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Quality Indices of Fluoride Concentration in Groundwater of Malkhaid Sub-basin, Gulbarga District, Karnataka

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ABSTRACT: Groundwater is the major source of drinking water in the study area., High fluoride content above permissible limit (>1.5 mg/l) are recorded at many places in groundwater samples of study area resulting in health hazards, causing dental and skeletal fluorosis. The major litho-units of study area are limestone, shales and Deccan traps. Integrated quality indices, multi-criteria decision making and sensitivity function analyses are used to analyze the groundwater samples using mathematical modelling. The geochemistry of groundwater relating major ionic constituents with fluoride using statistical analysis are carried out to understand the source and mechanism of enrichment of fluoride in groundwater. Based on multi-criteria decision making approach, the majority of the samples fall under the category of decreased quality region. Results of sensitivity function analyses indicate, waters belong to less recommended range. Saturation indices of fluoride minerals are interpreted using Chadha's diagram. The geochemical analysis indicates the alkalis, viz., Ca^{2+} and Mg^{2+} indicated negative correlation with fluoride. This could be due to the oversaturation of carbonate minerals as inferred from saturation indices. Positive correlation between F^- with that of Na^+ ions and pH is observed, which may be due to the rock dissolution processes. From the above studies it is interpreted that the mineral dissolution through rock water interaction is the major controlling process of fluoride enrichment in groundwater. Water treatment and de-fluorination at village levels are to be considered for using groundwater for drinking purpose.

KEYWORDS: Groundwater chemistry, fluorosis, integrated quality indices, rock dissolution, de-fluorination.

I. INTRODUCTION

Natural contamination due to particular geological environments can be an important factor in limiting the available water resources. Groundwater is the major source of potable water supply in arid to semi-arid areas and its availability may be threatened not only by introduction of contaminations by human activity but also by natural processes [1].

The link between fluoride geochemistry in water in an area and the incidence of dental and skeletal fluorosis is well established relationship in medical geology. While the essentiality of fluoride for human health is still being debated, its toxicity has now caused considerable concern in many lands where fluoride is found in excessive quantities in the drinking water. As in the case of some essential trace elements, the optimum range of fluoride varies within a narrow range and this causes fluoride imbalances, very often in large populations, mostly in developing countries of the tropical belt. In the case of many trace elements, food is the principal source. Much of the fluoride entering the body however is from water and the hydrogeochemistry of fluoride in surface and groundwater is therefore of major interest [2].

Groundwater is the major source of drinking water in Malkhaid sub-basin. High fluoride content above permissible limit (>1.5 mg/l) is recorded in groundwater samples of study area causing health hazards. Fluoride is the most

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electronegative and chemically reactive element of all halides. The occurrence of fluoride in groundwater may be due to natural or anthropogenic activities and the real source of contamination is often not clear. The availability of fluoride and its enrichment in the groundwater is mainly dependent on the dissolution of fluoride bearing minerals such as fluorite, apatite, flourapatite, topaz, amphibole, cryolite, villiamite, micas and clays over a period of time. The aim of the present study is to evaluate the possible sources of fluoride in groundwater samples of the study area through estimation of quality indices.

II. STUDY AREA AND GEOLOGY

The study area (Fig. 1) falls between 17°12′12.24″ to 16°58′52.32″ N latitude and 77°8′50.64″ to 77°15′43.56″ E longitude and forms a part of Bhima basin in Gulbarga district of Karnataka. The aerial extent is around 150 sq kms. The main physiographic features are hills and plains. The altitude in the study area ranges between 400 to 560 meters. The general slope of the area is towards north. The area experiences arid to semi-arid climatic condition with less rainfall. It shows sub-dendritic to sub-parallel drainage pattern flowing towards north. Limestone is the dominant geology of the study area with patches of shale and deccan trap in southern region.

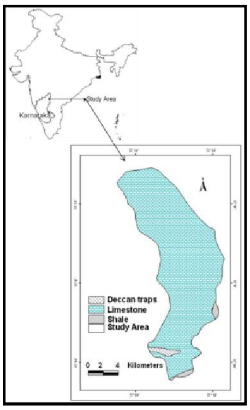

Fig. 1: The location and geology map of the study area

III. DATA USED AND METHODOLOGY

Premonsoon (January 2011) water analysis data of groundwater sample is used in the present study. A quality interval criterion of the multi-criteria decision making approach using mathematical modelling is adopted to categorize the water samples with respect to the concentration of fluoride in the samples. The sensitivity function analysis is used to bifurcate the water samples into suitable for drinking or not recommended for drinking purpose. Statistical analysis is carried out to understand the source and mechanism of enrichment of fluoride in groundwater. Stoichiometric approach has been used to know the source of enrichment of elements in the groundwater.

IV. RESULTS AND DISCUSSION

Statistical Analysis of water quality data

The statistical analysis (Mean, Median, Standard deviation etc) of major ionic constituents were analysed and the results are given in Table 1 to summarize the general composition of the groundwater samples. It was carried out for the Premonsoon (January 2011) water analysis data. The fluoride concentration in the groundwater samples of the study area ranges between 0.9 to 3 mg/l. The mean and median value is greater than the permissible limit of fluoride concentration for drinking purpose. The concentrations of other elements are within the permissible limit.

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Table 1: Statistical analysis of chemical constituents for the Premonsoon (January 2011) groundwater samples				
In mg/l	**Range**	**Mean**	**Median**	**SD**
Ca	40-260	103	80	65
Mg	60-360	149	120	82
Na	16-159	77	67	43
K	2-29	12	12	7
Cl	150-410	225	220	78
CO_3	0-120	21	0	32
HCO_3	230-800	448	460	150
SO_4	7-393	72	40	97
Fe	0-1	0.4	0.3	0.4
F	0.9-3	2	2	1

Comparison of Fluoride concentration with Standards

The comparison between the fluoride concentration of the study area and the water quality standards are matched in Fig. 2. The fluoride concentration is found to be higher when compared with the maximum permissible limit of Indian Drinking Water Standards (1.0 mg/l) [3] and World Health Organization (1.5 mg/l) [4].

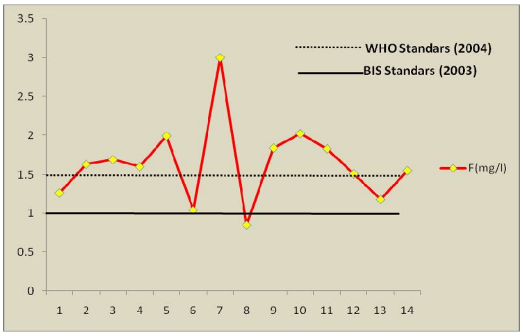

Fig. 2: WHO (2004) and BIS (2003) standards and Fluoride concentration in study area

Quality Indices

The suitable quality of water for different utilization is always lacking behind. It is essential to classify the water into zones on the basis of detailed study. The study has been carried out by M.S. Alam et al. [5], to classify the waters into different categories. In the present study same criteria has been used to know the impact of fluoride on groundwater of the study.

Integrated quality indices of groundwater samples are estimated on the basis of multi-criteria decision making approach. The quality interval and sensitivity numbers have been calculated using simple mathematical formula.

Quality Interval: Every system parameter has its own recommended value (r) or recommended range ($r1 \leq r \leq r2$) and also minimum (l) and maximum (u) permissible limits and these are used in mathematical language to categorize the samples into three groups as shown in Table 2 i.e., Excellent, Decreasing and Increasing quality regions. The results of quality interval for the parameters in the study area is shown in Fig. 3 indicates, 73% of samples fall under decreasing water quality region (DQR) and 27% of water sample are in excellent quality region (EQR).

Table 2: Quality Interval Criteria for categorising the groundwater samples		
EQR	$r1 \leq r \leq r2$	Excellent quality region
DQR	$r1 \leq r \geq r2$	Decreasing quality region
IQR	$r1 \geq r \leq r2$	Increasing quality region

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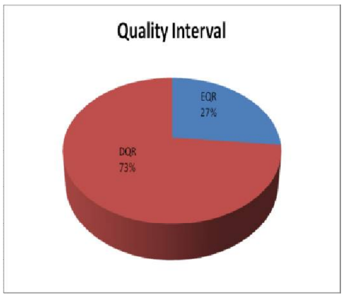

Fig. 3: Results of Quality Interval from the study area

Sensitivity Number: The sensitive number analysis is carried out using the mathematical criteria shown in Table 3. According to Table 3, the negative sensitivity number indicates that the value of the parameter is less than the recommended value; whereas the positive value indicates that the value of the same is more than the recommended range or value. The zero sensitivity number shows that the value of the parameter lies in the recommended range. In the present study area, the sensitivity number has been calculated and the results is shown in Fig. 4 indicates, 86% of the samples from the study area are in more than recommended range (MRR) and 14% of the samples are fall under recommended range (RR).

Table 3: Sensitivity Number analysis criteria for categorising the groundwater quality

RR	0	$r1 \leq r \leq r2$	Recommended range
LRR	- 1	$r1 \geq r \leq r2$	Less than Recommended range
MRR	+ 1	$r1 \leq r \geq r2$	More than Recommended range

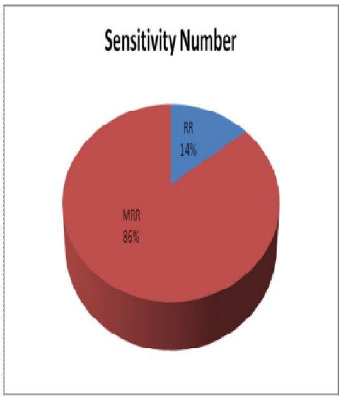

Fig. 4: Results of Sensitivity Number from the study area

Spatial distribution of Fluoride concentration

The spatial distribution map of fluoride (Fig. 5) has been prepared using the GIS software to have the better understanding of distribution of fluoride in the study area. It is observed from the spatial distribution map that the fluoride in almost entire study area is more than the permissible range (>1.5mg/l). The entire study area is under threat with respect to fluoride concentration.

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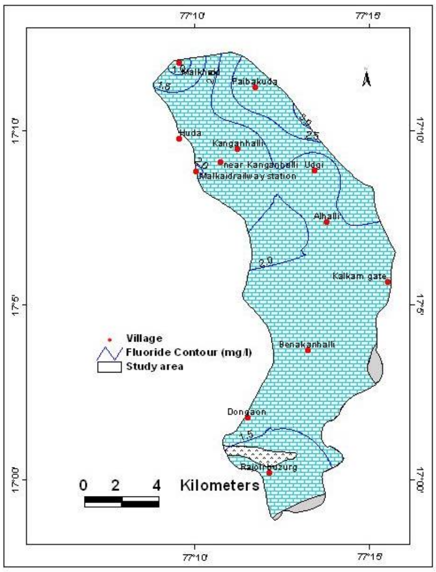

Fig. 5: Fluoride concentration contours showing distribution around the study area

Gibbs plot

Since the study region experiences dry and semiarid climatic condition, evaporation may also contribute to changes in water chemistry in the study region. Hence, to identify and to differentiate the influences of rock-water interaction, evaporation and precipitation process, and mechanisms affecting the chemistry of groundwater from the study area, Gibbs [6] plot representing the ratios of Na:(Na^{+}+Ca^{+2}) and Cl^{-}:(Cl^{-}+HCO_3^{-}) as a function of TDS was used. Samples fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock-forming minerals. 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.

In Fig. 6, the mechanism controlling quality of water is due to rock weathering i.e., rock dominance (chemical weathering with dissolution of rock-forming minerals) and only one sample falls in evaporation dominance region. Main source for the enrichment of fluoride concentration may be the water-rock interaction.

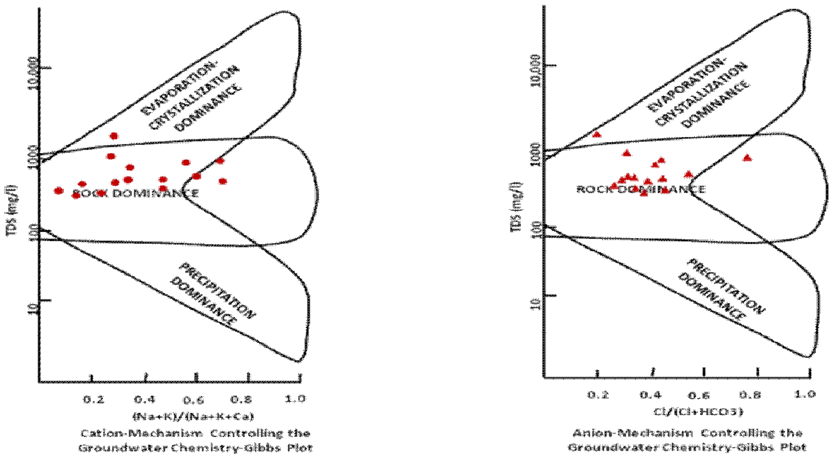

Fig. 6: Gibb's diagrams showing mechanism controlling quality for groundwater samples of the study area

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Saturation Indices

The status of fluoride ion released into the groundwater is controlled by the degree of saturation of fluorite and calcite minerals in groundwater. Geochemical simulation model WATEQ4F [7] has been used to determine the saturation indices with respect to fluorite and calcite. The Fig. 7 shows that groundwater samples of the study area are oversaturated with respect to calcite and under saturated with respect to fluorite. With respect to saturation indices of fluorite it is known as the fluorite mineral is still under dissolution process and the concentration of fluoride may increase further in groundwater of the study area.

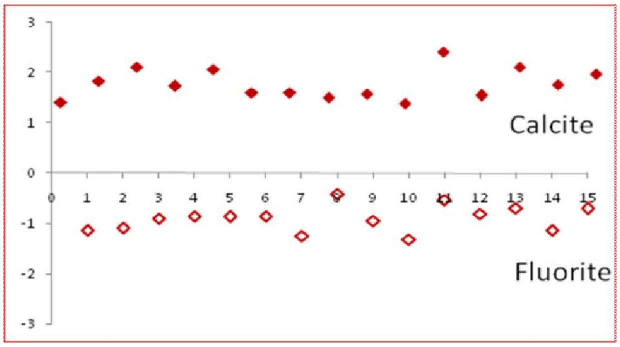

Fig. 7: Saturation index of Calcite ($CaCO_3$) and Fluorite (CaF_2) represents oversaturated and under saturated in groundwater samples of the study area

Plots of F^- v/s pH, Ca^{+2}, Na^+ and HCO_3^-

The R-squared values for the correlation of fluoride with some inorganic ingredients were plotted in Fig. 8. The Ca^{2+} showed poor negative correlation with F^-. This may because the groundwater in the study area is was predominantly rich in Ca^{2+}. Negative correlation of F- with Ca^{2+} and Mg^{2+} is expected due to low solubility of fluorides of these ions. The alkali metal ions, viz. Na^+ and K^+ showed positive correlation with fluoride. A moderate positive correlation was observed between F^- and pH showed negative correlation with Ca^{2+} and HCO_3^- and positive correlation with pH and Na^+. Therefore, fluoride forms complexes with sodium under alkaline condition while calcium precipitates due to oversaturation.

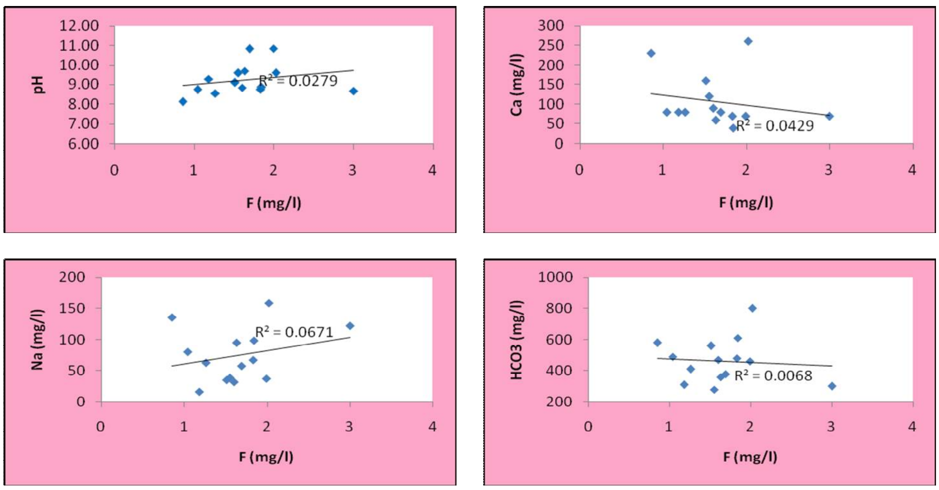

Fig. 8: Scatter diagram of F^- v/s pH, Ca^{+2}, Na^+ and HCO_3^- for groundwater samples of the study area

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Impacts

The impact of fluoride on health issues is given in the Table 4. In the study area 29% of the samples fall in permissible limit where as 71% of the samples are fall above permissible limit in the range of 1.5 to 4.0 mg/l, which results in dental fluorosis.

Table 4: Impact of fluoride on health (WHO, 1971)(cited in Medical geology of fluoride 2009)

Category	Concentration of fluoride in drinking water	Impact on health
1	0.0-0.5 mg/L	Limited growth and fertility, Dental caries, Promotes dental health resulting in healthy teeth
2 (29%)	0.5-1.5 mg/L	Prevents tooth decay
3 (71%)	1.5-4.0 mg/L	Dental fluorosis (mottling of teeth)
4	4.0-10.0 mg/L	Dental fluorosis, Skeletal fluorosis
5	>10.0 mg/L	Crippling fluorosis (pain in back and neck bones)

V. CONCLUSION

The fluoride concentration is found high (3mg/l) in Malkhaid sub-basin. Entire Malkhaid sub-basin is under threat with respect to fluoride level in groundwater samples. Groundwater is the only reliable source of drinking water for the people residing in the study area. The excess fluoride concentration in the groundwater of the study area implies that there is an urgent need to implement suitable remedial measures and defluoridation of the pumped water seems to be a viable option for immediate relief. In addition, such information should be made available to health professionals in order to avoid feasible over medication.

Acknowledgment

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