High Fluoride in the Ground Water in Parts of Khurda and Nayagarh District of Odisha

Laxmidhar Panda*, Dr. B.B. Kar**
Research Scholar, Professor (Chemistry)**,
School of Applied Sciences ,KIIT University, Bhubaneswar, Odisha, India

***Abstract*:- Fluoride contamination of ground water is global phenomenon. In India nearly half of the states are affected by the fluoride contamination of ground water and in Odisha nearly 20 states of the 30 districts and nearly 4 million people are affected by the menace of fluorosis ,which is characterized by deformed body with bending of legs, mottling of teeth along with ageing problems. One of the most affected and publicized area in the state which has drawn worldwide attention for fluorosis menace is the area comprising parts of Begunia and Bolagarh blocks of Khurda District and Bhapur Block of Nayagarh District. In view of the importance of the burning problem and it veracity of its impact on the local people we have chosen this particular area and the subject for our study. Water samples were collected from the affected area and these are analyzed for fluoride and other chemical parameters. Attempt has been made to correlate the occurrence of high fluoride in ground water of the area to local conditions including the geochemical source of fluoride in ground water.**

Keywords: Fluoride, Fluorosis, Ground Water, Leachability. Anthropogenic, Geogenic.

I. INTRODUCTION

Fluoride accounts for about 0.06 to 0.09% of the earth's crust. Fluoride bearing rocks are abundant in India. It is the leaching of fluoride from these fluoride containing rocks that is mainly responsible for contamination of the adjacent ground water and soil resources. Depending upon its source of origin, the cause of fluoride contamination can be anthropogenic or geogenic. When fluoride contamination is caused by human activities, it is referred to as anthropogenic pollution whereas significant presence of the fluoride in water, soil and air is by natural means is referred to as geogenic fluoride pollution [1].

The concentration of fluoride in drinking water depends mainly on the basic chemical composition of soil, the time of contact between the source of minerals and the water source, leaching of fluoride from rocks, calcium-poor aquifers, volcanic rocks, granite rocks and the amount of water withdrawn from the source over a period of time. Generally, surface water has lower fluoride content in comparison to ground water. River water near industries/mines like bauxite, graphite, aluminum, phosphate and fertilizer does contain some fluoride. But ground water is the single biggest contributing factor for the spread of fluoride and fluorosis. Fluoride occurs in soil in the form of minerals such as biotitic, muscovite and hornblende etc. which usually originate from micas, apatite and tourmaline. The fluoride content of soil is largely dependent on the mineralogical composition of the soil, inorganic fraction and the extent of clay and pH [1].

II. SAFE LIMIT OF FLUORIDE

Water is the major source of fluoride contamination. According to the 1984 guidelines published by the World Health Organization (WHO) ,the permissible upper limit for fluoride in drinking water is set at 1.5 mg/l. The WHO guideline value for water is not universal. In India, for instance, the permissible upper limit was lowered from 1.5 ppm to 1.0 ppm in 1998.Scientists working on issues related to fluoride in India have made a strong case for the lowering of the upper limit for fluoride to at least 1 ppm, since there is enough evidence to prove that constant exposure to fluoride even at the level of 0.7 mg/l could lead to fluorosis and other allied diseases. At concentrations of above 1 mg/l, fluoride in drinking water can be positively dangerous to human health and lead to dental and skeletal fluorosis, a disease that can cause mottling of the teeth, calcification of ligaments, crippling bone deformities and many other physiological disorders that might ultimately result in death. According to UNICEF, fluorosis is endemic in at least 25 countries around the world with India, China and Africa being the countries with the highest prevalence rates. The most disturbing fact about fluorosis is that it has no cure so far and prevention is thus the only means of controlling the disease. Developing effective and inexpensive techniques for the removal of fluoride in groundwater is a major challenge the world over [1]. The present study aims at finding the causes of fluoride contamination in the ground water of the affected area with due acknowledgement of the works of previous researchers on the mater.

III. DESCRIPTION OF THE STUDY AREA

The area came into lime light when the people of Balasinghpur were affected by a mysterious disease way back in 1987-88 and some even died of the dreaded disease. Later on it was established that that disease is nothing but fluorosis .Analysis of the ground water by some State Government Agencies then revealed that fluoride level in the water in the village tube wells was 3.18 mg/l while it was as high as 7.10 mg/l and 10.55 mg/l in the water in the open wells and ponds. Hundreds of people have died of fluorosis since then. The dreaded disease has resulted in drastic fall in their productivity. Fluorosis not only has affected the human population who are suffering from swelling of the joints, general weakness and premature death but also the cattle that are found to have lesser ability to procreate and to give milk. Agricultural fields have also not been spared by the menace [1] .

The area under study covers from 20°N to 20° 23'N latitude and 85° 12'E to 85° 32'E longitude .This area forms a part of the Eastern Ghats super group of rocks and the major rock types of the area being granite gneiss, charnockites and its derivatives. Recent alluvial soil cover dominates rest of the area[2].Agriculture is the main stay of the people of the area and due to the non-existence of major river and also due to not so abundant rain fall people of area are dependent upon ground water. They usually dig wells of low deep (shallow dug wells) on their own costs and use the water from such shallow wells for drinking, feeding their domestic animals and also for agriculture. Abnormal levels of fluoride are supposed to be present in fractured hard rock zone composed mainly of minerals like flourappatite, fluorite, and replaceable hydroxyl ion in ferromagnesian silicates.

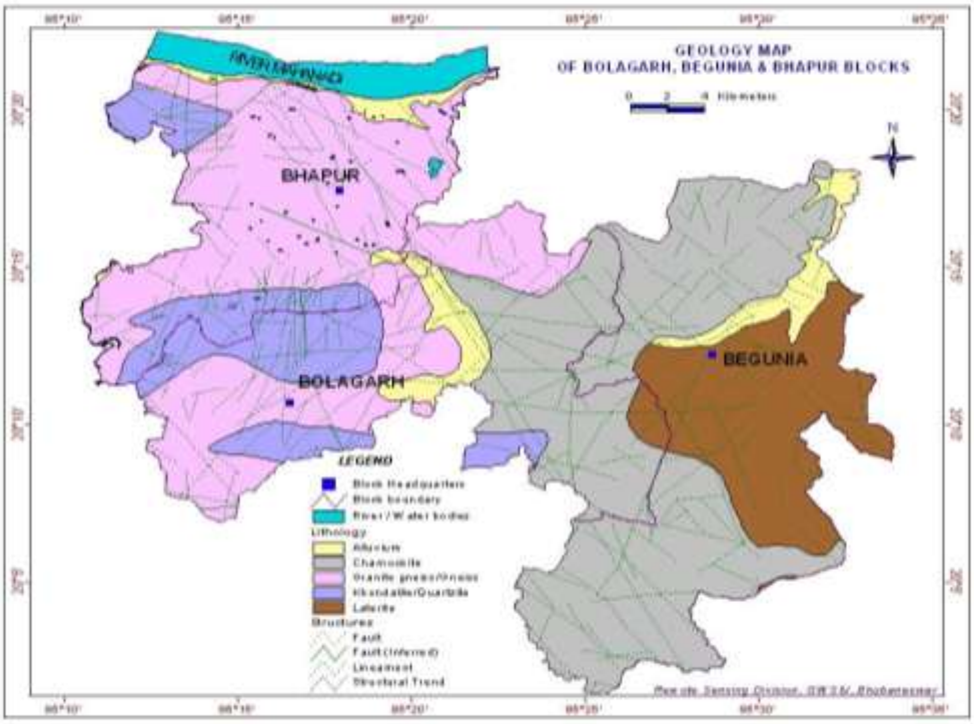

Figure-1: Lithological Map of Bhapur Block of Nayagarh , Begunia and Bolagarh Blocks Of Khurda[2]
Courtesy: Remote Sensing Division, Ground Water Survey Unit, Bhubaneswar

IV. METHODOLOGY

Ground water sampling locations were established in such a way that different physiographic regions, geological formations are represented and wells are more or less uniformly distributed in the study area. For assessment of groundwater quality it was ensured that maximum villages of the study area were covered for sampling, so as to arrive at meaningful and realistic analysis with reference to F-contamination in groundwater. Water samples from the dug well & bore wells of the contaminated sites were collected in 1 liter polythene bottles and these were subjected to chemical analysis employing standard methods. The PH, Temperature and electrical conductivity were determined on the site itself, pH by using portable PH meter and EC by using ECmeter.Total Hardness (TH) was measured by titrimetric method using standard (0.1M) EDTA solution. Na^+

and K^+ were analysed by flame photometer.Ca^+ and Mg^+ ion concentrations were measured by titrimetric method using EDTA solution. Carbonate (CO_3^{--}) and Bicarbonate (HCO_3^-) were estimated by titration with H_2SO_4.Sulpahtae, Nitrate, Fluoride and chloride were analyzed by spectrophotometer.

V. RESULT AND DISCUSSION

Chemical Analysis of groundwater samples:

The pH,EC,TDS,TH and other parameters of the water samples collected from the borewells and the dugwells of the affected areas are given in table-1.

Table-1:-Chemical Analysis of groundwater samples of the study area (values in mg/l)

Village name	**Source**	**PH**	**EC**	**TDS**	**TH**	**HCO3-**	**F-**	**Cl-**	**SO4--**	**CO3--**	**Ca2+**	**Mg2+**	**Na+**	**K+**
Haladipada	BW	8.1	1446	568	340	464	1.84	149	188	0.7	28	66	154	1.4
C Prasad	BW	6.8	1457	930	515	170	0.53	228	26.8	0.6	159.6	28.6	35.5	3.2
	DW	6.8	4	2	1254	135	0.45	826	40.2	0.2	353.2	90.3	109.5	28.1
Golapokhari	BW	7.7	218	138	71	120	0.28	36.3	0.1	0.3	22.7	3.6	13.9	3.0
Nihalprasad	DW	7.6	1733	989	391	303	0.93	254	16.8	0.8	92.0	39.2	153.4	2.4
Mahualia	DW	7.3	3	22	553	232	1.1	670	32.3	0.3	116.8	63.3	279.7	51.5
	DW	7.6	610	390	276	185	0.85	205	15.1	0.5	59.9	30.8	144.2	19.9
	BW	7.1	862	552	768	86	0.3	552	34.2	0.1	190.1	71.3	117.7	2.6
Begunia	DW	6.8	397	255	114	70	0.25	42.8	0.2	0.0	40.2	3.3	15.2	14.1
	BW	7.5	552	352	249	160	0.67	26.5	0.1	0.9	49.1	18.0	19.0	1.6
Tarabalo	DW	7.6	3	52	445	252	0.64	425	36.3	0.7	101.5	46.7	142.8	247.1
	DW	7.5	103	67	502	282	0.78	133	35.7	0.6	107.2	57.1	117.9	122.6
Elaparha	DW	7.4	1133	725	346	208	0.96	152	17.5	0.3	92.4	28.1	57.4	4.7
	DW	7.4	706	452	283	65	0.72	81.2	8.1	0.1	78.7	20.9	43.5	3.5
	BW	7.7	106	68	268	150	1.15	16.3	4.8	0.5	46.4	37.0	28.9	2.8
Marichia	DW	6.9	4	22	642	108	0.48	35	16.5	0.1	180.7	46.1	177.1	255.6
Karadapalli	BW	7.6	100	64	432	110	0.29	247	12.9	0.3	144.7	17.6	38.5	2.9
Parbatipur	BW	7.4	201	129	255	137	0.62	44.6	6.0	0.2	62.4	23.9	82.9	2.4
Pathapur	DW	7.2	190	122	59	86	0.16	14.0	3.6	0.1	18.0	3.4	7.7	5.1
Tangisahi	DW	7.1	980	911	361	170	0.34	282	14.5	0.1	111.3	20.3	74.5	60
Krushnapalli	BW	7.1	107	65	40	84	0.25	7.52	1.5	0.1	11.5	2.7	10.8	2.0
Khaudapalli	BW	6.3	159	102	27	58	0.18	16.7	4.8	0.0	6.3	2.9	14.1	1.5
	DW	7.0	4	33	969	154	0.36	968	74.7	0.1	268.9	96.3	156.6	93.2
Bhalukhai	BW	7.6	620	397	128	130	0.39	9.2	1.4	0.3	35.3	9.6	15.6	2.0
Sagargaon	BW	7.6	904	579	123	366	3.06	42.1	5.0	1.1	37.5	7.0	124.0	1.9
	BW	7.6	86	54	126	366	2.71	45.3	4.8	1.1	37.5	7.0	130.6	2.1
Biswanathpur	DW	8.2	1110	356	210	488	2.04	49	28	0.5	36	29	160	6
Kaliaka prasad	DW	7.6	3800	578	980	659	1.73	918	134	1.1	212	109	430	2.4
Balasinghpur	DW	7.2	792	508	195	454	7.3	3320	18.6	.5	44.5	20.4	199.5	3.0
	BW	7.7	1633	948	51	232	4.64	33.3	2.2	.7	14.1	3.7	137.6	1.6
	BW	7.8	97	61	132	285	4.07	184	16.5	1.4	30.1	13.8	152.3	1.7
	BW	8.2	655	417	54	315	5.35	37.1	1.0	2.4	15.2	3.9	144.4	1.7
	DW	7.5	17	20	299	369	10.5	698	44.9	1.1	66.7	32.0	431.9	1.7
	DW	7.5	66	40	510	325	2.8	1148	116.5	1.0	93.1	67.4	647.6	74.2
	DW	7.5	3	52	288	362	8.49	420	247.5	1.1	64.7	30.7	388.4	9.5
Bhabanipur	BW	8.5	2000	879	340	537	3.12	227	218	1.1	28	66	338	8.6
Belapadar	BW	7.6	1940	497	660	561	1.63	192	300	0.1	112	92	180	14
Akhupada	BW	8.1	1456	579	340	450	1.8	142	186	1.2	30	72	146	1.6
Radha kantapur	BW	7.5	1956	486	672	552	1.63	187	302	0.8	117	87	186	13.5
Srichandapur	BW	7.21	919	375	280	304	1.53	121	18	0.7	48	39	89	1.4
Bolagarh	BW	8.3	638	456	150	281	2.58	37	24	1.0	24	22	62	6.5
Dabardhua-patna	DW	8.1	1115	347	220	481	2.01	57	29	0.6	40	28	167	5.7
Mean		7.5	735.35	348.54	355.19	269.19	1.93	316.16	54.48	0.60	81.60	37.07	145.82	25.96

BW-Bore well, DW-Dug well, TDS-Total Dissolved Solids, TH-Total Hardness, EC-Electrical conductivity in µS/cm at 25°C.

The present analysis shows that the occurrence of high fluoride which varies from 0.18 to 10.5 is not uniform throught the area and is rather sporadic. The incidence of very high fluoride are limited to certain patches of Bolagarh and Bhapur block and is scattered in Begunia block.Balasinghpur Of Begunia Block shows highest fluoride content of an average 6.1mg/l.The ground water quality is also evaluated by comparing the range of values of different geochemical parameters with drinking water standards of both Indian(ISI,1983) and WHO (1984), which is tabulated in Table-2 .

Table-2:-Comparison of ground water Quality with Indian and WHO standards

Parameter	Minimum	Maximum	Mean	Indian Standard(ISI,1983)		WHO(1984)
				Highest desirable limit	Maximum permissible limit	
pH	6.3	8.5	7.5	7.0-8.5	6.5-9.2	6.5-8.5
EC	3	3800	735.35	500	2000	1400
TDS	2	989	348.54	500	1500	500
TH	27	1254	355.19	300	600	500
HCO_3^-	58	659	269.19	-	-	-
F^-	0.18	10.5	1.93	0.6-1.2	1.2	1.5
Cl^-	7.52	3320	316.16	200	1000	500
SO_4^{--}	0.1	305	54.48	150	400	400
CO_3^{--}	0.0	2.4	0.6	-	-	-
Ca_2^{++}	6.3	353.2	81.60	75	200	75
Mg_2^{++}	2.7	109	37.07	30	100	150
Na^+	7.7	647.6	145.82	-	-	200
K^+	1.4	255.6	25.92	-	-	-

The average pH of ground water of the area is above 7 which indicates the alkaline condition and which in turn favours the solubility of fluorine bearing minerals. The electrical conductivity in most of the samples lies in the WHO prescribed range. The values of chloride, sulphate ,calcium, magnesium , sodium and potassium in most of the samples are within the permissible range. The TDS varies from 2mg/litre to 989mg/litre , the main constituents of TDS in water being Ca^{2+}, $Mg^{2+}$and Cl^- .Total hardness (TH) which denotes the concentration of calcium and magnesium ions and are important criteria for determining the usability of water for domestic supplies, shows a positive and significant corelationship with Ca^{2+}, $Mg^{2+}$and Cl^- . Bicarbonate varies from 58mg/litre to 989mg/litre.This high value indicates the intense chemical weathering of the parent granite rock. Fluoride from those weathered rock minerals like fluoroapatite, fluorite and fluoride replaceable hydroxyl ion in ferromagnesian silicates (Fluoride being of the same size as that of hydroxyl ion,1.34°A) leach into the ground water and contribute to the high fluoride concentration. Solubility of fluoride from fluoride bearing minerals is relatively low under normal conditions but slow process of dissolution enhances leaching and Fluoride enrichment in ground water part of F^- may occur in ground water as a result of fluorite(CaF_2) dissolution.the solubility product of fluorite (K_{fluor}) can be determined according to te following formula.

$CaF_2=Ca^{2+}+2F-$ (1)

$K_{fluor}=[\mathbf{a}_{Ca2+}]*[\mathbf{a}_{F-}]=10^{-9.07}$ at 25^oC (2)

Where $[\mathbf{a}_{Ca2+}]$ and $[\mathbf{a}_{F-}]$are the activity coefficients of the corresponding ions and K is the equilibrium constant.Due to the relatively low solubity of F^-, the occurrence of aqueous F^- is mainly controlled by the availability of free Ca^{2+} ions in water.the dissolution constant of $CaCO_3$ is much larger than the fluorite.

$CaCO_3(s)+H^+=Ca^{2+}+HCO_3^-$ (3)

$K_{Cal}=[\mathbf{a}_{Ca2+}]*[\mathbf{a}_{HCO3-}]/[\mathbf{a}_{H-}]=0.97*10^2$ (4)

Since the solubility product of fluorite is constant, the activity of F^- is directly proportional to that of HCO_3^- if pH is constant. While calculating the thermodynamic equilibrium in the ground water system in contact with both calcite and fluorite, the combined equation is given below.

$CaCO_3(s)+H^++2F^- = CaF_2(s)+HCO_3^-$ (5)

$K_{cal\text{-}flour} = [\mathbf{a}_{HCO3-}]/[\mathbf{a}_{H+}]*[\mathbf{a}_{F-}]^2 = 1.06*10^{-11}$ (6)

It is clear from the above chemical equation that if there is more sodium ion in the sample, the lesser will be the calcium and consequently an increase in the level of fluoride and vice versa which is validated from the observed data. The ground water results also suggests that the country rocks in which fluorine is strongly absorbed are the main source of fluoride.There is a positive correlation between fluoride content and pH m in the ground water. High fluoride is also related to residual alkalinity ($Ca^{++}<HCO_3^-$) and saturation with respect to fluoride. Hardness is less than alkalinity in many samples. The ground water samples with high fluoride values show an increase in Na/Ca ratio due to lowering of Calcium activity in the area[3].

From the equation it is concluded that $K_{cal\text{-}flour}$ is a constant and pH of water being reasonably constant, any increase or decrease in bicarbonate concentration is accompanied by corresponding changes in fluoride concentration. This also shows the inverse relationship between Ca^{2+} and $F^{-.}$ The high fluoride in the study area is derived primarily from the country rock, i.e. hornblende biotite gneiss, since no man made pollution is visible in the area. The alkaline water depleted in Calcium is capable of releasing fluoride from the fluorine bearing minerals. Intensive and long-term irrigation, comparatively low rainfall, an alkaline environment, longer residence time of water in the aquifer zone and a low rate of dilution are the favorable factors for the dissolution of fluorine bearing minerals in the ground water. When the water is saturated with respect to or is at equilibrium with fluorite, the low calcium concentration leads to higher fluoride concentration [3,4].

VI. CONCLUSION

The present study shows that high fluoride in ground water poses serious health problems. As far as the origin of fluoride contamination is concerned, it is due geogenic and not anthropogenic .High fluoride in the shallow ground water zone is attributed to geochemical factors. The occurence of fluoride is also influenced by high ambient temperature, alkanity, calcium and magnesium in the ground water. Abnormal level of fluoride in water is common in fractured granitic, khondalitic & charnockitic rocks.Generally the ground water contains more fluoride than surface water due to greater contact time with fluoride bearing minerals. The incidence of fluoride concentration is always point specific as is seen from Balasinghpur where different wells of the village show wide variation in fluoride content. N. Kundu et al in their paper "Geochemical Appraisal of Fluoride contamination of ground water in the Nayagarh district of Orissa,India"has analysed the water from the nearby Hot Spring at Tarabalo, the second largest Hot Spring in Asia and has found excess fluoride in the hot spring water. On that basis they have opined that the high fluoride in the ground water of Balasinghpur(which they mentioned as Singhpur)and Sagargaon are due contamination of nearby hot spring water. However, Sagargaon is situated upslope and Balasinghpur is nearly horizontal as Tarabalo and also due to the fact that dental and skeletal flourosis has been reported from only Balasinghpur village and not from Sagargaon , it is difficult to accept the Hot Spring contamination theory.

Thus to conclude the weathering of fluoride bearing rocks, local hydrological conditions favourig such weathering and leachability of the fluoride are mainly responsible for the high fluoride content in the ground water. The longer the residence time of water in the aquifer zone, caused by a high rate of evapotranspiration and a weathered zone of low hydraulic conductivity, are the supplementary factors that activate the dissolution of fluorine bearing minerals to further increase the fluoride content in the ground water [1-4].

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