

Chemistry of Ground Waters Containing High Fluoride in Boudh District, Orissa

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ABSTRACT: *Monitoring of National Hydrograph Network Stations of Central Ground Water Board, in Boudh district has been used in identifying the high Fluoride containing wells in Harbhanga Block. Detailed reappraisal studies with a closer sampling in the particular area revealed presence of high Fluoride along two tracts. Analysis of the data has been used to study the geochemistry of ground waters and the probable source of high Fluoride in these waters.*

I. INTRODUCTION

National Ground water quality monitoring networks are generally used to inventory and monitor diffuse source of contamination in ground water¹. Any indication of a contamination ion in a network well should be viewed seriously with an objective to study atleast its origin and distribution in the particular area. Considering the origin to be a diffuse source, a study was conducted on the occurrence and distribution of high fluoride concentrations in Harbhanga Block of Boudh district, Orissa.

Water quality standard violations with respect to F (Fluoride) ion were observed while monitoring the water quality of NHS (National Hydrograph Stations) wells in Harbhanga block of Boudh district, Orissa. A further extension of above study was carried out at the block level by increasing the density of samples in the identified area. The results have been used to find out the origin of Fluoride ion and its behavior in the natural waters of the study area. Ground water is a dependable source for the people of the block for their day to day needs, hence the area of high fluoride has been demarcated in order to use an alternative source to avoid health hazards.

II. Geology and Source of Fluoride

Earlier geological survey revealed² that Harbhanga Block is mainly dominated by Granite Gneiss in the north and north – western portion and with Charnockite in the whole of south with some out crops of Granite Gneiss and Khondalite in between, towards southeastern part. Alluvium has been observed only along the river course.

Studies³ on the source of high Fluoride was reported in Anugul district, which is to the north – east of Harbhanga Block. In spite of presence of some major industries at Anugul, studies indicate that high Fluoride concentrations are mainly attributable to geological sources. The geological sources of Fluoride in Ground waters are mainly the Fluoride containing minerals i.e. Fluorite (Ca F_2), Fluor apatite [$3 \text{ Ca (PO}_4)_2 \text{ Ca F}_2$], Cryolite ($\text{Na}_3 \text{ Al F}_6$) etc. Other minor rock forming minerals are of Amphibole group having general formula $\text{M}_7 [\text{Si}_4\text{O}_{11}]_2 [\text{OH}]_2$ & minerals of Mica group with [OH] group incorporated in between two tetrahedral layers. Substitution of F ion in place of OH group in these minerals along with the resistate sedimentary formations containing volcanic ash is the other sources of Fluoride⁴. Anthropogenic sources, in the absence of any chemical and fertilizer industries, mainly is the use of phosphatic fertilizers for agricultural purpose.

III. CLIMATE

Standard limit has been set for Fluoride by BIS (1991)⁵, keeping in view the climatic conditions of certain regions. A limit of 1.5 mg/L Fluoride is for regions having normal ambient temperatures and humidity. Average daily intake of water in the regions with higher ambient temperatures is more; hence the limit of one mg/L of Fluoride has been set for such areas. Reports indicate⁶ that although the mean daily minimum temperature at Harbhanga Block during winter season is 2 °C, the mean daily maximum temperature during summer has been found to be 40 °C. Relative humidity varies between 71% to 91% throughout the year. So the average daily intake of water may be assumed to be more than normal intake. Hence the limit of 1 mg/L of Fluoride has also been considered.

IV. METHODOLOGY

Initially a detailed National Hydrograph Survey of Boudh district was carried out. A total of 58 samples were analysed from the district. After detecting the problem in Harbhanga Block, closer sampling was done during reappraisal survey. A total of 39 dug well samples were collected in Harbhanga Block (Fig.1) and analysed for E.C, pH, CO₃²⁻, HCO₃⁻, F⁻, Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, SiO₂, PO₄³⁻ using standard methods⁷. This survey was carried out in pre monsoon season of 1992 – 93. Problematic area was then identified and a still closer sampling was carried out (Fig. 2). Samples from shallow aquifer represented by about 12 dug wells other than the regular monitoring wells, aquifers of upto 30 metres depth represented about 7 hand pumps and samples from deeper aquifer i.e. 3 exploration wells constructed by Central Ground Water Board in the same block, were collected and analysed in 1997. Surface water samples were collected from the canals used for irrigation in the identified area and from Mahanadi river near Harbhanga (Fig. 2).

V. RESULTS AND DISCUSSION

SURFACE WATER

Five samples were collected from surface water sources like the irrigation canals and Mahanadi river in the study area (Fig. 2). These water bodies form a potential source of recharge to the ground water in the effected area. The data hence helps in identifying the source of high fluoride in the ground water . Chemical analysis data shows that water from all the surface water sources is of Ca (HCO₃)₂ type , with Fluoride concentrations below 1 mg/L (ranging between 0.29 to 0.67 mg/L) . The concentrations of Nitrate (as NO₃⁻)and Potassium have been found to be very low (Below 3 mg/L). These results confirm the absence of any contamination from fertilizers.

GROUND WATER

Chemical data analysis (Table – 1) reveals the presence of three types of waters in the study area viz., NaHCO₃, Ca(HCO₃)₂ and a Mixed type. A detailed analysis of the results was used, to identify the source of high Fluoride and its relationship with other ions in the aquifer.

NaHCO₃ type of water

Dug wells yielding these waters tap aquifers of weathered residuum with the Charnockite as the under ground formation. Analysis of the chemical data reveals that a positive correlation exists between F⁻ and HCO₃⁻ ; a fact well established by other workers.⁸ NaHCO₃ appears to play an important role in the presence of high Fluoride in these waters. Further presence of high concentration of silica in the NaHCO₃ type of water along with high F⁻ points the source towards amphibole group of minerals, i.e., Arfvendsonite , apart from the well established source i.e. Cryolite.

Ca (HCO₃)₂ TYPE OF WATER

These types of waters are encountered mainly in the wells with granite gneiss and in some places with charnockite formations. Fluoride concentrations have been found to be low i.e < 1.0 ppm, much contrary to the findings reported in Anugul district.

VI. MIXED TYPE OF WATER

Characteristics of these waters have been found to resemble both NaHCO₃ type and Ca (HCO₃)₂ type waters. Fluoride concentrations from 0.41 to 2.6 ppm. Have been observed in these wells

In view of the complexity of relationship between F⁻ and other ions in the three types of waters, graphs were plotted between F⁻ vs. Ca/Mg (Fig. 3). From the figure it is clear that in NaHCO₃ type of waters, high concentrations of F⁻ i.e >1.0 ppm occurs, only when the ratio of Ca/Mg is above 0.4 . Similarly the concentration of F⁻ in Ca(HCO₃)₂ type waters, is limited to below 1mg/L,when the ratio is above 0.4 . Both situations co exist in the mixed type of waters.

The correlation coefficient calculated (Table 2) between F⁻ ions and other dependent ions show that a positive correlation exists between F⁻ and other ions in NaHCO₃ type and Ca(HCO₃)₂ type of waters ,but in case of mixed type of waters, the correlation is negative between F⁻ and HCO₃, Calcium and Magnesium indicating probable dilution of high F⁻ waters of NaHCO₃type waters with low F⁻ waters of Ca(HCO₃)₂ type.

Table 2: Correlation coefficient values between Fluoride and other ions in different types of water from Boudh district.

Parameter	NaHCO ₃ type	Ca(HCO ₃) ₂ type	Mixed type
HCO ₃	0.27	0.59	-0.10
Na	0.36	0.48	0.38
Ca	0.23	0.44	-0.36
Mg	0.03	0.48	-0.33

Apparently from the above results, High bicarbonate concentrations are an indication of the surface water recharge to the aquifers subsequently bringing about three types of changes in the chemical quality of the ground water in the area:

1. Complete change where in the $\text{Ca}(\text{HCO}_3)_2$ type surface water, while percolating down the subsurface material, extracts the F^- from the Fluoride rich minerals, exchanges Ca^{+2} with Na^+ ions, finally appearing as NaHCO_3 type of water with high Fluoride content.
2. Partial change wherein the surface water is partly converted into NaHCO_3 type and a considerable quantity percolates down unchanged resulting in a Mixed type of water.
3. No change where the surface water percolates down directly unchanged, resulting in $\text{Ca}(\text{HCO}_3)_2$ type of water with low Fluoride concentrations.

Rock forming minerals with high Fluoride content can be classified depending upon their constituent cations. Mainly two groups are prominent: They are

- Calcium containing fluorite and fluorapatite
 - Sodium containing cryolite
 - Other minor rock forming minerals of Amphibole and Mica group like Arfvedsonite & Glaucofanite.
1. Dissolution of Fluorapatite can be ruled out since the initial survey shows low PO_4^{3-} concentrations.
 2. Alternatively dissolution of Fluorite (sparingly soluble) could result in enrichment of Ca^{2+} and F^- ions in the solution. Ion exchange taking place in the soil further gives rise to two situations
 - Ion exchange phenomenon where Adsorption of Ca^{2+} and release Na^+ , occurs thus yielding only NaHCO_3 type water with high F^- concentration. Here generally a negative correlation is obtained between F^- and Ca^{2+} ions. But in NaHCO_3 type of water positive correlation has been observed between F^- and Ca^{2+} ions (Table no. 2).
 - Saturated condition where the Ca^{2+} rich water from the surface as well as from fluorite containing subsurface formations, percolates down directly with very little ion-exchange. Subsequently yielding ground water with low Na^+ , high fluoride and high Calcium concentrations, a situation which has not been observed in the present study.
 3. Dissolution of Cryolite enriches the solution with Fluoride and Sodium. A positive correlation exists between Fluoride & Sodium ions (Table no. 2) in the NaHCO_3 type of water. Hence, Cryolite forms a probable major source of Fluoride in the ground water of the study area.

VII. AREA DEMARCATION

Local sampling was carried out in the identified area during pre monsoon season 1997. The study has revealed that most of the shallow aquifers and aquifers tapped by hand pumps along Baisparha -- Chatrang -- Jharkamal tract & Chatrang -- Baliagora -- Harbhanga (shown in Fig. 2) are contaminated with high Fluoride ($> 1.5 \text{ mg/L}$). Comparative values of Fluoride (presented in Fig. 4) between the dug wells and tube wells show lower concentrations of Fluoride in tube wells throughout the tract. Deep bore holes drilled by CGWB, at Purunakatak, Charichhak and Harbhanga show that concentration of Fluoride are 1.1, 0.99, 0.86 mg/L respectively. Hence deeper aquifers form a better alternative source for the domestic use in this area.

VIII. CONCLUSION

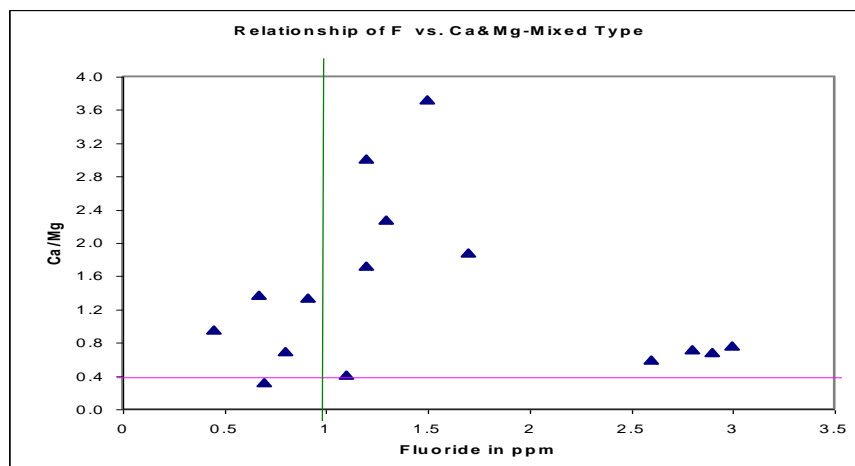
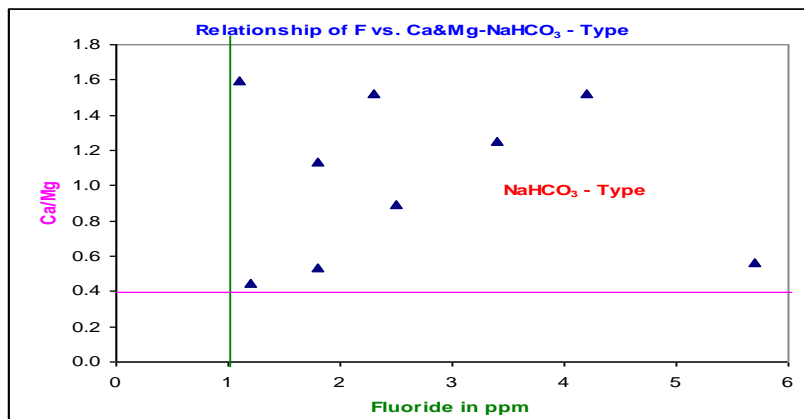
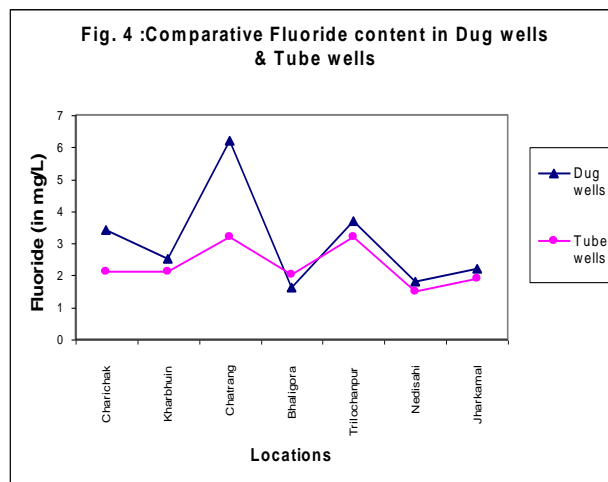
High concentrations of F^- ions were observed in the ground waters of Harbhanga block of Boudh district, Orissa. Detailed analysis of the chemical data has further revealed the presence of three types of waters in the area viz. NaHCO_3 , $\text{Ca}(\text{HCO}_3)_2$ and mixed type. High concentration of F^- was mainly observed in NaHCO_3 type of waters which lead to the speculation of its probable source being the F^- bearing minerals of Amphibole group apart from Cryolite. Fluoride concentration, below 1mg/L was most prominent in $\text{Ca}(\text{HCO}_3)_2$ type of waters. The mixed type of waters appear to be the diluted NaHCO_3 type (having high F^-) and the dilution is caused by low F^- containing $\text{Ca}(\text{HCO}_3)_2$ type of waters. Further studies in the area indicated that high Fluoride concentration are present both in the dug wells and tube wells of the Baisparha -- Chatrang -- Jharkamal tract & Chatrang -- Baliagora -- Harbhanga tract. Deep bore wells are better alternative source that can provide low Fluoride water to the region.

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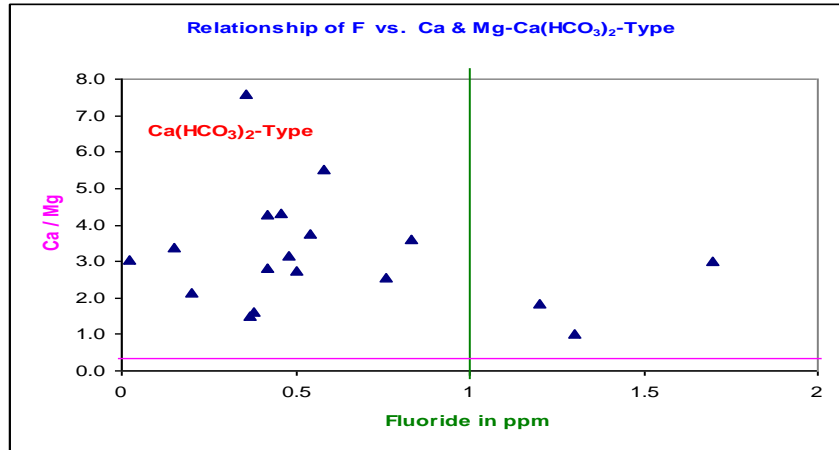


Fig. 3 Diagram showing relationship between F, Ca & Mg in different type of waters

Table 1: Chemical data of different locations (dug wells) in Harbhanga block, Boudh district.

Sl.No.	LOCATION	pH	EC	CO ₃	HCO ₃	Cl	F	PO4	TH	Ca	Mg	Na	K	SiO ₂
NaHCO ₃ – Type		μS/cm			-----mg/L-----									
1	Charichhak	8.02	1128	0	653	39	4.2	0.82	125	30	12	209	2.3	86
2	Birnarsingpur	8.24	980	0	476	67	1.2	0.12	245	30	41	129	1	97
3	Charichhak	8.2	811	0	451	35	3.4		90	20	9.7	161	2	
4	Bagchipara	7.44	352	0	177	25	2.3		25	6	2.4	71	1.6	
5	Tilkupa	7.52	229	0	153	11	1.1		65	16	6.1	32	1.6	
6	Kharbhuin	8.2	617	0	329	11	2.5		115	22	15	106	2	
7	Chatrang	7.67	751	0	378	46	1.8		130	28	15	115	4.1	
8	Chatrang	8.17	723	0	336	32	1.8		100	14	16	127	1.8	
9	Trilochanpur	8.19	667	0	281	89	5.7		165	24	26	92	1.2	
Ca(HCO ₃) ₂ - Type														
1	Adengarh	7.32	175	0	92	11	0.15	0.01	65	20	3.6	12	1.6	42
2	Baispada	7.89	463	0	238	21	0.46	0.01	160	52	7.3	35	2.7	40
3	Chatrang	7.28	2169	0	323	312	1.3		665	134	80	166	6.6	
4	Kusanga	7.32	1128	0	250	195	0.58	0.01	400	136	15	59	2	46
5	Landibandh	7.75	490	0	177	39	0.42	0.13	185	60	8.5	17	2.1	80
6	Karadakotha	8.24	425	0	238	11	0.76		160	46	11	27	1.8	
7	Karadakotha	7.93	603	0	207	46	0.54		190	60	9.7	35	10	
8	Marding	7.93	278	0	92	25	0.36		85	30	2.4	13	6.4	
9	Pedohali	7.92	441	0	214	21	0.42		145	44	9.5	29	1.6	
10	Jingakata	7.72	480	0	293	11	0.37		225	54	22	12	1.6	
11	Geramunda	7.68	422	0	244	14	0.5		185	54	12	13	1.2	
12	Ranipathar	8.01	251	0	153	11	0.2		110	30	8.5	10	1.4	
13	Ranipathar	7.8	534	0	268	28	0.38		225	56	21	17	0.8	
14	Sunkulai	7.77	651	0	317	18	1.2		270	70	23	13	16	
15	Thakurmunda	7.99	284	0	140	18	0.83		115	36	6.1	9.7	1.2	
16	Dhunjamunda	8.12	361	0	146	35	0.48		125	38	7.3	21	7.6	
17	Baliagara	7.5	567	0	323	14	1.7		215	64	13	38	1.2	
18	Dharmanagar	7.69	467	0	244	25	0.2		215	60	12	17	0.8	
Mixed - Type														
1	Thuklunda	7.76	705	0	293	57	0.91	0.01	200	46	21	69	2.1	80
2	Chatrang	8.16	592	0	275	43	3	0.01	175	30	24	63	2	89
3	Dholpur	8.23	343	0	128	25	1.2	0.04	95	24	8.5	37	1.2	83
4	Tileswar	8.24	806	0	177	99	0.7	0.04	210	20	39	35	68	58
5	Thidkajhor	8.19	632	0	348	21	1.1		210	24	36	54	0.8	
6	Kamalpur	7.6	555	0	305	25	1.2		160	48	9.7	54	2.1	
7	Karanjakata	7.88	624	0	378	14	2.6		215	32	33	58	2.1	

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8	Chatrang	8.22	389	0	214	18	2.8		120	20	17	41	1.2	
9	Chatrang	8.19	478	0	214	35	2.9		125	20	18	53	1.2	
10	Nadisahi	7.85	406	0	232	28	1.7		115	30	9.7	48	5.3	
11	Arakhpada	7.86	931	0	421	71	1.3	0.01	310	86	23	77	1	61
12	Harikrishnapur	8	520	0	238	28	0.45	0.04	215	42	27	20	11	51
13	Singanibera	7.57	798	0	458	21	0.8		320	52	46	41	1.6	
14	Lundrujor	7.07	966	0	275	99	0.67		380	88	39	32	0.8	
15	Kharbhuin	8.16	1079	0	354	14	1.5		330	104	17	46	78	
16	Dharmanagar	7.69	467	0	244	64	1.2							
17	Nuapada	8.08	598	0	342	60	0.8	0.03	240	38	35	35	5.7	62
18	Nunibahal	8.02	623	0	323	18	0.9	0.05	230	40	32	47	2	72
19	Jharkamal	7.65	406	0	207	35	2.6		115	34	7.3	44	1.6	
20	Bharipathro	8.2	490	0	232	32	0.53		175	36	21	26	1.2	
21	Thidkajhor	7.59	646	0	354	32	0.7		255	40	38	35	1.6	
22	Kalahandi	7.41	571	0	342	14	0.41		265	44	38	37	2.3	
23	Jharajing	8.02	475	0	293	14	0.64		200	16	39	25	1.2	
24	Barajhuli	7.57	656	0	342	50	1.5		220	52	22	54	1.2	