploration*, vol.93 issue.1, pp.1–12, 2006. DOI: 10.1016/j.gexplo.2006.07.001
- [16] Al-Amry, A.S., "Fluorosis Study in Selected Villages of Taiz Governorate", Technical report prepared as part of the National Programme on Integrated Water Resources Management, UNDP-NWRA/Sana'a, Yemen, 2009.
- [17] Pillai, K.S., and Stanley, V.A., "Implications of fluoride an endless uncentrinity", *Journal of Environmental Biology*, Vol.23, pp.81-87, 2002.
- [18] Subba Rao, N., Prakasa Rao, N. S., John Devadas, J., Srinivasa Rao, K. V., Krishna, C. and Nagamalleswara Rao, B., "Hydrogeochemistry and groundwater quality in a developing urban environment of a semi-arid region, Guntur, Andhra Pradesh, India", *Journal of the Geological Society of India*, vol.59, pp.159–166, 2002. DOI: 10.1007/s002540100431
- [19] Subba Rao, N., "Groundwater quality: focus on fluoride concentration in rural parts of Guntur district, Andhra Pradesh, India", *Hydrological Sciences Journal*, vol.48, issue 5, pp.835-847, 2003. DOI:10.1623/hysj.48.5.835.51449.
- [20] Rainfall data, Chief planning office, Guntur district. Book edition. 2012
- [21] APHA. "Standard Methods for Examination of Water and Wastewater", American Public Health Association WWA, Washington, D.C. 2005.
- [22] Domenico, P.A., and Schwartz. F.W., "Physical and chemical Hydrogeology", Wiley, New York, 1990. ISBN 0 471 50744 X; 0 471 52987 7
- [23] Stallard, R.F., and Edmond, J.M., "Geochemistry of the Amazon River—the influence of the geology and weathering environment on the dissolved load", *Journal of Geophysical Research*, Vol.88, pp.9671–9688, 1983. DOI: 10.1029/JC088iC14p09671
- [24] Hem, J.D., "Study and interpretation of the chemical characteristics of natural Water", USGS, Water Supply Paper pp. 2254, 264, 1985. <https://pubs.usgs.gov/wsp/wsp2254/pdf/wsp2254a.pdf>.
- [25] Bouwer, H., "Groundwater Hydrology", McGraw-Hill. New York. 480 pp, 1978. ISBN-10: 0070067155
- [26] Miller, G.T., "Living in the Environment". Wadsworth Publishing Company, Belmont California, 1979.
- [27] Craig, E., and Anderson, M.P., "The effects of urbanization of ground water quality. A case study of ground water ecosystems", *Environmental Conservation*, Vol.30(2), pp.104–



- 130,1979. DOI: 10.1111/j.1745-6584.1979.tb03341.x
- [28] Srinivasamoorthy, K., Vijayaraghavan, K., Vasanthavigar, M., Sarma, V.S., Rajivgandhi, R., Chidambaram, S., Anandhan, P. and Manivannan, R., "Assessment of groundwater vulnerability in Mettur region, Tamilnadu, India using drastic and GIS techniques", *Arabian Journal of Geosciences*, 2010. DOI: 10.1007/s12517-010-0138
- [29] WHO, "Guidelines for drinking water quality", 4th edn. World Health Organization, Geneva, 2006
- [30] BIS, "Bureau of Indian Standards Drinking water-specification", IS: 10500, New Delhi, 2003.
- [31] Hounslow, A.W., "Water quality data: analysis and interpretation", CRC, Boca Raton, FL, 1995.
- [32] Dhiman, S.D., and Keshari. A.K., "GIS assisted inverse geochemical modeling for plausible phase transfers in aquifers", *Environmental Geology*, Vol.50, pp.1211–1219, 2006. DOI:10.1007/s00254-006-0293-2
- [33] Shaji, E., Viju, B.J. and Thambi, D.S., "High fluoride in groundwater of Palghat District, Kerala", *Current Science.*, Vol.92(2), pp.240–246,2007.<http://www.iisc.ernet.in/currsci/jan252007/240.pdf>
- [34] Saxena, V., and Ahmed, S., "Inferring chemical parameters for the dissolution of fluoride in groundwater", *Environmental Geology*, Vol.43(6), pp.731–736, 2003. DOI:10.1007/s00254-002-0672-2
- [35] Robinson, W.D., and Edington. G., "Fluorine in soils", *Soil Science*, vol.61, pp.341–353, 1946. DOI.org/10.1097/00010694-194605000-00001
- [36] Hem, J.D., "Study and interpretation of the chemical characteristics of natural water", Washington, DC: U.S. Gov. Print. Office, 1991.<https://pubs.usgs.gov/wsp/wsp2254/pdf/wsp2254a.pdf>
- [37] Reddy, A.G.S., and Rao. P.N., "Occurrence, behaviour and genesis of fluoride in groundwater of Wailpalli watershed in Nalgonda District, Andhra Pradesh, India", *Journal of Applied Geochemistry*, vol.8, issue 2A, pp.618–630, 2006. Print ISSN: 0972-1967 Online ISSN: 2319-4316
- [38] Raju, N.J., Shukla, U.K. and Ram, P., "Hydrogeochemistry for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India". *Environmental Monitoring and Assessment*, Vol.173, pp.279–300, 2011. DOI: 10.1007/s10661-010-1387-6
- [39] Deshmukh, A.N., and Chakravarti, P.K., "Hydrochemical and hydrological impact of natural aquifer recharge of selected fluorosis endemic areas of Chandrapur district", *Gondwana Geology Magazine*, vol.9, pp.169–184, 1995. ISSN: 0970-261X.
- [40] Brown D.W., and Roberson, C.E., "Solubility of natural fluorite at 25°C", *USGS Journal Research*, 5, 4, 506–517, 1977.
- [41] Kundu, N., Panigrahi, M.K., Tripathy, S., Munshi, S. M. A., and Powell and Hart, B.R., "Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa, India", *Environmental Geology*, Vol.41, pp.451–460, 2001. DOI: 10.1007/s002540100414
- [42] Gupta, S., Banerjee, S., Saha, R., Datta, J.K., and Mondal, N., "Fluoride geochemistry of groundwater in Birbhum, West Bengal, India", *Fluoride*, vol.39, pp. 318–320, 2006.
- [43] Hu, S., Luo, T., and Jing, C., "Principal component analysis of fluoride geochemistry of groundwater in Shanxi and Inner Mongolia, China", *Journal of Geochemical Exploration*, vol. 135, pp.124–129 2013. DOI: 10.1016/j.gexplo.2012.08.013
- [44] Ramamohana Rao, N. V., Suryaprakasa Rao K., and Schuiling R.D., "Fluorine distribution in waters of Nalgonda district, Andhra Pradesh, India", *Environmental Geology*, vol.21, pp.84–89,1993. DOI: 10.1007/BF00775055
- [45] Subba Rao, N., "Groundwater quality in crystalline terrain of Guntur district, Andhra Pradesh, India", *Visakha Science Journal*, vol.2, pp.51–54, 1998.
- [46] Subba Rao, N., "Groundwater chemistry in two different hydrogeologic environments", *Journal of Applied Geochemistry*, vol.4, pp.61–70, 2002
- [47] Subba Rao, N., "Geochemistry of groundwater in parts of Guntur district, Andhra Pradesh, India", *Environmental Geology*, vol.41, pp.552–562, 2002. DOI: 10.1007/s002540100431.
- [48] Handa, B.K., "Geochemistry and genesis of fluoride containing ground waters in India", *Groundwater*, Vol.13, issue 3, pp.275-281, 1975. DOI:10.1111/j.17456584.1975.tb03086.x
- [49] Piper, A.M., "A graphic procedure in the geochemical interpretation of water analysis", *Transactions - American Geophysical Union*, 25,914-923,1944. DOI: 10.1029/TR025i006p00914
- [50] Karanth, K.R., "Quality of groundwater and groundwater exploration", Tata McGraw – Hill Publishing Co.Ltd, New Delhi, pp. 217–275, 437–509,1987. ISBN 0074517120, 9780074517123
- [51] Jeon, S.K., Kim, J.M., KO, K.S., Yum, B., and Chang, H.W., "Hydrogeochemical characteristics of groundwater in a mid-western coastal aquifer system, Korea", *Geosciences Journal*, Vol.5, pp.339-348, 2001. DOI: 10.1007/BF02912705
- [52] Mercado, A. "The use of hydrogeochemical patterns in carbonate sand and sandstone aquifers to identify intrusion and flushing of saline

- waters.” *Ground Water.*, v.23, pp.635-645 Dixon and Chiswell, 1992 DOI: 10.1111/j.1745-6584.1985.tb01512.x
- [53] Vengosh, A., Starinsky, A., Melloul, A., Fink, M., and Erlich, S., “Salinization of the coastal aquifer water by Ca-chloride solutions at the interface zone, along the Coastal Plain of Israel”, *Hydrological Service, Jerusalem*, 1991
- [54] Gibbs, R.J., “Mechanisms controlling world water chemistry”, *Science*, Vol.170, pp.1088–1090, 1970.  
<https://doi.org/10.1126/science.170.3962.108>
- [55] Garrels, R.M., and Mackenzie, F.T., “Origin of the chemical compositions of some springs and lakes”, In: W. Stumm (Ed.), *Equilibrium concepts in natural water systems*. American Chemical Society, pp.222–242, 1967. DOI: 10.1021/ba-1967-0067.ch010
- [56] Rasouli, F., KianiPouya A., and Cheraghi, S.A.M., “Hydrogeochemistry and water quality assessment of the Kor-Sivand Basin, Fars province, Iran”, *Environmental Monitoring and Assessment*, vol.184, pp.4861–4877, 2012. DOI: 10.1007/s10661-011-2308-z
- [57] Singaraja, C., Chidambaram, S., Prasanna, M.V., Paramaguru, P., Johnsonbabug T.C., and Thilagavathi, R., “A study on the behaviour of the dissolved oxygen in the shallow coastal wells of Cuddalore District, Tamilnadu, India”, *Water Quality Exposure and Health*, vol.4, pp.1–16, 2012a. doi:10.1007/s12403-011-0058-3
- [58] Thilagavathi, R., Chidambaram, S., Prasanna, M.V., Thivya, C., and Singaraja, C., “A study on groundwater geochemistry and water quality in layered aquifers system of Pondicherry region, southeast India”, *Applied Water Science*, 2012. DOI:10.1007/s13201-0120045-2
- [59] Andrade A.I.A.S.S., and Stigter, T.Y., “Hydrogeochemical controls on shallow alluvial groundwater under agricultural land: case study in Central Portugal”, *Environmental Earth Science*, vol.63, pp.809–825, 2011. DOI: 10.1007/s12665-010-0752-7
- [60] Nosrati K., and Van Den Eeckhaut, M., “Assessment of groundwater quality using multivariate statistical techniques in Hashtgerd Plain, Iran”, *Environmental Earth Science*, vol.65, pp.331–344, 2012. DOI: 10.1007/s12665-011-1092-y
- [61] Rajmohan, N., and Elango, L., “Identification and evaluation of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basin, southern India”, *Environmental Geology*, vol.46, pp.47–61, 2004. DOI: 10.1007/s00254-004-1012-5
- [62] Sreedevi, P.D., Ahmed, S., Made, B., Ladous, E., and Gandolfi, J.M., “Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India”, *Environmental Geology*, vol.50 pp.1–11, 2006. doi:10.1007/s00254-005-0167-z
- [63] Gupta, S., Banerjee, S., Saha, R., Datta, J.K., and Mondal, N., “Fluoride geochemistry of groundwater in Birbhum, West Bengal, India”, *Fluoride*, vol.39, pp.318–320, 2006.