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Journals, Poland, Directory of Research Journals

International Journal of Earth Sciences and Engineering

www.cafetinnova.org

ISSN 0974-5904, Volume 09, No. 05

October 2016, P.P.1947-1951

Anomalously High Fluoride Content in Groundwater from Basalt Aquifer: A Case Study from Kakalghar, Maharashtra, India

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Abstract: Groundwater occurring in basalt aquifer, in general, contains fluoride content within the limit drinking water standard prescribed by the World Health Organization. In addition, groundwater in aquifers located in high rain fall regions also contains low content of fluoride. On the contrary, groundwater occurring in basalt aquifer in Kakalghar, located within the Deccan volcanic province, that receives > 3000 mm of rain has registered > 3 ppm of fluoride. This case is similar to Karbi-Anglom district of Assam that receives > 3000 mm of rain, where the alluvial aquifer contains > 15 ppm of fluoride. Children drinking this water are suffering from dental fluorosis and adults have developed kidney stones. In this paper we analyze the causes for high fluoride in groundwater in basalt aquifer. This study demonstrates that water quality and aquifer characteristics should be assessed thoroughly before the communities are supplies drinking water under rural water management programme.

Keywords: *Fluorosis, Kidney stone, Kakalghar, Deccan Traps, Basalt aquifer, xenoliths*

1. Introduction

High fluoride content in groundwater is very common in arid and semi-arid parts of India [1] and nearly 62 million people in India drink high fluoride groundwater, with fluoride content varying between 1 to 20 ppm and hence are prone to dental and skeletal fluorosis [2,3]. Fluorine exists in a variety of rocks and minerals and can enter groundwater due to water-rock interaction processes. Nearly 70% of rural world population suffering from fluorosis depends on groundwater. According to WHO [4] guidelines, in areas with warm climate, the optimal fluoride concentration in drinking water should be below 1 ppm, while in cooler climatic regions it could be up to 1.2 ppm. Since the threshold limit of fluoride to cause dental fluorosis is 1.5 ppm, WHO sets the upper limit of fluoride in drinking water at 1.5 ppm. However this guideline is not universal. For example in India this value is set at 1 ppm [4]. Fluorosis in India is much more severe than arsenic poisoning in west Bengal. According to recent statistics the number of people subjected to arsenic poisoning in India is 38 million and confined to West Bengal [**5]** and comparatively far less than those affected by fluorosis. While the source of arsenic in west Bengal is not well understood [6,7] the source of fluoride is well defined and is geogenic. The distribution of fluorosis in India is shown in figure 1.

In general, groundwater in regions with high rainfall, such as Assam, western parts of Karnataka and coastal Konkan regions contain < 1.5 ppm of fluoride. The Karbi-Anglong district in Assam, that receives ~ 2000 mm of rain annually and falling under less endemic state (Figure 1), recorded > 15 ppm of fluoride [8] that is far above the prescribed value (1.5 ppm) for drinking water [4]. Several cases of dental and skeletal fluorosis have been reported from the above two districts of Assam (Fig. 2 a & b). In Assam, the high fluoride groundwater occurs in deeper, granite aquifers while the groundwater occurring in shallow alluvial aquifer contains < 1.5 ppm of fluoride [8].

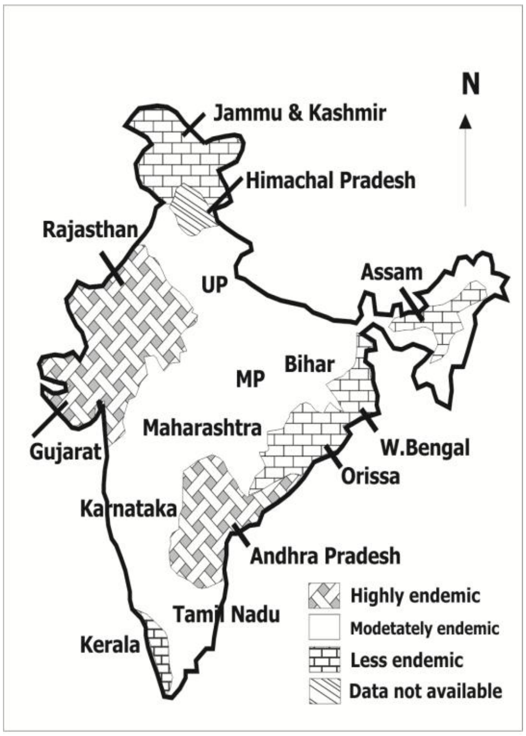

Figure 1 *Status of fluorosis in India (modified after [2]).*

Figure 2 *Incidence of a) skeletal and b) dental fluorosis in men and children, Assam [8]*

During regular surveillance of groundwater samples in India, a similar case was discovered along the west coast of India, where the groundwater drawn from bore-wells drilled into basalt aquifer recorded > 3 ppm fluoride. This region too receives > 3000 mm of rain. It is unusual to find groundwater occurring in basalt aquifer with high fluoride content (above drinking water permissible limit) and a large population, especially children of age 5 to 15, suffer from dental fluorosis and in certain cases incidence of kidney stone in adults is recorded. Groundwater occurring in basalt aquifers generally contain fluoride concentration below 1 ppm [9,10,11] and never posed any health related issues like dental and skeletal fluorosis. This paper focuses on the reasons for high fluoride content in groundwater in basalt aquifer and suggests mitigating measures to safeguard the health of the rural population, especially children of this region.

2. Description of the field area

Kakalghar (18° 30'N72° 57'E), a small village, located south of Mumbai, along the west coast of India (Fig. 3), has a population of 518 (2011 census) with 255 females. 8.5 % of this population is children < 6 years age group. Agriculture is the main activity that supports the families. The local populations depend on groundwater, drawn from open dug wells and bore wells, for domestic and agricultural purposes. The open dug wells are shallow with water table occurring at about 1-10 m depth. The bore wells penetrate the basalt hard rock aquifer from depth of about 200 to 300 m (Fig.4). The groundwater level in the open dug wells reaches near surface level (fig. 4) during monsoon season (June-August) and during the non-monsoon season the dug wells nearly go dry due to steep drop in the water level in the top basalt aquifer while the bore wells provide continuous supply of groundwater.

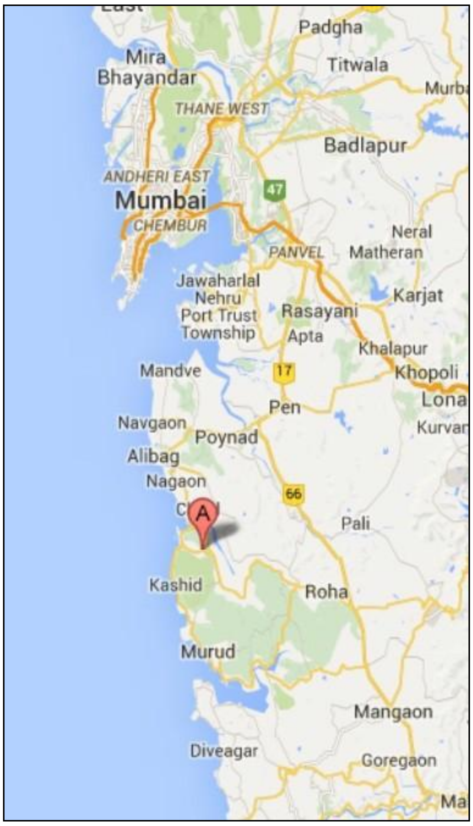

Figure 3 *Google Map showing the study area, south of Mumbai. Kakalghar location is indicted (A: 18° 30'N72° 57'E).*

Figure 4 *Open dug well (top) and bore well (bottom) in Kakalghar*

3. Hydrogeology

The study area falls within the Deccan volcanic terrain that consists of basalt flows. Groundwater occurs in the vesicles and fractures of the basalt aquifer. These flows often are covered by thick 2 to 5 meters weathered horizon. This weathered horizon acts as the top unconfined aquifer while the fractured and vesicular basalt flows constitutes the hard rock aquifer. The top weathered and the hard rock aquifers are separated by a layer of clay that separates these two aquifers. These two aquifers may have hydraulic connection that may cause flow of water from the top unconfined aquifer to the hard rock aquifer. Dug wells tap the top unconfined weathered aquifer while the bore wells tap the deeper hard rock aquifer. A schematic diagram showing these two aquifers in the study area is shown in figure 5.

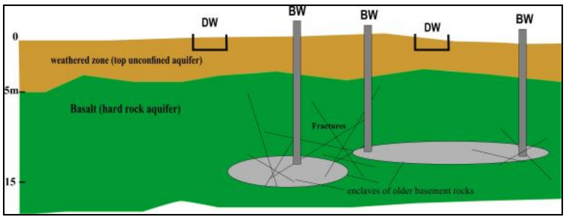

Figure 5.*Schematic diagram showing the two aquifers in Kakalghar. The grey patches indicate large enclaves of older basement rocks emplaced in the basalt flows.*

The basalt flows enclose large xenoliths of older basement crustal rocks. These rocks include granulites, pyroxinites, lamprophyres and diorites. All these rocks contain mica group of minerals (e.g muscovite, phlogophite and biotite) and accessory minerals like apatite ($Ca_5(PO_4)_3$ (F,Cl,OH)), fluorite (CaF_2) and zircon ($ZrSiO_4$). The phlogophite ($KMg_3(AlSi_3O_{10})(F,OH)_2$) contains 7200 ppm of fluorine [12,13] while apatite contains 1000 to 8000 ppm of fluorine. At some places, these xenoliths outcrop over the surface.

4. Hydrogeochemistry

The chemical composition of groundwater samples collected from dug wells, bore wells and stream are shown in Table 1.

On the Piper [14] tri linier diagram, the water samples fall in two distinct fields (Fig.6). The shallow dug wells and the stream waters typically are Ca-HCO_3 rich while the bore well waters are typically Na-HCO_3 and Na-SO_4.

Table 1 *Chemical data of water samples (ppm) from Kakalghar: Post monsoon (post: Oct 2014) and Pre monsoon (pre; May 2015) periods*

S.No	pH	ond µS/cm	Na (ppm)	K	Ca	Mg	Cl	HCO_3	SO_4	F	
BW1	9.6	278.8	59.8	0.3	1.9	0.2	19.5	110.0	66.2	3.5	Post
	8.9	294.0	66.0	0.2	1.2	0.1	30.0	120.0	8.9	3.6	Pre
BW2	9.7	455.0	89.1	0.4	2.0	0.0	90.0	65.0	333.6	3.9	Post
	9.9	488.0	99.0	0.6	1.9	0.2	30.0	85.0	36.9	3.5	Pre
BW3	9.6	8.6	81.2	0.4	1.6	0.1	60.0	80.0	276.4	5.2	Post
	10.0	436.0	89.0	0.6	1.7	0.3	85.0	25.0	29.0	4.7	Pre
DW1	6.8	241.0	11.0	0.3	27.1	11.0	25.0	125.0	13.2	0.1	Post
	8.2	257.0	11.0	0.9	34.0	9.9	30.0	190.0	433.0	0.1	Pre
DW2	7.4	363.0	12.2	0.6	49.8	14.8	15.0	195.0	37.4	0.1	Post
	7.9	366.0	13.0	0.6	51.0	19.8	25.0	150.0	7.9	0.1	Pre
Stream	7.8	141.7	7.4	0.2	13.1	5.9	5.0	65.0	14.5	0.1	Post
	7.3	169.0	8.5	0.5	18.3	8.4	15.0	100.0	1.2	0.1	Pre

The Ca-HCO_3 water is typical of basalt aquifers [15] and hence the dug wells located in the zone of weathering of basalts are of this type (Fig 6). However, the bore wells although located within the basalts, show composition entirely different from the dug well and fall in the $NaHCO_3$ and $NaSO_4$ fields. Two samples, especially (BW2 and BW3, samples 2 and 3 in figure 6) record very high SO_4 values over HCO_3, that is unusual for groundwater in basalt aquifers. Seasonal change has no influence on the chemical signature of the ground waters (Table 1). The fluoride content in the bore well samples do not show any correlation with the Ca or SO_4 (Table 1) indicating different sources for these two ions.

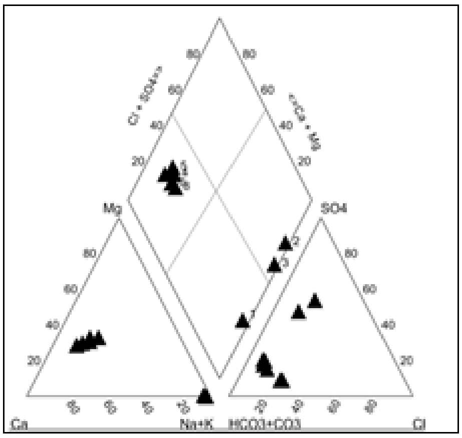

Figure 6.*Piper [14] diagram showing the chemical signatures of groundwater and surface samples.*

From the Table 1 it is apparent that the dug wells and the stream provide water with the dissolved chemical constituents within the limits prescribed by [4] for drinking water, while the bore wells, drilled into the basalts, contain large amount of fluoride that is far above the limit of 1.5 mg/l prescribed by [4] for drinking water. Thus it is interesting to note that dug wells drawing water from basalts has low fluoride while bore wells drawing water from basalts from deeper depths has higher concentration of fluoride.

5. Bore wells and dental fluorosis

The shallow dug wells (Figs. 4 and 5) dry up during summer (April-July) due to fall in the water table levels. The population is water stressed during these four months. In order to ease the drinking water problem to the local population, the local government (known as Panchayat) drilled bore wells to tap the hard rock basalt aquifers. This project was a great success as bore wells are able to provide constant supply of water for domestic purpose throughout the year. However, the water quality was never tested by the local government officials as groundwater in basalt aquifers in general is of good quality and do not pose any severe health problems. Over a period of 5 years, after the bore wells started meeting the domestic water demand, it was noticed by a dental surgeon (Dr Ulhas Wag) during his routine rural health checkup, that the children are having discolored teeth. On closer examination more and more cases of dental fluorosis, emerged as shown in figure 7.

6. Fluoride content, fluorosis and kidney stone

The fluoride concentration in the bore well water samples is higher than that in shallow dug wells and stream, and varies from 3.5 to 4.7 mg/l (Table 1) and is far above the limit of 1.5 ppm prescribed for drinking water by [4]. The sulphate content as well as fluoride content makes the bore well waters distinct from other waters. These bore wells were drilled in 1996, and those children born after 1996 and consuming bore well water are affected by fluorosis. With the help of a local social organization, more than 25 children were examined for fluorosis. Discoloration, irregular teeth growth and gum liaison are typically seen in the children (Fig. 7). Fluorosis is not prevalent in adults. However, incidence of kidney stone is reported in one case. The kidney stone from a male (54 yrs), drinking the bore well water since 1996, recovered and analyzed using x-ray diffraction technique and the result is shown in figure 8. The data shows that the kidney stone is whewellite (Ca $C_2O_4.H_2O$), a calcium oxalate (organic) compound that accumulates in kidneys in adults drinking fluoride rich water [16,17,18].

7. Source and mobilization fluorine

The fluorine is present in apatites and phlogophite occurring in the xenoliths described above. When these xenoliths weather, fluorine is easily mobilize into the percolating groundwater recharging the hard rock aquifers. A schematic diagram showing the position of the bore wells tapping fluoride rich water is shown in figure 9.

Figure 7.*Dental fluorosis and growth deformation of teeth in young girls of Kakalghar (Photo by D.Chandrasekharam)*

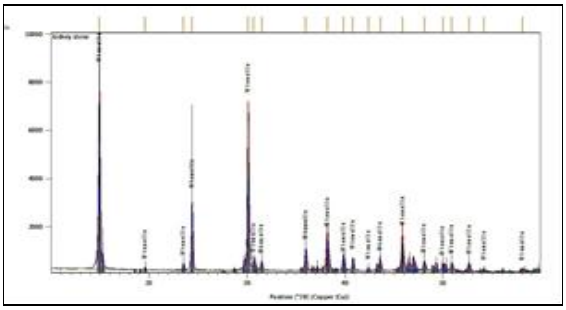

Figure 8 *X-ray diffractograph of kidney stone (whewellite)*

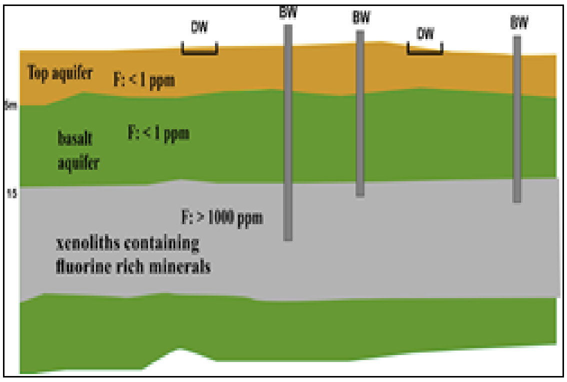

Figure 9.*Schematic cross section showing the position of bore wells drawing high fluoride groundwater*

As there is no correlation between fluoride and Ca in the bore well samples, it is apparent that the Ca and fluorine are supplied from different sources; Ca from the plagioclases in the basalts and fluorine from the xenoliths. The bore wells are also used for washing clothes by the local communities. The SO_4 enrichment in the bore well perhaps may be due to contamination from the detergents.

8. Discussion

It is well known that groundwater occurring in granite aquifers contain high concentration of fluoride [2]. A common problem in all the fluoride endemic states shown in figure 1 is that, groundwater is drawn from granite aquifer that contain fluorine rich minerals listed in section 3. In Kakalghar only bore wells tapping the fluorine rich hard rocks (rocks of granitic composition) have the problem of high fluoride content. To mitigate this problem, bore wells should be drilled into basalts instead of the xenoliths shown in figure 9. Geophysical investigation can locate zones free from such xenoliths. Alternately, streams can be impounded to create storage tanks to store water for the inhabitants. Both fluorosis in children and formation of kidney stones in adults can be mitigated. Such cases appear to be common in Deccan volcanic province where bore wells drilled into basalt flows tap granite hard rock aquifer with high fluoride content [19]. Similar situation must be prevailing in several regions of the world (e.g. east African countries like Tanzania) where groundwater is drawn from granite aquifers located below the basalt flows.

Acknowledgements

This work form a part of M. Sc thesis by C Behra. We thank the Director, IITB for supporting this work. Thanks are due to the head of "Anganwadi" of Kakalghar who helped the team during the sampling campaign. Thanks are due to Dr. Chandrasekhar Azad and Dr Hemant Singh for taking photographs. The authors thank Prof L. Elango, Prof N J Pawar and Dr Gayen for their constructive comments and Prof D V Reddy for his encouragement during the course of this work.

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