



# Monitoring of Groundwater Quality with Respect to Fluoride Contamination Around Hindalco Industries Ltd. Renukut, Sonbhadra District, Uttar Pradesh, India

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## ABSTRACT

In the era of industrial advancement, fluoride is mainly contributed through runoff and leaching of phosphate fertilizers in agricultural land and liquid waste from industrial sources. Persistent use of fluoride contaminated coal in the thermal power plants and aluminium smelter plant can also heavily contribute fluoride in the groundwater. Since there are no major studies in the recent past, the present study was carried out to understand the groundwater quality in the investigated area. Groundwater samples were collected from 25 different locations around aluminium smelter plant from wells, shallow hand pump and deep hand pump during the month of June to September 2008 in Renukut district Sonbhadra for determining various parameters (pH, EC, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Total Dissolved Solids, fluoride). The fluoride content in groundwater of Renukut ranged from 1.23 to 2.79 mg/L with average of 1.82 mg/L. 95% of the groundwater samples in the study area had crossed the permissible limit of fluoride in drinking water i.e., 1.5mg/L. The fluoride contamination to the groundwater during the post-monsoon season is mainly due to the seepage, moving and percolation of fluoride contaminated water nearby aluminium smelter plant and dissolution of fluoride bearing mineral under alkaline condition is the major source of fluoride in groundwater.

## INTRODUCTION

Fluorine is one of the most important essential nutrient elements that has a prominent place in human health. Fluoride is among the substances for which there are both lower (0.6 mg/L) and upper (1.5 mg/L) limits of concentration in drinking water, with identified fluoride (< 0.6 mg/L) in water promote tooth decay. However, when consumed in higher doses (> 1.5 mg/L), it leads to dental fluorosis or mottled enamel and excessively higher concentration (> 3.0 mg/L) of fluoride may lead to skeletal fluorosis. The severity of fluorosis depends on the concentration of fluoride in drinking water, daily intake, continuity and duration of exposure and climatic conditions. It is not only water through which fluoride is ingested, but also from the food that is consumed by the people. The crops, particularly cereal and vegetables have high rates of fluoride absorption from soil. Plants that grow in the soils and utilize undergroundwater, where fluoride levels are high, will enter into plants and may be accumulated in the edible parts.

India is one of the 28 countries identified by UNICEF as having serious health problems associated with fluoride in drinking water. About 62 million people in India suffer from dental, skeletal or non-skeletal fluorosis (Susheela 2001).

Of these, 6 million are children below the age of 14. In India, about 20 states (viz., Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Uttar Pradesh, Rajasthan, and Tamilnadu etc.) have been identified with a problem of excess fluoride in groundwater. The origin of fluoride in groundwater is through weathering of alkali, igneous and sedimentary rocks. The common fluoride bearing minerals are Fluorspar (CaF<sub>2</sub>), Cryolite (Na<sub>3</sub>AlF<sub>6</sub>), and Fluor-apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>Ca (FCl)<sub>2</sub>). Fluorite (CaF<sub>2</sub>) is the principle bearer of fluoride and is found in granite, granite gneisses and pegmatite (Deshmukh et al. 1995 and Rao 2009). Apart from natural sources, a considerable amount of fluoride may be contributed due to anthropogenic activities. Burning of coal, manufacturing process of aluminium, steel, bricks, phosphatic fertilizer industries, often contain fluoride as an impurity and are being leached down to the groundwater (Deshmukh et al. 1995, Anderson et al. 1991, Smith & Hodge 1979, Tailor & Chandel 2010).

## MATERIALS AND METHODS

**Study area:** The study was conducted during 2007-2009 around the Hindalco Industries Ltd., situated at Renukut in the central part of Sonbhadra district. The study area is situ-

ated between 24°8'N-24°18'N latitude and 83°58'E - 83°06'E longitude. It has an average elevation of 283 metres and 1,400 feet above from sea level, with nearby hills exceeding 2000 feet. Summers peak in May and June. Rain starts around the third week of June. Renukut has the largest integrated aluminium plant in Asia. Renukut lies in one of the most important industrial belts of India constituting of cement factories, aluminium industry, chemical industries, hydel power projects, thermal power projects. To name a few, there exists Hindalco, India's largest aluminium company, and then in the same belt around some 40 km away is India largest NTPC plant. Monsoon generally sets in the first week of June and lasts up to last week of September. 90-95 % rainfall is received during June to September. The mean relative humidity is 60 per cent. The location map of study is represented in Fig. 1.

**Sampling and analysis:** Water samples from drinking and irrigation wells (open, dug wells and hand pumps) were collected from villages of Myorpur Block, Renukut near Hindalco Industries Ltd. The global position and samples location are presented in Table 1. Water samples were collected in clean plastic bottles of 500 mL capacity. The sampling bottles were soaked in 1:1 diluted HCl solution for 24 hours, washed with distilled water, and washed again prior to each sampling the filtrates of sample. In the case of bore wells, water samples were collected after pumping the water for 10 min. In the case of open wells, water samples were collected from 30 cm below the water level using a depth sampler. Samples collected were transported to the laboratory and filtered using 0.45 µm millipore filter paper.

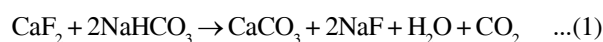
**Analysis of fluoride content in water:** Fluoride content in the water was determined electrochemically, using the direct ion sensitive electrode method. In this method, 25 mL of water sample and 25 mL of the TISAB solution (total ionic strength adjustment buffer) were taken in a 100 mL plastic beaker. Calibration was made with NaF as standard with the concentration range of 0.1-1000 mg/L and concentration of the solution was calculated (Page 1991) according to the derived calibration function.

**Preparation of TISAB solution for F<sup>-</sup>:** 58 mL of glacial

acetic acid and 12 g of sodium citrate were added to 300 mL distilled water and pH of the solution was adjusted to 5.2 using 6 N sodium hydroxide and then cooled and diluted to 1000 mL.

## RESULTS AND DISCUSSION

The results of chemical analysis of groundwater samples of Renukut are given in Table 2. Fluoride concentration in the study area varied between 1.23 to 2.79 mg/L, with average 1.82 mg/L. The permissible limit of fluoride in drinking water is 1.5 mg/L (ISI 1983). It is observed that nearly 95% of the groundwater of the study area exceeds the desirable limits. The pH value of groundwater in the study area varied from 6.7 to 7.6. It indicates a slightly alkaline condition in most of the cases, which favours the dissolution of fluoride bearing minerals in groundwater (Shaji et al. 2007, Handa 1975, Raju et al. 2009, Saxena & Ahmed 2001). While in acidic medium (acidic pH) fluoride is adsorbed in clay. The aqueous ionic concentrations of groundwater also influenced the fluoride solubility behaviour; for example, in the presence of excessive sodium bicarbonates in groundwater, the dissociation activity of fluoride will be high, and this can be expressed as in Equation 1 and suggesting the fluoride concentration in natural waters is inversely related to Ca concentration in Equation 2 (Saxena & Ahmed 2003).



The lower Ca content permits free mobility of the fluoride ion into the solution (Rango 2008). Fluoride concentration in groundwaters also depends on temperature, pH, solubility of fluorine bearing minerals, anion exchange capacity of aquifer materials (OH<sup>-</sup> for F<sup>-</sup>) and the nature of geologic formations drained by water and contact time of water with a particular formation. Minerals which have the greatest effect on the hydro geochemistry of fluoride are fluorite, apatite, mica, amphiboles, certain clays and villiamite. The permissible limit of fluoride in drinking water is 1.5 mg/L (ISI 1983). It is observed that nearly 95% of the groundwater of the study area exceeds the desirable limits. Total dissolved solids of the sample varied from 181 to 584 mg/L. It indi-

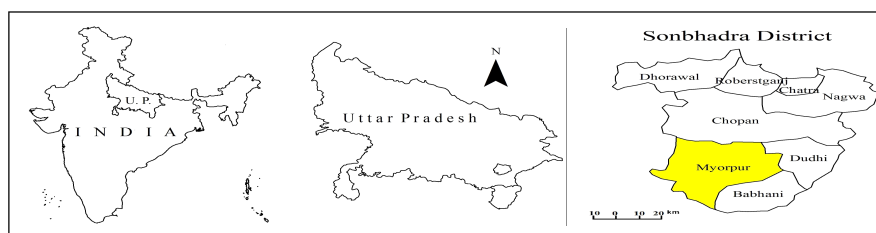


Fig. 1: Geographical representation of study area.

Table 1: Location and global position of groundwater samples of Renukut.

S. No.	Location	Global Position	S. No.	Location	Global Position
1	Renukut	N 24° 13.449' E 83° 02.381'	14	Myorpur	N 24° 07.789' E 83° 04.431'
2	Renukut	N 24° 13.493' E 83° 02.394'	15	Sendur	N 24° 12.491' E 83° 56.966'
3	Renukut	N 24° 11.373' E 83° 18.216'	16	Rajpahari	N 24° 09.271' E 83° 03.520'
4	Balliary	N 24° 07.524' E 83° 03.423'	17	Nawatola	N 24° 06.729' E 83° 04.857'
5	Renukut	N 24° 13.483' E 83° 02.357'	18	Rajpahari	N 24° 09.242' E 83° 02.892'
6	Labhari	N 24° 09.698' E 83° 02.457'	19	Patritola	N 24° 07.077' E 83° 02.892'
7	Myorpur	N 24° 07.370' E 83° 03.017'	20	Patritola	N 24° 07.094' E 83° 02.799'
8	Balliary	N 24° 07.404' E 83° 03.625'	21	Balliary	N 24° 06.498' E 83° 02.385'
9	Lucky PCO	N 24° 14.498' E 83° 03.438'	22	Myorpur	N 24° 07.360' E 83° 03.021'
10	Myorpur	N 24° 07.729' E 83° 03.031'	23	Turrya	N 24° 10.560' E 83° 57.027'
11	Patritola	N 24° 07.118' E 83° 02.741'	24	Myorpur	N 24° 07.495' E 83° 02.099'
12	Balliary	N 24° 07.080' E 83° 04.241'	25	Pippery	N 24° 11.490' E 83° 55.098'
13	Patritola	N 24° 07.156' E 83° 02.941'			

Table 2: Cations and anions content (mg/L) in groundwater of Renukut.

S.No	pH	EC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	TDS	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Fluoride
1	7.2	0.765	130	232	122	490	12	24.4	114	1.93
2	7.3	0.502	104	129	147	321	18	36.6	85	2.00
3	7.3	0.400	80	241	168	256	12	24.4	57	1.28
4	7.2	0.339	44	171	191	217	24	48.8	43	1.70
5	7.3	0.827	108	167	104	529	12	24.4	128	1.80
6	7.5	0.503	82	132	106	322	21	42.7	57	1.57
7	7.0	0.707	128	129	212	452	18	36.6	142	1.81
8	6.7	0.582	98	187	133	372	18	36.6	71	1.53
9	7.5	0.331	48	100	168	212	12	24.4	43	2.23
10	6.7	0.574	104	232	30	367	24	48.8	85	1.90
11	7.6	0.283	50	177	225	181	12	24.4	43	2.79
12	6.8	0.473	72	161	140	303	18	36.6	71	1.89
13	7.0	0.331	156	106	120	212	18	36.6	71	1.80
14	7.2	0.62	112	103	113	397	12	24.4	71	1.70
15	7.2	0.765	96	206	179	490	24	48.8	71	1.67
16	7.1	0.795	134	183	110	509	30	61	85	1.94
17	7.2	0.593	112	174	120	380	12	24.4	99	1.97
18	7.6	0.736	112	254	221	471	15	30.5	71	2.77
19	7.1	0.347	98	135	191	222	12	24.4	57	1.45
20	7.6	0.374	130	93	209	239	27	54.9	43	1.80
21	7.1	0.741	98	193	97	474	12	24.4	99	1.92
22	7.0	0.913	160	161	145	584	27	54.9	128	1.32
23	7.0	0.388	98	167	179	248	12	24.4	43	1.23
24	7.1	0.891	130	148	152	570	21	42.7	43	1.63
25	7.2	0.516	76	138	140	490	12	24.4	142	1.89

cates the intense chemical weathering of the minerals bearing rocks. It may be due to stagnant or low flow of groundwater and accumulation of dissolved salts during summer season (Reddy et al. 2009, Manahan 1993). The values of Ca<sup>2+</sup> plus Mg<sup>2+</sup> ions in groundwater were found 148 - 366 mg/L, resulted from dissolution or weathering of respective minerals from rocks. It may be attributed to dilution effect of rain through seepage and percolation of surface or sub-surface water (Sengupta 1993). Similarly the chloride ion concentration varied from 43 to 142 mg/L due to accumulation of salt concentration, chloride, especially from evaporation or loss of water in unsaturated zone during summer

season. Bicarbonate concentration varies from 24 mg/L to 61 mg/L in the water samples and this is well within the permissible limit of 600 mg/L of ISI standard. Bicarbonate is mainly derived from rock weathering (80%), pollution contributing only 2% (Maybeck 1979). While in the case of Na<sup>+</sup>, the concentrations were found in the range of 29 to 225 mg/L due to percolation or seepage of agricultural and domestic wastewater (Saxena & Ahmed 2001).

**Correlation study of fluoride and chemical composition of groundwater:** The data on correlation of fluoride content in groundwater with electrochemical properties, anions and cations composition in groundwater study area are pre-

Table 3: Correlation between water properties with fluoride content in ground waters of Renukut.

Properties	pH	EC	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	RSC	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SAR	Fluoride
pH	1.000												
EC	-0.121	1.000											
CO <sub>3</sub> <sup>2-</sup>	-0.045	0.364	1.000										
HCO <sub>3</sub> <sup>-</sup>	0.113	0.281	-0.065	1.000									
RSC	0.370	-0.440*	0.046	0.200	1.000								
Cl <sup>-</sup>	0.003	0.558**	0.081	0.189	-0.094	1.000							
SO <sub>4</sub> <sup>2-</sup>	0.000	0.243	0.374	0.222	-0.029	-0.063	1.000						
Ca <sup>2+</sup>	-0.269	0.544**	0.188	-0.039	-0.693**	0.360	0.058	1.000					
Mg <sup>2+</sup>	-0.298	0.224	-0.151	-0.182	-0.827**	-0.141	0.036	0.173	1.000				
Na <sup>+</sup>	-0.142	0.246	0.302	-0.185	0.014	0.284	0.175	0.132	-0.119	1.000			
K <sup>+</sup>	0.180	0.042	-0.048	0.335	0.424*	-0.102	0.484*	-0.292	-0.339	0.062	1.000		
SAR	-0.125	0.216	0.299	0.198	0.071	0.284	0.173	0.081	-0.159	0.995**	0.108	1.000	
Fluoride	-0.201	0.533**	0.629**	0.191	-0.115	0.072	0.233	0.257	0.012	0.319	-0.032	0.281	1.000

Note: Significant at only 5%; \*\*Significant at 1% and 5

sented in Table 3. The correlation analysis indicated that F<sup>-</sup> is negatively correlated with Ca<sup>2+</sup> and Mg<sup>2+</sup>. A positive correlation with CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> with F<sup>-</sup> was also found in groundwater. This was in agreement with the earlier findings of Kundu et al. (2001). These findings were also in agreement with earlier observations (Handa 1975) that elevated fluoride in groundwater was generally associated with low calcium and high amount of bicarbonates. The dissolution of fluorite (mineral) is suppressed when the concentration of Ca is above the limit of fluorite solubility. The electrical conductivity (EC) was found negatively correlated with fluoride content in groundwater due to the common ion effect (i.e. Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> etc.) during the process of dissolution of F<sup>-</sup> bearing minerals.

## CONCLUSIONS

The 95 percent of the groundwater samples in the study area have crossed the permissible limit of fluoride in drinking water i.e. 1.5mg/L (ISI 1983). The study revealed that anthropogenic activities are the major sources of fluoride incidence in groundwater. The groundwater samples near Hindalco and Thermal Power Plants are evidenced with excess fluoride concentration in groundwater during the post-monsoon season which is mainly due to the seepage, moving and percolation of fluoride contaminated water nearby aluminium smelter plant and rock-water interaction. It clearly shows that the water is not good for human consumption who are also struggling for their existence. So there is an immediate need of restoration, improvement and proper management of these secret water bodies for the human and environment.

## REFERENCES

Anderson, M.A., Zelazny, L.W.M. and Bertsch, P.M. 1991. Fluoro-aluminium complexes on model and soil exchangers. *Crop Sci. Soc. America J.*, 55(1): 71-75.

- Deshmukh, A.N., Shah, K.C. and Sriram, A. 1995. Coal ash: a source of fluoride pollution, a case study of Koradi thermal power station, district Nagpur, Maharashtra. *Gondwana Geological Magazine*, 9:21-29.
- Handa, B.K. 1975. Geochemistry and genesis of fluoride containing ground waters in India. *Groundwater*, 13: 275-281.
- Indian Standard (IS: 10500). Drinking Water Specification (Reaffirmed 1993). Bureau of Indian Standards, New Delhi.
- Kundu, N., Pamgrahi, M.K., Tripathy, S., Munshi, S., Powell, M. A. and Hart, B.R. 2001. Geochemical appraisal of fluoride contamination of ground water in Nayagarh district of Orissa, India. *Environ. Geol.*, 41: 451-460.
- Manahan, S.E. 1993. *Fundamentals of Environmental Chemistry*. 2nd edition, Lewis Publishers, Boca Raton, Florida 844.
- Page, A.L. 1991. *Methods of Soil Analysis*, 2nd Edn. Am. Soc. Agron. & Soil Sci. America, Madison, Wisconsin, USA on the content of fluorides in soil and grass. *Polnohospodarstvo*, 10: 257-262. (In Slovak.)
- Ramam, P.K. and Murty, V.N. 1997. *Geology of Andhra Pradesh geological society of India*, India. ISI (1983). Indian Standard Specification for Drinking Water. ISI 10500, BIS, New Delhi.
- Rango, T., Bianchini, G., Beccaluva, L., Ayenew, Tenalem and Colombani N. 2008. Hydrogeochemical study in the main Ethiopian Rift: new insights to the source and enrichment mechanism of fluoride. *Environmental Geology*, 58 109-118.
- Raju, N., Dey, S. and Das, K. 2009. Fluoride contamination in groundwaters of Sonbhadra District, Uttar Pradesh, India. *Current Science*, 96(7): 979-985.
- Reddy, A.G.S., Kumar, K.N., Rao, S.D. and Rao, S.S. 2009. Assessment of nitrate contamination due to ground water pollution in north eastern part of Anantapur district, A.P. India. *Environmental Monitoring and Assessment*, 148(1-4): 463-476.
- Shaji, E., Bindu, J.V. and Thambi, D.S. 2007. High fluoride in groundwater of Palghat District, Kerala. *Current Science*, 92(2): 240-245.
- Saxena, V.K. and Ahmed, S. 2001. Dissolution of fluoride in groundwater: a water-rock interaction study. *Environmental Geology*, 40(9): 1084-1087.
- Sengupta, M. 1993. *Environmental Impacts On Mining, Monitoring, Restoration And Control*. Lewis Publishers, Boca Raton, Florida 194.
- Susheela, A.K. 2001. *A Treatise on Fluorosis. Fluorosis Research and Rural Development Foundation*, New Delhi.
- Tailor, G.S. and Chandel, C.P.S. 2010. To assess the quality of ground water in Malpura Tehsil (Tonk, Rajasthan, India) with emphasis to fluoride concentration. *Nature and Science*, 8(11): 2026.