Geochemical Analysis of Flouride in Ground water using GIS

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***Abstract* - Water is essential natural resource for sustaining life and environment which we have always thought to be available in abundance and free gift of nature. However, chemical composition of surface or sub surface, is one of the prime factors on which the suitability of the water for domestic, industrial or agriculture purpose depends. Fluoride is a chemical element that has shown beneficial effects on teeth at low concentrations, it can also be quite detrimental at higher concentrations. High concentrations of fluoride (up to 6.2 mg/L) are recognized features of the study area. The basement rocks like granitic gneiss, schist, shale and sandstone provide abundant source of fluoride in the form of silicates, biotite, hornblende and glaucaphase. A correlation study of water quality parameters with Fluoride content is performed on groundwater samples from Gadag and Bagalkot district. The study suggests that the water samples with higher F − concentration generally have relatively higher pH value, implying that alkaline environment favours the replacement exchangeable F − in fluoride rich minerals by OH − in groundwater. The positive correlation of TDS implying that dissolved solids gives more opportunity for fluoride to be present and most of the metal fluoride are soluble. Since nitrate is an oxidizing agent it increases the solubility of fluoride in groundwater. Hardness of water is mainly due to calcium salts in water. As the hardness increases, formation of calcium fluoride (CaF 2) which is an insoluble salt increases.. Thus the origin of the fluoride is mostly from weathered gneiss, schist shale and sand stone. In this study arcGIS approach to develop maps based on the groundwater quality has been found to be very useful. GIS data base also helps in decision making process by identifying the most sensitive zones that need immediate attention.**

***keywords* - Ground water, Fluoride, Ion exchange process, GIS.**

1.Introduction

Water is the most precious gift of nature, the most crucial for sustaining life and is required in almost all the activities of man - for drinking and municipal use, for irrigation, to meet the growing food and fiber needs for industries, power generation, navigation and recreation. Moreover, the rainfall is mostly confined to the monsoon season and is unevenly distributed both in space and time even during the monsoon season. As a result, the country is affected by frequent droughts. Nearly one third of the country is drought prone. In the very near future, water will be a scarce resource and therefore, needs to be harnessed in the most scientific and efficient manner. The surface water is subjected to various threats like discharge of effluents from different industries in the vicinity, encroachment of surface water sources like pond, river, stream etc. Groundwater is the major source of drinking water in both urban and rural India. The demand for water has increased over the years and this has led to water scarcity in many parts of the world.. In India, many people including children suffer from fluorosis because of consumption of water with high fluoride concentrations. Excess fluoride affects plants and animals also. The severity of injury is determined by duration of fluoride exposure and concentration. The major sources of fluoride in groundwater are fluoride bearing rocks such as amphibole, biotite, fluorite and apatite [6]. Fluoride is a common constituent of rocks, soils and waters with rock being the primary reservoir and ultimate source. The presence of fluoride in groundwater is governed by several factors like igneous rocks formation, magmatic processes i.e. and formation of magma, pegmatite, hydrothermal fluids, metamorphic rocks and weathering processes.

In the present study we have selected whole Gadag district area, since the ground water in this area is adversely contaminated with fluoride and other water chemical parameter. So we are interested to study the geochemical analysis of fluoride and the ion exchange process taking place in the ground water. Using the GIS software by interpreting the laboratory results of fluoride and other chemical parameter mapping can be done, so that we can easily analyse the variation of groundwater chemical parameter in the area. This study will help to know causes for fluoride generation in the groundwater and also keep the people aware about health effects of excess fluoride in the area.

1.1 Study Area

The district of Gadag is situated entirely in the North Karnataka, which is a part of the larger Deccan plateau. Located in north central Karnataka, Gadag is surrounded by Koppal district to the east, Bagalkot district to the north, Haveri district to the south, Dharwad district to the west. It is positioned at 15º15'N 75º20'E/ 15º45'N 75º47'E and covers an area of 4656 km_2. Gadag district has 5 talukas–Gadag, Mundargi, Shirahatti, Ron and Naragund. The area of the district is plain to gently undulating terrain varies in altitude from 508m to 750m from msl. The climate is warm and dry throughout the the year and the rainfall is scarce. Gadag district receive the lowest rainfall annually in Karnataka. The months of September to December account for about 53% of the total annual rainfall.

Gadag lies in the semi arid region. The district is apart of Krishna basin, divided into two sub basins namely Malaprabha and Tungabhadra. Soil in the area can be categorized as either the majority black or minority red. Black cotton soilretains moisture and is often used for the cultivation of cotton, Bengal gram, ground nut, maize and jowar. Common rock types in the region includes granitic gneiss, quartzite gneiss, dharwar schis, conglomerates, gray wackes and sand stone. Gold ore is also found in the Kappatagudda hills. The average rainfall in the region is approximately 613 mm annually. Fig 1.1 shows the map of Gadag district

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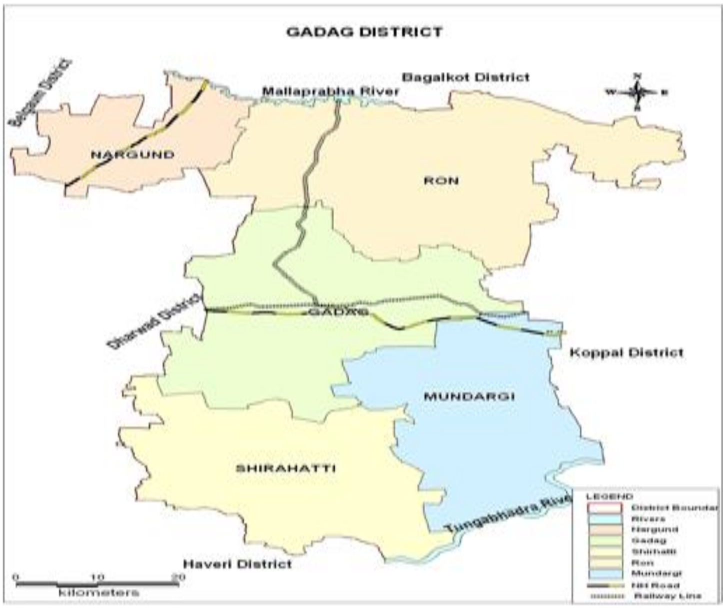


2.MATERIALS AND METHODS

Ground water geochemical analysis for fluoride and various chemical parameter and its representation in the GIS mapping involves 3 steps

- **Field study**
- **Laboratory study**
- **GIS based interpretation of the data**

2.1 Field study

In this phase we are selecting the bore well points at various places in the district, to locate bore well point GPS reading is taken for GIS mapping purpose.

Samples from bore well water were collected in high grade plastic bottles of one litre capacity. The bore well is pumped and allow to run the water, after 5 minutes the bottles are filled in order to flush out the stationary water. Using the water level indicator a static ground water level is measured. Surface soil information around the bore well were collected, meanwhile geological formation of the area were studied and collected the information.

The water samples are analysed for chemical parameters.

2.2 Laboratory study

In recent years, the growth of industry, technology, population, and water use has increased the stress upon both our land and water resources. Locally, the quality of ground water has been degraded. Municipal and industrial wastes and chemical fertilizers, herbicides, and pesticides not properly contained have entered the soil, infiltrated some aquifers, and degraded the ground-water quality. Water from some wells and springs contains very large concentrations of dissolved minerals and cannot be tolerated by humans and other animals or plants. Many parts of the Nation are underlain at depth by highly saline ground water that has only very limited uses. A clean and pure water is the greatest need for all human kind. Therefore, it is very important to know whether the water is fit for human utility or not and it can be determined by analyzing chemical properties of water.

In the laboratory study water samples were analysed for eight chemical parametres Viz.

pH, Total hardness, Fluoride, Total dissolved, Chloride, Total alkalinity, Nitrate, Sulphate

By the standard methods as per IS 3025 Part1- part37 methods of sampling and test (physical and chemical) for water have been adopted for analyzing the quality parameters and the results were tabulated in appendix.

2.3 Geology of the area:

Gadag: In this region most of the area is covered with granitic gneiss, the area covering under Kappata gudda hill consisting of schist belt .These schist generally show a foliation dipping angle of 50^{o} to 70^{o}in the east direction. These rock formations show a folding as well as micro folding along with veins of quartzite, quartz and dykes. These helps in the improvement of the ground water level.

The weathering of the schist rock is taking place at a depth of 20 to 30m, and that of the gneiss is around 30 to 45m.Due to the weathering of these rock formation in the earth crust the alkalinity of the ground water increases.
Mundargi: In this region large area is covering under granitic gneiss towards west direction Gadag- Dambal schist rock strata is being covered. In the schist rock strata shale, banded ferruginous quartzite, conglomerate, are being inter bedded which helps in the improvement of the groundwater level.
Naragund: the area is covered under granitic gneiss, schist belt, these rock formation extend from Naragund to Chikka naragund in the direction from NE to NW . these schist beds show a foliation dipping by an angle 50⁰ to 70⁰ towards SW. there is a rock bed formation of conglomerate near sankdal.
The weathering of the schist taking place at a depth of 20m to 30m,and that of gneiss taking place at 30 to 40m.there is a lineament formation near surkod which helps in the improvement of the groundwater. Since the groundwater is contaminated with alkalinity it is not used for potable and irrigation purpose.
Ron: The area covers under gneiss and granitic gneiss formation except in the direction of SW, wherw the formation of sand stone are found. The sand stones are foliation dipping by an angle 5⁰ to 10⁰ in the direction of SW. The sand stone depth range from 15 to 30m. Weathering of granitic gneiss improves the groundwater in the hilly region.
Shirahatti: The area covered by shale, schist, conglomerate, gray wacke, gneiss, quartz. These rock formation show a folding as well as micro folding along with a veins of quartz, quartzite and dykes helps in the improvement of the groundwater level. The rock bed covers in the direction of NE to NW and foliation dipping by an angle of 50⁰ to 70⁰ towards east. There is a lineament found in the places of Battur, Kadkol, Devihal, Machenahalli which helps in the improvement of the groundwater level.
The hydrogeology map of Gadag district is shown in Fig. 2.1

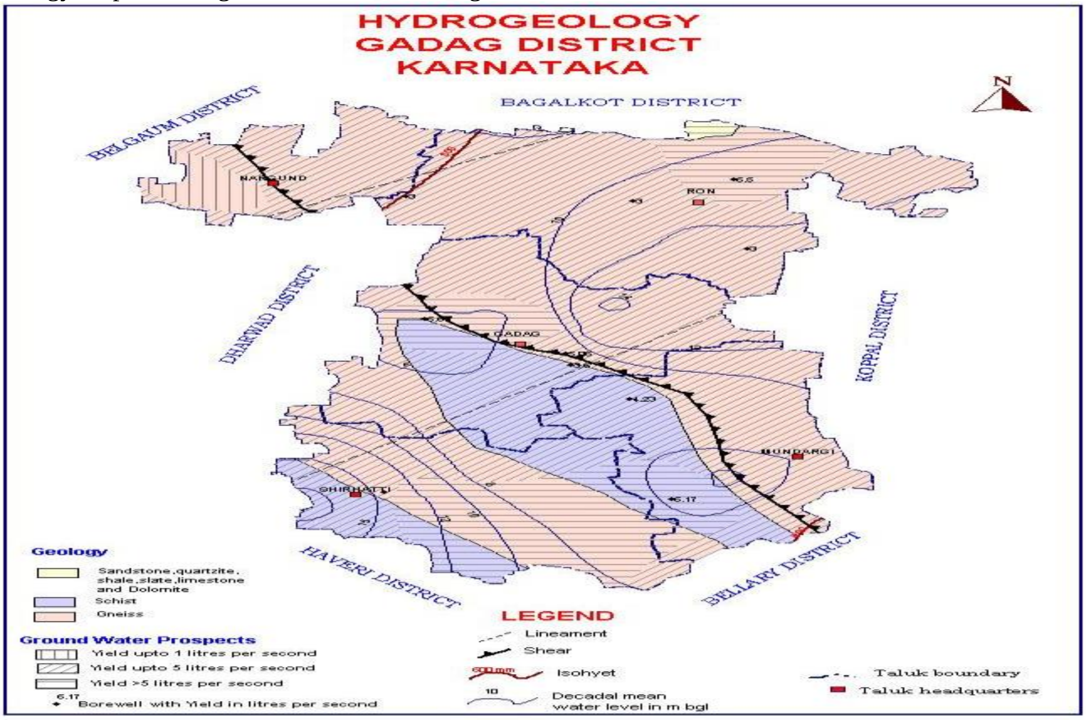


Fig. 2.1 Hydrogeology map of Gadag district

2.3 In the study area mainly 3 types of soils were observed:
They are
1. Red loamy soil
2. Red gravelly clay soils
3. Black cotton soil

Table2. 2: Properties of the soil

S.No	Type of soil	Content
1	Red loamy soil	Granite, gneisses, iron oxide, iron and magnesium bearing minerals
2	Red gravelly clay soils	Granite, gneisses, schist, quartzites, phyllites, charnockites
3	Black cotton soil	High proportions of Ca, Mg, Basalt,Ferroginous schist and gneisses. The base exchange capacity of black soil is generally fairly high.

RESULTS AND DISCUSSION
Gadag district covers an area of 4656 km_2. Through out the entire area depending upon the contamination of ground water we have collected water sample from 186 bore well points, mean while GPS reading has taken for location of the place in GIS map.In order to analyse the geological formation an information regarding rock strata formation and surface soil around the bore wells has taken. Since ground water is the major source for potable and irrigation purpose in the area, it is necessary to know

the chemical parameters of the ground water .collected ground water samples have been tested for chemical parameters like pH, fluoride total hardness, total dissolved solids, nitrate, sulphate, alkalinity and chloride in the laboratory according to the standard methods. The results have been compared with the Indian standard drinking water specifications (IS 10500 :1991).[22]

Table 4.1 Indian standard drinking water specifications (IS 10500 :1991).

S.No	Chemical parameter	Desirable limit (mg/l)	Permissible limit in the absence of alternative source (mg/ l)
1	pH	6.5 – 8.5	
2	Total alkalinity	200	600
3	TDS	500	2000
4	Total hardness	300	600
5	Fluoride	1.0	1.5
6	chloride	250	1000
7	nitrate	45	100
8	sulphate	200	400

TDS : Total dissolved solids

Table 4.2 Summary of ground water quality parameters

S. No.	Chemical parameter	No. of samples within desirable limit	No. of samples within permissible limit in the absence of alternative source	No. of samples above permissible limit
1	pH	180	06	
2	Total alkalinity	92	72	22
3	TDS	72	86	28
4	Total hardness	54	110	22
5	Fluoride	25	72	89
6	Chloride	103	83	Nil
7	Nitrate	156	30	Nil
8	Sulphate	160	26	Nil

By observing the results we come to know that the groundwater from many villages in the district are not suitable for potable purpose.The pH of the groundwater sample are in the range of 6.73 to 8.92,most of the samples are within the desirable limit of 8.5, 6 samples have crossed the desirable limit in Mundargi taluk i.e in Kalkeri, Mustikoppa and in Gadag taluk i.e in Balganur and Harlapur have been contaminated. The Total hardness in the groundwater has the permissible limit of 600 mg/L. 22 samples have crossed the permissible limit, most of the samples are in the range of permissible limit where the alternate source of safe drinking water is not available. Considering the fluoride, where 89 samples have crossed the permissible limit of 1.5 mg/L. The samples are in the range of 0.5 ppm to 6.12 ppm, around 26 samples being collected from Gadag taluk and Mundargi taluk have crossed the range of 3.0 ppm. The geological formation in this area is covering under dharwar schist and gneiss, these are composed of minerals like feldspar, hornblende, chlorite, biotite, glaucaphase etc. These minerals are containing fluoride in their chemical composition ,because of the mining activity weathering of the rock takes place and the fluoride ion released into the ground water. So the concentration of the fluoride observed is more in this area. Sulphate being the most important chemical present in the groundwater which has a desirable limit of 200ppm and permissible limit of 400 ppm. If the concentration is more than the desirable limit it may cause gasto intestinal irritation.28 samples are above the desirable limit. Nitrate have the desirable limit of 45ppm and permissible limit of 100ppm, it ranges from 5ppm at Chabbi and 68ppm at Hallikeri , 30 samples are in the permissible limit, if the concentration exceeds the desirable limit it may cause methaemoglobinimia. Total dissolved solids are distributed in the range of 183ppm to 3346ppm, 28 samples are above the permissible limit.it is observed that fluoride concentration is higher, where the total dissolved solids are highly concentrated. In the study area sulphate is distributed in the range of 17 ppm to 423 ppm . 15 samples are in the range of permissible limit.

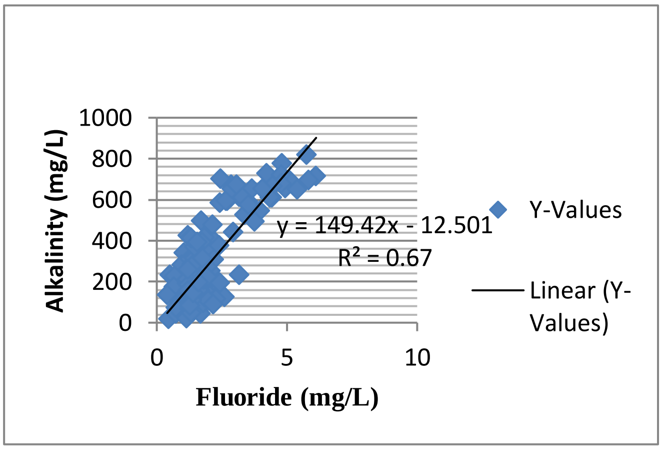


Fig 4.1 Correlation study of fluoride with other chemical parameters

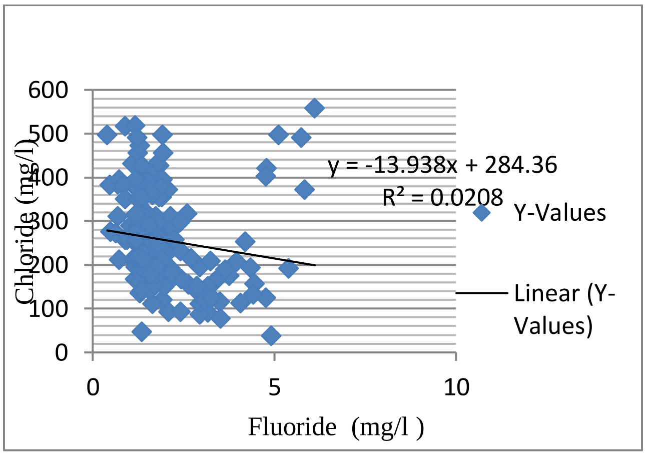
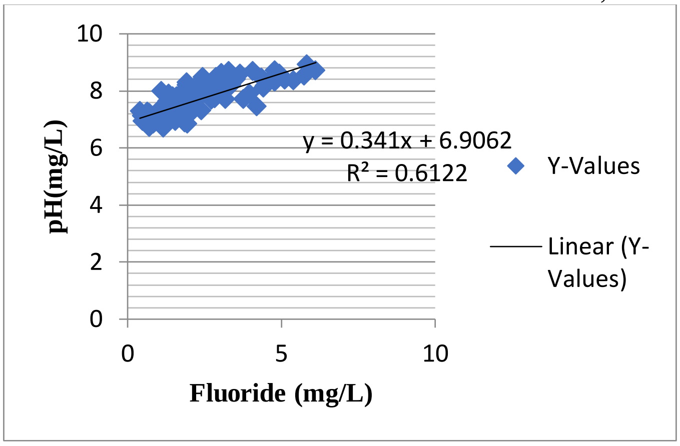


Fig. 4.2 Fluoride Vs Chloride

The positive correlation between alkalinity and the and the fluoride might be due to the release of hydroxyl and bicarbonate ions simultaneously during the leaching and dissolution process of fluoride bearing minerals into the groundwater.ie more and more leaching of minerals lead to increase in the fluoride ion concentration with high level of alkalinity From the graph it shows that fluoride is negatively correlated with chloride, since the fluoride is highly electro negative than chloride as the fluoride concentration increases chloride concentration decreases, due to the exchange of fluoride with chloride.



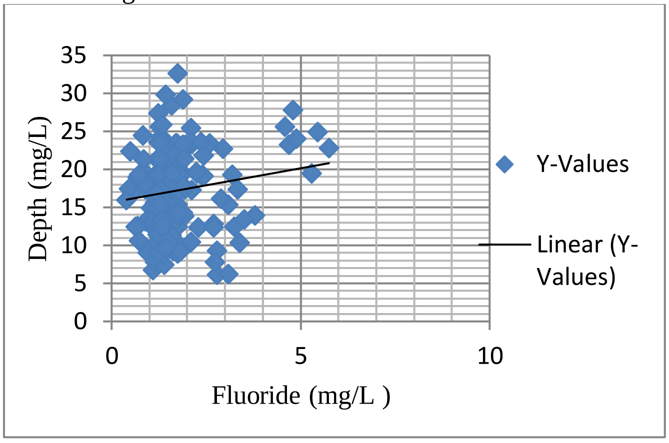
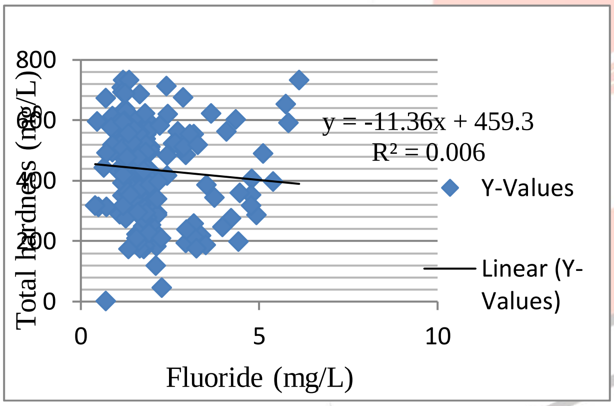


Fig. 4.3 Fluoride Vs pH Fig. 4.4 Fluoride Vs Depth

From the graph it shows a positive correlation between fluoride and the pH.
Since metal fluorides do under go hydrolysis, release metal hydroxides. Hence the increase is pH with the increase in fluoride content is observed.

It may be contemplated that as the depth of the bore well increases the contact area and time increases. Hence it may be concluded that fluoride content increases with increase in depth of bore wells.



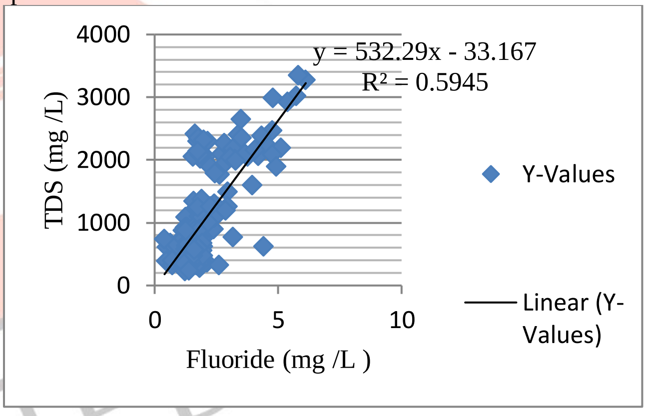
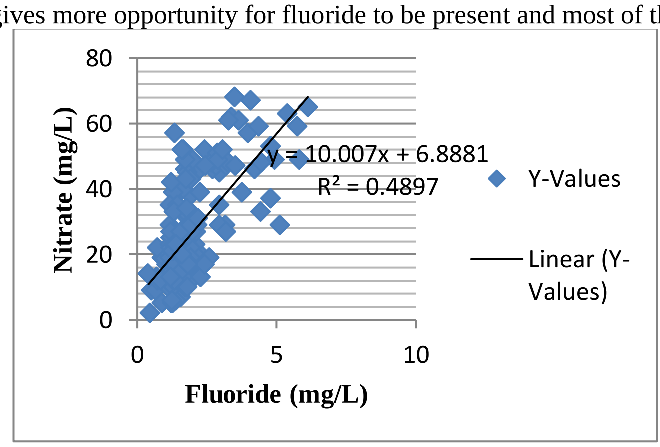


Fig. 4.5 Fluoride Vs Total hardness Fig.4.6 Fluoride Vs Total dissolved solids

From the graph it shows a negative correlation between fluoride and the total hardness. Hardness of water is mainly due to calcium salts in water .As hardness increases formation of calcium fluoride (CaF_2) an insoluble salt formation increases. Therefore decrease in fluoride content as the increase in hardness of water is observd.

From the graph it shows a positive correlation between fluoride and the total dissolved solids. Since dissolved solids gives more opportunity for fluoride to be present and most of the metal fluoride are soluble.



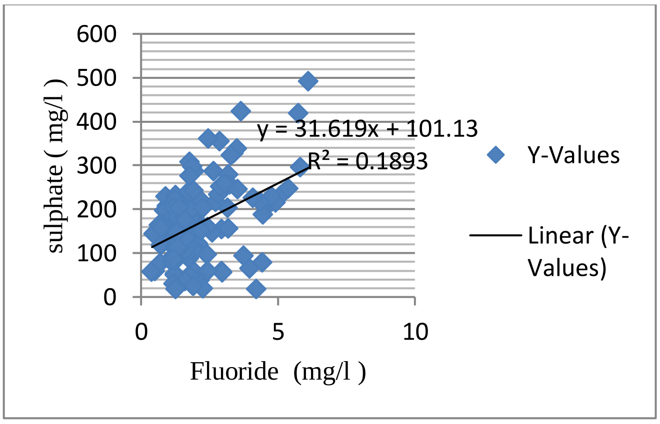


Fig 4.7 Fluoride Vs Nitrate Fig. 4.8 Fluoride Vs sulphate

From the graph it shows a positive correlation between fluoride and the nitrate. Since nitrate is an oxidizing agent it increases the solubility of Fluoride in groundwater. The sulphate is positively correlate with fluoride concentration

4.2 Ion exchange process

Minerals containing fluoride present in the soil are in the form of complex salts which will under go several chemical changes. During the process strong acid formation, strong base formations do occur in nature. This environment provides dissolution of fluoride in water in the form of NaF through a complex reaction involving H_4SiO_4(silisic acid) which will undergo neutralization with Na_2CO_3/ NaOH to give NaF, which will be present in the water. All these reactions taking place in accordance with chemical equilibrium.

$2HF + Na_2CO_3 \rightarrow 2NaF + CO_2 + H_2O$

$HF + NaHCO_3 \rightarrow NaF + H_2O + CO_2$

Fluoride present in the water as fluoride ion, due to the almost complete dissociation of the parent fluoride compounds. The solubility of CaF_2 that is present in the minerals increases with the increase in total alkalinity in the ground water according to the following reactions. [3]

$CaF_2 + CO_3^{2-} \rightarrow CaCO_3 + 2F^-$

$CaF2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$

The carbonate and bicarbonate are also hardness producing ions. A positive correlation of total alkalinity with fluoride elucidates leaching of fluoride from fluoride bearing minerals into groundwater at alkaline environment or in other words increase of pH of the water enhances the leaching of fluoride from the minerals containing fluoride. Even though alkalinity and pH are the important factors that has influence on fluoride ion concentration in drinking water, because increase of alkalinity is due to the increase of carbonate and bicarbonate ions , these ions not having direct influence on pH level like hydroxyl ion, so increase of alkalinity does not increase the pH level linearly.

F^- is the most electronegative element and thus it reacts immediately to form fluoride compounds and therefore making presence of free F^- an obsolete possibility but under favorable physicochemical conditions with long residence time it may occur as dissolved salt from groundwater. At acidic pH the F^- is adsorbed on the surface of the clay. A higher value of pH favors the enrichment of F^- in groundwater. The OH^- in groundwater with high value of pH can replace the exchangeable F^- of fluoride containing minerals (muscovite) thus can increase the concentration of fluoride in groundwater.The hydroxyl ions replace F^- from muscovite as shown below: Muscovit [23]

$KAl_2[AlSi_3 O_{10}]F_2 + 2OH^{-1} \rightarrow KAl_2[AlSi_3 O_{10}[OH]_2 + 2F^-$

Lowest pH values are found in groundwaters with lowest TDS values. These represent recently recharged groundwater. Most groundwaters are of Na- Ca- HCO_3 type,reflecting the importance of reaction of silicate minerals, notably sodic feldspar in the presence of acid generated from soil derived CO_2.[6]

$2NaAlSi_3O_8 + 2H^+ + 9 H_2 \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4$

Zeolites are the cage like structures made from silicates. They have empty space in their structures into which ions can fit. As with the ordinary ion exchange, sodium ions are the normal residents in the holes. When hard water passes over the zeolites the calcium ions displaces the sodium ions. The zeolite is regenerated by swamping it with salt water. [20]

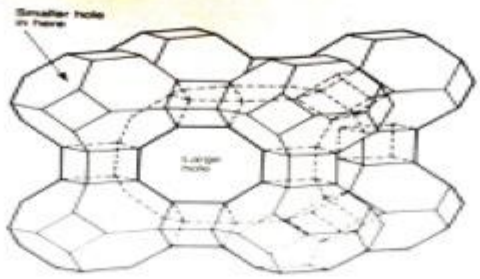


Fig.4.18 The cage structure of zeolite with formula $Na_{12}(AlSi_{12}O_{48})$ 27H_2O.

The cage structure of zeolite with formula $Na_{12}(AlSi_{12}O_{48})$ 27H_2O.

The structure is based on a combination of cubes and octahedral. There is a large hole in the centre and smaller ones inside the other frame works, in which atoms, molecules, or ions can be trapped.

CONCLUSIONS

Fluoride bearing minerals like feldspar, quartz, hornblende, glaucaphase, plagioclase etc are found in the granite, gneiss, schist, shale, sandstone and conglomerate rock formations. These minerals in the sub surface provide a significant source of fluoride in groundwater. Climatic conditions such as semi aridity and high temperature, favours effective chemical weathering of these rocks. Thus the origin of the fluoride is mostly from a weathered gneiss,schist,quartz and conglomerate. In the study area fluoride is high, with concentration ranging from 0.4 to 6.12 mg/l, 50% of the samples contained fluoride concentration that exceed the drinking water standard of 1.5 mg/l set by WHO.Ground water in the study area is also containing high TDS and nitrate concentration which may cause gastro intestinal irritation and methahaemoglobinimea respectively. Geographic information system(GIS) approach to develop spatial information knowledge based on the groundwater quality of study area has been found to be very useful. GIS data base also helps in decision making process by identifying the most sensitive zones that need immediate attention.

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