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Geochemical Assessment and Impact of Fluoride Contents in Groundwater of Selected Area of Mayurbhanj District, Odisha, India

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Groundwater quality of a remote and relatively unnoticed area of Mayurbhanj district, Odisha with special reference to fluoride contamination was reported. Groundwater of three villages of Kusumbandh panchayet showed fluoride concentration above permissible limit. Most of the people of different age group in theses villages are found affected due to regular consumption of fluoride contaminated water. The fluoride concentration in the groundwater showed positive correlation with Na^+ and negative correlation with Ca^{2+} and total hardness. Analyses of rock sample of the affected area by XRF, XRD and FT-IR revealed that the presence of fluorapatite is the most likely reason for fluoride contamination. Since groundwater is only source for drinking and domestic uses, remedial measures is necessary in the study area.

Keywords: Fluoride contamination, Dental and skeletal fluorosis, Granite rock, Groundwater.

INTRODUCTION

Fluoride is a natural component of the earth crust and occurs in almost all waters at varying levels [1]. Fluoride in groundwater is mostly of geogenic origin arising from the weathering and subsequent leaching of different fluoride-bearing minerals *viz*. fluorite, apatite, mica, amphiboles, certain clays and villiamite present in rocks and soils [2,3]. The concentration of fluoride in groundwater is a function of several factors such as the climate of the area, chemistry of water and the presence of accessory minerals in the rocks/soils through which groundwater is circulating. In addition, the anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes generated by thermal power plants, rubber, fertilizer and semiconductor manufacturing, glass and ceramic production and electroplating industries also contribute to fluoride ions in groundwater.

Depending on the concentration and duration of continuous uptake, fluoride in drinking water can be beneficial or detrimental to mankind [4,5]. At concentrations below (< 0.6 mg/L) fluoride is known to prevent dental carries and essential for mineralization of hard tissues. On the other hand, the uptake of higher concentrations of fluoride has injurious effects in human beings. These effects are mostly found in hard tissues and most common ones are mottling of teeth in mild cases, dental and skeletal fluorosis in severe cases. Advanced skeletal fluorosis may result in crippling fluorosis, which is the most severe type whereby victims face restricted mobility. Fluoride is also known to attack soft tissues and can lead to non-skeletal fluorosis. As the main source of fluoride uptake in human body is through drinking and cooking waters, the maximum permissible limit for fluoride in drinking water are set by each country depending partly on its economic and technological powers [4,5]. The WHO recommended the optimal fluoride concentration in drinking water should remain below 1 mg/L in the areas with a warm climate, while in cold climates it could go up to 1.2 mg/L.

India is among 23 nations in the world, where fluorosis is found to be prevalent. It had been estimated that more than 66 million people in 19 states of India are affected with different forms of fluorosis, which include dental and skeletal fluorosis [6]. A number of fluoride effected cases have been reported [7-13] mostly from the granite and gneissic complex of different states such as Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Odisha, Rajasthan and Tamil Nadu. As per latest available data, 27 out of the 30 districts in Odisha have higher concentrations of fluoride; as a result the state is in the high endemic category [13-15]. Groundwater of four blocks in Mayurbhanj district namely Udala, Saraskana, Kaptipada, Khunta are reported to

be affected with fluoride contamination out of total 26 blocks [13]. Due to geochemical reason and over withdrawal of ground water more and more areas in Orissa are coming under fluoride threat.

Keeping the above in view, the present study aims to assess the fluoride content groundwater of relatively unnoticed small area, Kusumbandh panchayet of Bangriposhi block, Mayurbhanj district, Odisha with special reference to the probable geochemical reason and impact due to consumption of fluoride contaminated water. To our best of knowledge, this is the first in-depth report of fluoride contamination in the area under study.

EXPERIMENTAL

Ground water samples were collected from 10 villages, at least two samples each from dug wells and hand pumps, during May 2009-June 2012. The samples were collected in pre-cleaned sterilized bottles and stored in an icebox. The common physical (EC and pH) and chemical (total dissolved solid, total alkalinity and total hardness) parameters were measured by standard methods [16]. Electrical conductivity and pH were measured using conductivity and pH meters (Systronics). Total dissolved solid was estimated by ionic calculation method. Total alkalinity, CO_3 and HCO_3 were estimated by titrating with HCl. Total hardness and Ca^{2+} were analyzed titrimetrically using standard EDTA. Na^+ and K^+ were measured by flame photometer. Fluoride was estimated spectrophotometrically using SPADN reagent. In case of some selective water samples, analyses of different anions along with fluoride was carried out by ion chromatograph available at CSIR-National Metallurgical Laboratory, Jamshedpur. AR grade chemicals/reagents were used throughout the study without further purification. The reagents and calibration standards were prepared in deionized distilled water. All the experiments were carried out at least in duplicate and the average values were presented. The results were reproducible within ± 3 % error limit.

A few rock samples, collected from the most affected village (Kurkutia), were grounded to powder. In one case the hydrous mineral-apatite-rich portions were hand-picked and powdered. The powdered sample was analyzed by X-ray fluorescence (Phillips, Axios 4 kW) available at Neelachal Ispat Nigam Ltd., Odisha. Powder XRD patterns were recorded on a Rigaku Miniflex X-ray diffractometer using CuK_α radiation. FT-IR spectra in KBr phase was taken using a Shimadzu (IR Affinity 1) FT-IR spectrophotometer with a nominal resolution of 2 to 4 cm^{-1} and averaging at least 44 scans to improve signal to noise ratio.

Frequent visits were made during May 2009 to July 2011 to the study area in order to collect the information with regard to impact on consumption of fluoride excess water and alternative water source provided in the affected areas. Photographs of affected people were also taken at regular intervals.

RESULTS AND DISCUSSION

The study area, located in the Bangriposhi block is about 45 km away from district headquarters of Mayurbhanj district Baripada with a pollution free climate where the average temperature varies in the range 10-40 °C. Rainfall is the main source of groundwater recharge in the study area.

The dug well and tube well are the major source of water for drinking and other house hold purposes. The depth of water ranges from 30 to 45 m below the ground surface. The depth of dug wells ranges from 30 to 45 ft while the maximum depth of the hand pump for drinking water use is about 160 ft below the ground level. The area around Bangriposi block belongs to a Precambrian terrain in Eastern India where the major rock-type is granite (commonly known as Mayurbhanj granite) [17] with subordinate phyllitic rocks, which is generally overlain by brownish to reddish soil. Usually the granite has a granophyric texture and consists mainly of feldspars, quartz, biotite and hornblende. The accessory minerals are apatite, magnetite, epidote, sphene and zircon, *etc*. The content of biotite and hornblende are so significant that these granophyric granites are classified in geological literature as biotite-granites or hornblende-biotite granites [17]. Therefore, it is quite obvious that apart from apatite, the occurrence of biotite-mica and hornblende, which are quite susceptible to weathering in a tropical climate might have contributed towards the fluoride content of the surface and ground waters.

The results of chemical analyses of the groundwater samples are presented in Tables 1 and 2. The pH values of groundwater in the study area are well within the expected pH values of natural water (5.79-8.32) and permissible limit (6.5-8.5) as per guidelines of WHO/BIS.

In general, the alkaline condition favours the solubility of fluorine-bearing minerals, which in turn increases the fluoride content in ground water. In acidic pH, fluoride is

TABLE-1
ANALYTICAL RESULTS* ON SELECTED PARAMETERS OF GROUNDWATER SAMPLES COLLECTED FROM KUSUMBANDH PANCHAYET

S. No.	Location	pH	EC (µS/cm)	TDS	Ca^{2+} (mg/L)	TH as $CaCO_3$	F^- (mg/L)	Na^+ (mg/L)
1	Asanbani	7.14 (6.98)	1234 (919)	682 (508)	89 (87)	362 (337)	0.47 (0.51)	57 (69)
2	Asansikhar	7.81 (7.41)	898 (867)	496 (479)	69 (73)	312 (328)	1.95 (1.89)	148 (1.43)
3	Basantpur	6.78 (6.85)	1191 (1326)	658 (733)	108 (97)	382 (420)	0.31 (0.45)	48 (56)
4	Gadrasahi	8.32 (7.87)	1094 (987)	604 (545)	57 (71)	282 (317)	2.71 (2.45)	149 (139)
5	Hizli	7.17 (6.98)	986 (934)	545 (516)	95 (89)	387 (364)	0.51 (043)	67 (75)
6	Jua	7.03 (7.13)	1078 (1121)	596 (619)	102 (98)	395 (334)	0.38 (043)	51 (58)
7	Kusumbandh	7.45 (7.23)	1201 (1298)	664 (717)	101 (107)	375 (407)	1.01 (0.95)	88 (98)
8	Kurkutia	8.04 (7.75)	1283 (1000)	709 (552)	54 (66)	265 (305)	2.78 (2.35)	167 (145)
9	Labania	7.57 (7.46)	879 (934)	486 (516)	81 (85)	328 (351)	1.01 (0.84)	103 (98)
10	Rangamatia	7.71 (7.47)	786 (843)	434 (466)	6 9 (78)	312 (335)	1.54 (1.46)	123 (127)

*Values presented in parentheses represent the results of tube well water while others represent for water sample collected from dug well.

TABLE-2
LOWEST AND HIGHEST ANALYTICAL VALUES OF HIGH FLUORIDE CONTAINING GROUNDWATER SAMPLES (6 TO 8 SAMPLES WERE COLLECTED FROM EACH VILLAGE)

Parameters	Asansikhar	Gadrasahi	Kurkutia
pH	7.36-7.89	7.29-8.38	7.66-8.19
EC (μS/cm)	767-904	817-1320	843-1280
Ca (mg/L)	67-91	47-76	45-68
TH as $CaCO_3$	286-336	201-326	248-322
Na (mg/L)	136-156	128-166	136-156
F^- (mg/L)	1.54-2.04	2.08-2.84	1.96-2.88
Cl^- (mg/L)	25-44	28-61	35-68
NO_3^- (mg/L)	9.1-15.3	11.1-16.5	10.5 -14.7
Br^- (mg/L)	1.62-1.82	0. 82-0.89	0.68-1.32
PO_4^{3-} (mg/L)	1.02-1.21	1.31-1.38	1.28 -1.46

adsorbed in clay while the alkaline medium favours the desorption of fluoride from fluoride bearing minerals, presumably due to favourable displacement of fluoride ion by hydroxyl ion [3,18,19]. The positive correlation of pH with fluoride suggests that pH is important in determining fluoride in ground water in agreement with earlier observations [9]. The EC, an index to represent the total concentration of soluble salts in water, is found to be less than 1000 μS/cm in about 50 % of the collected samples. Total dissolved solids, a salinity indicator for the classification of groundwater, varies from 434-733 mg/L in the study area and nearly 80 % samples show TDS values above the permissible limit (500 mg/L).

Calcium concentration is found in the range 54-108 mg/L in which about 55 % of the water sample are above permissible value (75 mg/L) of WHO/BIS. Except at two locations, sodium concentration was higher than the WHO's acceptable limit of 50 mg/L. Fluoride concentration in the groundwater samples varies in the range 0.31 to 2.78 mg/L (Table-1) indicating 40 % of the collected samples are having higher fluoride content than the maximum permissible limit (1.5 mg/L). It has been reported previously that elevated fluoride in the ground water is generally associated with relatively lower Ca^{2+} and higher Na^+ contents. It is also evident in this case that the concentration of fluoride is more for ground water samples with lower Ca^{2+} and higher Na^+ contents. A strong negative correlation between Ca^{2+} and F^- in the ground waters, required for the solubility of fluoride minerals, has also been observed earlier [7,20]. The dissolution of fluoride is often suppressed when the concentration of Ca^{2+} is above the limit of fluoride solubility due to the common ion effect. On the other hand, high concentration of Na^+ generally increases the solubility of fluoride-bearing minerals in the waters. More analytical results including ion chromatographic data of ground water samples, collected from three most affected villages, are presented in Table-2. Fluoride content (>1.5 mg/L) is found mainly in three villages namely Asansikhar, Gadrasahi and Kurkutia out of ten villages in Kusumbandh panchayet. The highest fluoride concentration (2.78 mg/L) is recorded from a dug well in Kurkutia village. Regular consumption of ground water due to want of safe drinking water supply, more and more people of these three villages in different age groups is getting affected with fluoride contamination. In the fluoride-affected villages, both children and adults suffer from health disorders like mottling of teeth, deformation of ligaments, bending of spinal column and ageing problem. In the rest of village, there is no noticeable impact of fluoride till date.

Since there is no anthropogenic source of fluoride pollution in the study area, the fluoride contamination is most likely from natural process, which involves the leaching of fluorine-bearing minerals. As such, selected part of the rock samples collected from the most affected area was subjected to XRF, XRD and FT-IR spectral analyses. The XRF analysis (Table-3) shows that the component of fluorapatite (like Ca^{2+} and P) are relatively higher compared to other rock sample indicating the presence of this minerals in the rock samples. Powder XRD pattern of the same sample is presented in Fig. 1, which shows the majority characteristic peaks of fluorapatite (JCPDS 15-876) and also matches well with the XRD pattern presented earlier for fluorapatite containing rock sample [3]. The presence of chemical constituents of apatite in the rock sample is further evident from the FT-IR spectra (Fig. 2).

The broad absorption bands at about 3450 cm^{-1} and moderately intense band at about 1650 cm^{-1} are attributed to

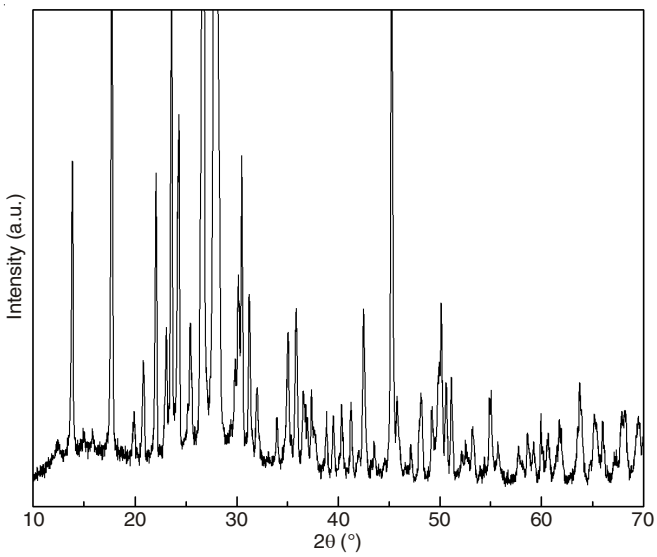

Fig. 1. Powder XRD of selected portion of rock sample

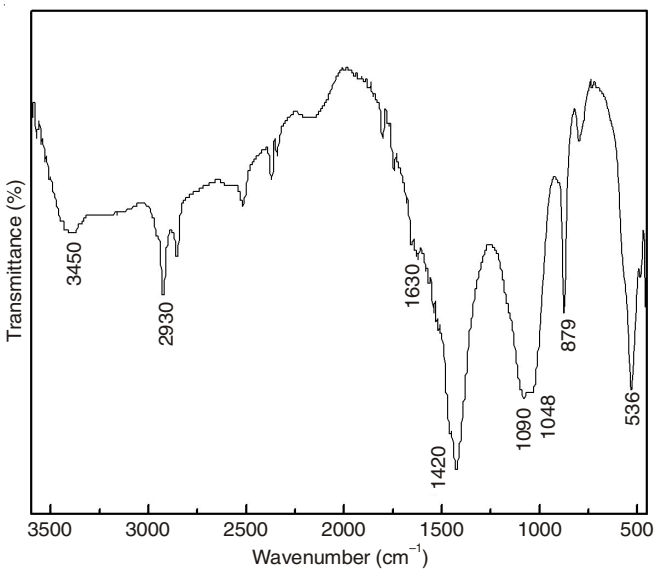

Fig. 2. FT-IR of selected portion of rock sample in KBr phase

TABLE-3
ANALYTICAL RESULTS OF SELECTED
PORTION OF COLLECTED SAMPLE BY XRF*

Constituents	wt. %	Constituents	wt. %
Na_2O	0.074	Cr_2O_3	0.287
MgO	1.613	MnO	0.335
Al_2O_3	1.451	Fe_2O_3	4.602
SiO_2	61.169	ZnO	0.05
P_2O_5	1.736	SrO	0.019
K_2O	0.576	ZrO_2	0.120
CaO	16.335	BaO	0.083
TiO_2	0.267	Cl	0.042

*The wt. % of different constituents present is expressed as oxides but they may be present in other forms.

O-H stretching and bending modes of vibrations, respectively [21]. Bands at 1090, 1048 and 539 cm^{-1} may be attributed to the existence of PO_4^{3-} group while those appeared at 1450 and 879 cm^{-1} are attributed to ν(C-O) and δ(OCO) modes of CO_3^{2-} group substituted partially for phosphate group of fluorapatite.

Conclusion

The present study showed that the groundwater quality with respect to fluoride concentration in the Kusumbandh panchayet of Bagriposhi block, Mayurbhanj varies in the range 0.31 to 2.88 mg/L. Relatively high fluoride concentration was found in about 32 % ground water samples comprising of three villages of Kusumbandh panchayet. Due to ingestion of fluoride contaminated water, the people of these villages are affected with dental and skeletal fluorosis. Fluoride concentrations in the groundwater of other villages are found within permissible range. Powder XRD and FT-IR study of rock sample collected from the study area, revealed that fluorapatite is most likely releases fluoride ion into the groundwater of the study area. Development of a simple and easy fluoride removal technique using locally available minerals as adsorbent can solve the problem to a great extent.

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