

## Saturation indices (SI) of the fluorite and calcite of water samples of Karli River basin, Southern part Sindhudurg district, Maharashtra.

Gaikwad S.K.<sup>++</sup> and Pawar N.J.\*

Shivaji University Kolhapur

<sup>++</sup>Department of Geology, University of Pune, Pune- 411 007.

Corresponding E-mail: njpawar@unipune.ac.in

### Abstract

In order to study the chemical equilibrium existing in groundwater and recognize the source of high fluoride concentration in groundwater from the study area, the concept of speciation modeling has been used. To study the Saturation Indices of groundwaters of Karli River Basin of Sindhudurg district, Maharashtra an analysis of 31 water samples from dug well, bore well, surface and spring water is carried out using High Performance Ion Chromatography (HPIC). The data for the saturation indices (SI) of fluorite ( $\text{CaF}_2$ ) and calcite ( $\text{CaCO}_3$ ) in the groundwater samples were calculated using PHREEQC Interactive, a computer programme of U.S. Geological Survey, version 2.8. Result shows that except one sample (DW-1), all of the samples are undersaturated with respect to calcite and fluorite during the Premonsoon season. During Postmonsoon season all samples are fluorite undersaturated except sample BW-24, which is oversaturated with respect to fluorite and calcite and 22% samples have been found oversaturated with respect to Calcite. Thus solubility control on the higher concentration of fluoride can be explained by the fact that fluoride ions in groundwater can be increased as a result of precipitation of  $\text{CaCO}_3$  at high pH, which removes  $\text{Ca}^{2+}$  from solution allowing more fluorite to dissolve.

**Keywords:** Saturation indices, fluorite, calcite, Karli River basin

### Introduction

To understand the geochemistry of fluoride bearing groundwater with the other major ions of the groundwater from the hard rock of Pre-Cambrian terrain of Karli river basin of Sindhudurg district of Maharashtra was a major aim to analyze the 31 samples of groundwaters. As the, quality of water along the course of its underground movement is dependent on the chemical and physical properties of surrounding lithologies, the quantitative and qualitative properties of through-flowing water bodies, and the products of anthropogenic activity (Matthess 1982). According to Handa (1975), F shows positive correlation with  $\text{Ca}^{2+}$  and F, till saturation with respect to fluorite is attained. After reaching saturation, it shows negative correlation.

### Study area and geology

The area under study is bounded by Karli Rivers in the Konkan Coastal zone covering an area of about 792.71 Km<sup>2</sup>. The study area lies between the longitude 73.48 to 74.03 E and latitudes 15.91 to 16.17 N on the western coast of India in the southern part of maharashtra state. It is on the eastern side of the Western Ghats forming narrow strip of land of about 40 Kms between the Sahyadris on the east and the Arabian Sea on the west. It is highly hilly and undulating, being cut up by many east-west trending ridges, some of which reach right to the coast. The area under investigation receives average of about 3,287mm (IMD, 1974).

Geologically, the area is endowed with a variety of lithological types ranging in age from Achaean to Recent (Fig.1). Litho types like gneisses, quartzites, and schists (Dharwar Super Group) are exposed while Cretaceous basaltic flows of Deccan Volcanics are present at higher elevations (Sarkar, 1986).

### Material and Methods

In all 31-surface and groundwater sampling wells based on random grid were selected to represent different aquifer types and the areas representing different land use and slope categories (Fig. 1). Two sets of samples have been collected during the period Pre-monsoon (May) 2005 and Post-monsoon (December) 2006. The sampling stations include 22 dug wells, 2 bore wells and 4 surface water and 3 spring water samples. Pre-cleaned plastic bottles of 1-liter capacity were used for the collection of samples. Standard procedures were used for analysis (APHA, 1998; Pawar *et al.*; 1989). The anions were analyzed by using Dionex-Dx-600 High Performance Ion Chromatography System (HPIC). Fluoride analyzed by using AS-II-HC analytical column.

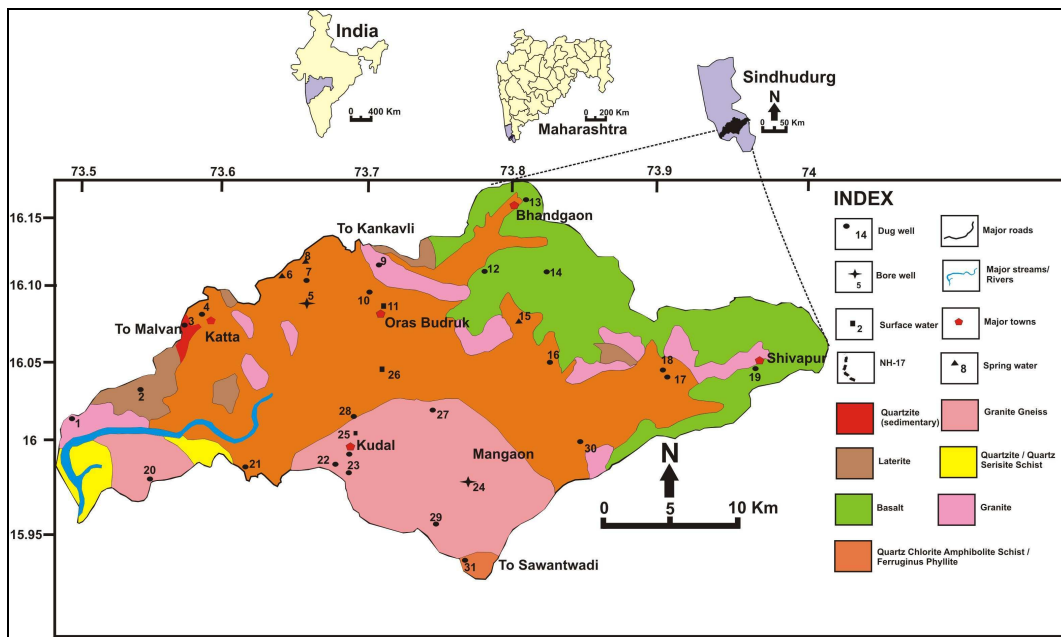


Fig.1. Sample locations, accessibility and geological variations in the Karli river basin.

**Results and discussion**

The chemistry of groundwater is the consequence of interaction between rain and the rock near the earth’s surface. In order to study the chemical equilibrium existing in groundwater and recognize the source of high fluoride concentration in groundwater from the study area, the concept of speciation modeling has been used. The most important results of speciation calculations are saturation indices (SI) for minerals, which signify whether a mineral should dissolve or precipitate. The solubility limits for fluorite and calcite provide natural controls on water composition in a view that calcium, fluoride and carbonate activities are interdependent (Kundu *et al.*; 2001). The data for the saturation indices (SI) of fluorite (CaF<sub>2</sub>) and calcite (CaCO<sub>3</sub>) in the groundwater samples were calculated using PHREEQC Interactive, (Parkhurst and Appelo, 1999) a computer programme of U.S. Geological Survey, version 2.8 (2003) and shown in Table.1

Saturation indices (SI) of fluorite (CaF<sub>2</sub>) and calcite (CaCO<sub>3</sub>) are plotted in Fig.2, which shows that except one sample (DW-1), all of the samples are undersaturated with respect to calcite and fluorite during the Premonsoon season. During Postmonsoon season all samples are fluorite undersaturated except sample BW-24, which is oversaturated with respect to fluorite and calcite and 22% samples have been found oversaturated with respect to Calcite (Fig.2).

respect to Calcite (Fig.2).

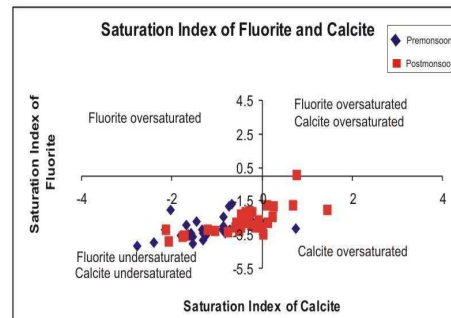


Fig.2: Plot of saturation indices (SI) of for fluorite (CaF<sub>2</sub>) vs. calcite (CaCO<sub>3</sub>) in the water samples of Karli River basin

| S.No  | Premonsoon    |                |      |           | Postmonsoon |           |               |                |
|-------|---------------|----------------|------|-----------|-------------|-----------|---------------|----------------|
|       | SI of Calcite | SI of Fluorite | pH   | F in mg/l | pH          | F in mg/l | SI of Calcite | SI of Fluorite |
| DW 1  | 0.76          | -3.12          | 8.47 | 0.17      | 8.89        | 0.36      | 1.46          | -2.05          |
| DW 2  | -2.14         | -3.19          | 7.01 | 0.43      | 8.24        | 0.31      | -2.13         | -3.18          |
| DW 3  | -2.77         | -4.18          | 6.45 | 0.15      | 7.63        | 0.23      | -1.72         | -3.57          |
| DW 4  | -1.31         | -3.81          | 7.12 | 0.12      | 7.95        | 0.18      | -0.5          | -3.29          |
| BW 5  | -0.85         | -3             | 7.30 | 0.28      | 7.79        | 0.35      | -0.29         | -2.47          |
| SP 6  | -1.57         | -3.58          | 6.91 | 0.15      | 8.05        | 0.16      | 0.01          | -3.1           |
| DW 7  | -0.87         | -3.24          | 8.05 | 0.27      | 8.26        | 0.12      | 0.04          | -3.49          |
| SP 8  | -1.24         | -3.57          | 7.18 | 0.15      | 8.16        | 0.62      | -0.21         | -2.19          |
| DW 9  | -1.53         | -3.64          | 6.75 | 0.12      | 7.93        | 0.28      | -0.32         | -2.8           |
| SW 10 | -1.3          | -3.44          | 7.13 | 0.17      | 8.09        | 0.33      | -0.47         | -2.78          |
| DW 11 | -0.73         | -3.29          | 7.31 | 0.15      | 8.17        | 0.25      | 0.13          | -2.82          |
| DW 12 | -0.2          | -2.82          | 7.52 | 0.16      | 7.78        | 0.24      | -1.04         | -3.29          |
| DW 13 | -0.85         | -3.13          | 7.18 | 0.20      | 7.98        | 0.22      | -0.24         | -2.91          |
| DW 14 | 0             | -2.76          | 7.73 | 0.21      | 8.03        | 0.18      | -0.16         | -3.09          |
| SP 15 | -0.49         | -3.24          | 7.39 | 0.16      | 8.38        | 0.61      | 0.69          | -1.72          |
| DW 16 | -0.82         | -3.45          | 7.19 | 0.13      | 8.28        | 0.77      | 0.25          | -1.84          |
| SW 17 | -0.7          | -3.24          | 7.42 | 0.17      | 8.00        | 0.35      | -0.56         | -2.76          |
| DW 18 | -1.54         | -4.02          | 7.17 | 0.13      | 7.97        | 0.40      | -0.31         | -2.46          |

|       |       |       |      |      |      |      |       |       |
|-------|-------|-------|------|------|------|------|-------|-------|
| DW 19 | -2.03 | -2.06 | 6.50 | 0.84 | 7.89 | 0.50 | -0.47 | -2.28 |
| DW 20 | -2.39 | -3.94 | 6.48 | 0.12 | 7.38 | 0.20 | -2.07 | -3.91 |
| DW 21 | -1.58 | -3.45 | 7.01 | 0.19 | 7.47 | 0.28 | -0.35 | -2.17 |
| DW 22 | -1.79 | -3.59 | 6.99 | 0.19 | 7.76 | 0.28 | -1.21 | -3.2  |
| DW 23 | -0.66 | -1.71 | 7.43 | 0.93 | 7.34 | 0.22 | -1.76 | -3.65 |
| BW 24 | -0.74 | -1.8  | 7.30 | 0.91 | 8.45 | 5.33 | 0.77  | 0.06  |
| DW 25 | -1.68 | -2.93 | 6.99 | 0.34 | 8.08 | 0.67 | -0.28 | -2.08 |
| SW 26 | -1.24 | -3.51 | 7.22 | 0.15 | 7.86 | 0.20 | -0.75 | -3.36 |
| DW 27 | -1.64 | -3.47 | 6.78 | 0.16 | 7.93 | 0.26 | -0.08 | -2.62 |
| SW 28 | -1.45 | -2.7  | 7.16 | 0.42 | 7.86 | 0.21 | -0.58 | -3.05 |
| DW 29 | -0.85 | -2.46 | 7.25 | 0.43 | 8.13 | 0.77 | 0.11  | -1.75 |
| DW 30 | -1.32 | -3.22 | 7.02 | 0.19 | 8.20 | 0.34 | 0.24  | -2.43 |
| DW 31 | -1.62 | -3.59 | 7.03 | 0.16 | 7.89 | 0.22 | -0.46 | -3.08 |

Table.1: The calculated saturation indices (SI) of for fluorite (CaF<sub>2</sub>) and calcite (CaCO<sub>3</sub>) in the water samples of Karli River basin

Thus solubility control on the higher concentration of fluoride can be explained by the fact that fluoride ions in groundwater can be increased as a result of precipitation of CaCO<sub>3</sub> at high pH, which removes Ca<sup>2+</sup> from solution allowing more fluorite to dissolve (Alamry, 2009; Gaikwad, 2012). As the average pH during premonsoon are 7.17 as compared to the 7.99 during the postmonsoon (Table.1). These released Ca<sup>2+</sup> ions combine with CO<sub>3</sub><sup>2-</sup> ions to further enhance the precipitation of CaCO<sub>3</sub>. During postmonsoon season fluorite undersaturation in groundwater of area under study might be due to the calcite saturation, preventing it by reducing calcium activity and allowing more fluorite to dissolve thereby increasing the F/ Ca ratio of solution (Alamry, 2009).

### Acknowledgements

SKG acknowledge Head, Department of Geology, University of Pune for the permission to carry out geochemical analysis and for publishing of this manuscript.

### References

- Alamry A.S., (2009), Study about the Fluorosis in Selected Villages of Taiz Governorate, Final Draft Mission Report prepared for NWRA, Yema, pp71.
- APHA., (1998), Standard methods for the examination of water and wastewater. (American Public Health Association), Washington DC, 20th edn.
- Gaikwad S K., (2012), Geochemistry of Fluoride Bearing Ground Waters from the Karli River Basin, Southern part of Sindhudurg District, Maharashtra. Unpubl. Ph.D. thesis, University of Pune, India.
- G.S.I., (2001), Geological Resource Map of Sindhudurg District.

Handa B K., (1975), Geochemistry and genesis of fluoride containing groundwaters in India, Ground Water, Vol. 13, 275-281.

India Meteorological Department (1974), Climate of Raigad district, In Climate of Maharashtra, pp 57–63.

Kundu N., Panigrahi M K., Tripathy S., Munshi S., Powell M A., Hart B R., (2001), Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa, India, Environmental Geology, Vol. 41, 451-460.

Matthess G., (1982), The properties of groundwater, John Wiley& Sons, New York.

Parkhurst D L and Appelo C A J., (1999), User's Guide to PHREEQC (Version 2) – A computer 576 program for speciation, batch reaction, one-dimensional transport, and inverse 577 geochemical calculations. U.S.G.S. Water Resources Investigations Report, 99-4259, 578, U.S.G.S, Denver, USA.

Pawar N J., Nagpal U., Phanaskar D. B., Phadke A V., and Soman G R., (1989), Manual of geochemistry techniques. Department of geology, University of Pune, India, pp 56.

Sarkar P K., (1986), Geology of the area around Katta, Sindhudurg District of Maharashtra, India. Unpubl. Ph.D. thesis, University of Pune, India, pp 243.