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FLUORIDE CONTAMINATION THREAT IN THE GROUNDWATER OF ASSAM, INDIA: A CASE STUDY IN THE HIGH CONCENTRATION ZONE OF NAGAON

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Abstract: This work focuses on the chemistry of groundwater in the district of Nagaon, Assam, India, which is a high concentration zone for fluoride; with areas of particular interest being the major ion chemistry, and identification of contamination levels with reference to fluoride. Fluoride concentration well above the WHO guideline value was found in several locations of the district with a range of values between 0.14 and 3.65 mg/L. About 60% of the samples studied had F^- content higher than the recommended maximum permissible level of 1.5 mg/L, while about 10% samples had it below the recommended level of 0.6 mg/L. The chemical characteristic of the groundwater study shows that the cationic chemistry is dominated by Ca^{2+} and Na^+ while anionic chemistry is primarily dominated by Cl^- ; the geological formation of the area is the basic cause of high fluoride content in its groundwater.

Keywords: groundwater quality; fluoride; fluorosis; water pollution

1. Introduction:

97% of the water on Earth is salt water and only 3% is fresh water. Slightly over 67% of this fresh water is frozen in glaciers and polar ice caps. The remaining unfrozen fresh water is found mainly as groundwater, which constitutes 30% of the freshwater on Earth. Only a small fraction is present above ground or in the air. Though fresh water is a renewable resource, yet the world's supply of groundwater is steadily decreasing, with depletion considered to be occurring most prominently in Asia and North America. Moreover, groundwater quality is constantly decreasing due to various anthropogenic as well as geogenic causes, and water quality crisis is a rampant problem the world over.

Excess fluoride in drinking water has appeared as a serious problem around the world. Around 200 million people, from 25 nations of the world, are under the dreadful fate of fluorosis. Presence of high levels of fluoride in groundwater of India too poses a great threat to the health of the people. Fluorosis was first reported in the country as early as in 1937 in Andhra Pradesh. Assam also faces severe contamination of fluoride in its groundwater. The presence of high concentrations of fluoride in the drinking water in many parts of Assam, particularly Nagaon and Karbi Anglong districts, is a great concern for health; with about 20,000 young people in the state suffering from endemic fluorosis [1], and other harmful effects due to excess fluoride in drinking water.

Fluorosis is an endemic disease due to long term intake of excessive fluoride. Two main kinds of fluorosis, namely dental fluorosis and skeletal fluorosis have been identified so far. Patients with dental fluorosis chronically develop yellowing of teeth, and pitting/mottling of enamel. Skeletal fluorosis is a bone disease caused by consumption of fluoride exceeding 4-8 mg/L. Symptoms may include increase in bone density, calcification of ligaments, rheumatic or arthritic pain in joints and muscles, stiffness and rigidity of joints, bending of vertebral column etc [2]. There are several commonly accepted causes for endemic fluorosis such as long term intake of high fluoride groundwater and exposure to high fluoride gas from coal burning. Apart from environmental concerns and threat to human health, fluoride in groundwater also poses geochemical problems.

Fluoride occurs naturally in groundwater. A common natural source is the dissolution of fluoride bearing minerals such as fluorite, apatite etc. into aquifers. Hence the problem occurs in areas where fluoride bearing minerals are most abundant in the host rocks; because the chemical quality of groundwater is influenced to a great extent by the chemical composition of the rocks and the soil mass through which it moves under various physico-chemical conditions [3]. In recharge areas, the soil zone undergoes a net loss of mineral matter to the flowing water. As groundwater moves from recharge to discharge areas, its chemistry is altered by the effects of a variety of geochemical processes.

2. Materials and methods:

The groundwater samples were collected from shallow tube wells (STW), deep tube wells (DTW), dug wells (DW), and hand pumps (HP) from various locations of the district during the pre- and post-monsoon seasons. Pre-washed polythene bottles were used for sample collection, and the samples were then pretreated and stored following standard procedures (Table 1). One part was acidified with conc. HNO_3 for cation analysis, and the unacidified part was used for analyzing the dissolved anions.

Table 1: Table showing the various methods used for sample preservation:

Parameters	**Container used**	**Preservation method**
pH	Polythene	Analyzed immediately
Fluoride	Polythene	None required, analyzed within 28 days
Chloride	Polythene	Refrigerated, analyzed within 6 hrs
Sulphate, Nitrate	Polythene	Refrigerated, analyzed within 24 hrs
Calcium, Magnesium	Polythene	Acidified with HNO_3 to pH < 2, analyzed within 30 days
Sodium, Potassium	Glass, rinsed with 1+15 HNO_3 and deionized water	None required, analyzed within 7 days

The groundwater samples were analyzed for pH, major cations and anions following standard methods [5] (APHA 1989, 17th edition). pH was determined immediately after sample collection with a digital pH-meter (Elico pH Meter) using standard buffers for calibration. F^- content was determined by using SPADNS method using UV-visible spectrophotometer (Shimadzu UV-1800) at 570 nm, calibrating against blank and standard NaF solutions. This method is based on the reaction between fluoride and a zirconium-dye lake. F- reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}). As the amount of fluoride increases, the color produced becomes gradually lighter. Ca content was estimated by EDTA complexometric method and Mg was calculated by the difference in the hardness and Ca. Cl^- was estimated by argentometric titration method using $AgNO_3$. SO_4^{2-} and NO_3^- were analyzed by UV-visible spectrophotometer (Shimadzu UV-1800). SO_4^{2-} was estimated by turbidimetric method by measuring absorbance of reaction mixture at 420 nm, while for NO_3^- measurement was carried out at 220 nm and 275 nm wavelengths. Na^+ and K^+ were determined with flame photometer (Elico CL-361) using standard calibration procedure. All chemicals used were of analytical grade (Merck, India).

3. Results and Discussion:

The results of analysis of the ions and other parameters of some selected samples (mostly having high fluoride concentrations) of groundwater in the district are given in Table 2 below.

Table 2: Ranges of chemical parameters analysed from the samples and their comparison with WHO guideline values for drinking water:

Chemical parameter	**Minimum value**	**Maximum value**	**Average**	**WHO standard (1997)**	
				desirable limit	**permissible limit**
pH	6.8	8.5	7.71	7	9.2
F^- (mg/L)	0.14	3.65	1.55	0.9	1.5
Cl^- (mg/L)	39.76	69.58	54.90	250	600
SO_4^{2-} (mg/L)	8.67	80	44.33	200	600

NO_3^- (mg/L)	0.02	10.15	5.75	50	-
Ca^{2+} (mg/L)	8.016	32.064	22.42	75	200
Mg^{2+} (mg/L)	7.308	21.92	14.61	30	150
Na^+ (mg/L)	11.75	67.62	35.23	50	200
K^+ (mg/L)	2	13.50	5.25	10	12

Except that of fluoride in some samples, the concentrations of various other ions, are either low or moderate and within the guideline values of WHO [6]. However, the fluoride content in the analyzed samples was found to vary from 0.14–3.65 mg/L with an average value of 1.55 mg/L. The WHO guideline value for fluoride in drinking water is 0.6-1.5 mg/L. The pH of the analyzed samples varied from 6.8 to 8.5 with an average value of 7.7, implying that the groundwater is mostly alkaline in nature. In general, pH of groundwater samples is alkaline. Among the cations, Ca^{2+} and Na^+ were found to be the dominant ions, with Ca^{2+} having values between 8.016 to 32.064 mg/L with an average of 22.42 mg/L. Na^+ content varied from 11.75 to 67.62 mg/L with average value of 35.23 mg/L, followed by Mg^{2+} (average 14.61 mg/L) and K^+ (average 5.25 mg/L). Among the anions, Cl^- was found to be the dominant ion, having a range of 39.76 - 69.58 mg/L (average 54.90 mg/L), followed by SO_4^{2-} with a range 8.67 – 80 mg/L (average 44.33 mg/L), and $NO_3^{\,-}$ with a range 0.02 –10.15 mg/L (average 5.75 mg/L).

From the analysis, it was observed that about 60% of the groundwater samples had F^- content higher than the recommended maximum permissible level of 1.5 mg/L while about 10% samples had it below 0.6 mg/L (fig.1). Only 25% samples had fluoride levels within the permissible guideline values of WHO[6] (0.6-1.5 mg/L).

Fig. 1. Fluoride concentrations in the water samples

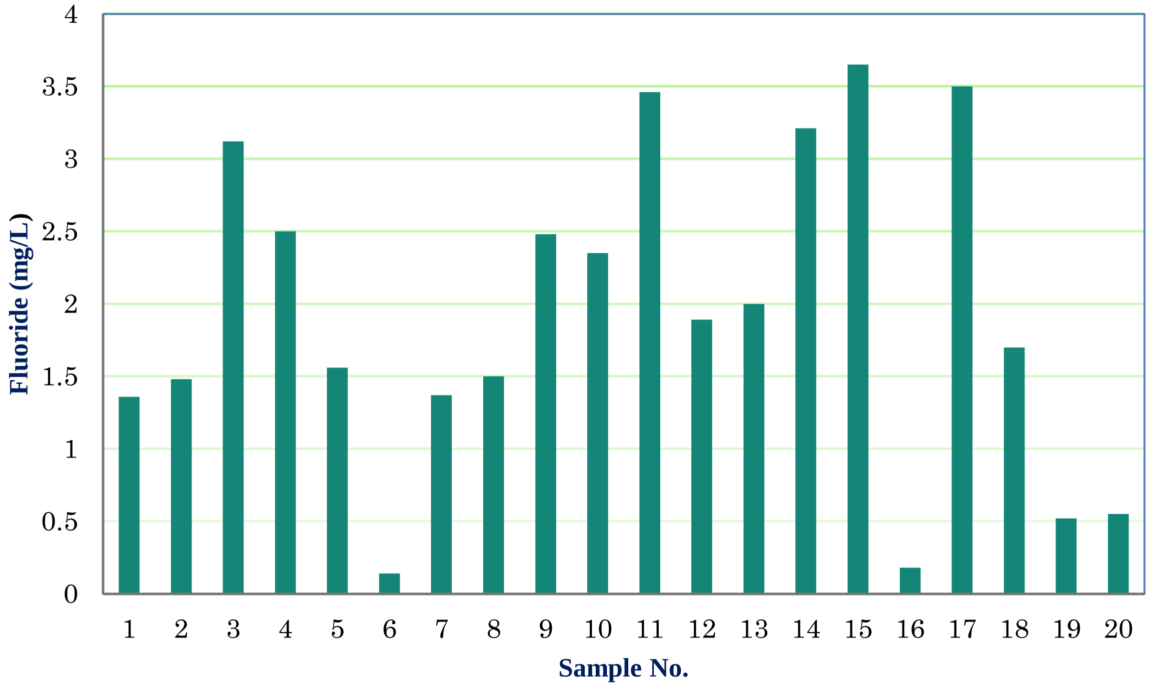

Figure 1: Bar diagram depicting the range of concentrations of F^- in the samples taken from a single region.

The correlation of some select ions and other parameters with fluoride were studied and R-squared values were plotted. The alkaline earth metal ion Ca^{2+} showed positive correlation with fluoride (fig.2). This may be attributed to the presence of limestone in the sampling areas [7,8]. Chakraborti *et al* also reported positive correlation of fluoride with Ca^{2+} in groundwater in parts of Nagaon and Karbi Anglong districts of Assam [9]. However, poor negative correlation of Ca^{2+} with F^- has also been reported in some parts of Nagaon district, which may be attributed to the presence of predominantly Ca^{2+} - Mg^{2+} - HCO_3^- type of groundwater in those areas [10].

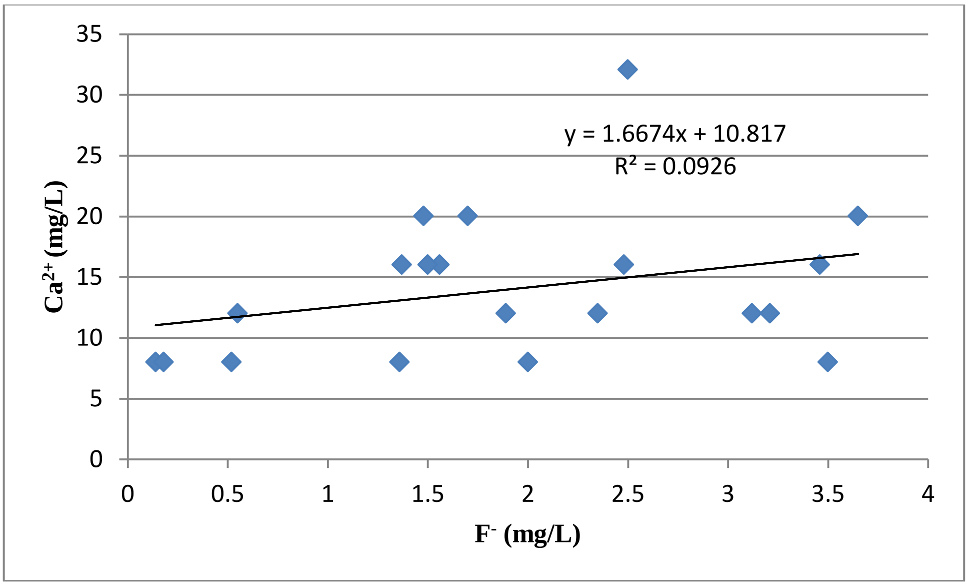

Figure 2: Correlation of Ca^{2+} vs F^- in the samples.

Mg^{2+} showed negative correlation with fluoride content (fig.3). Negative correlation of fluoride with Mg^{2+} is expected due to low solubility of fluorides of the ion in groundwater [11,12].

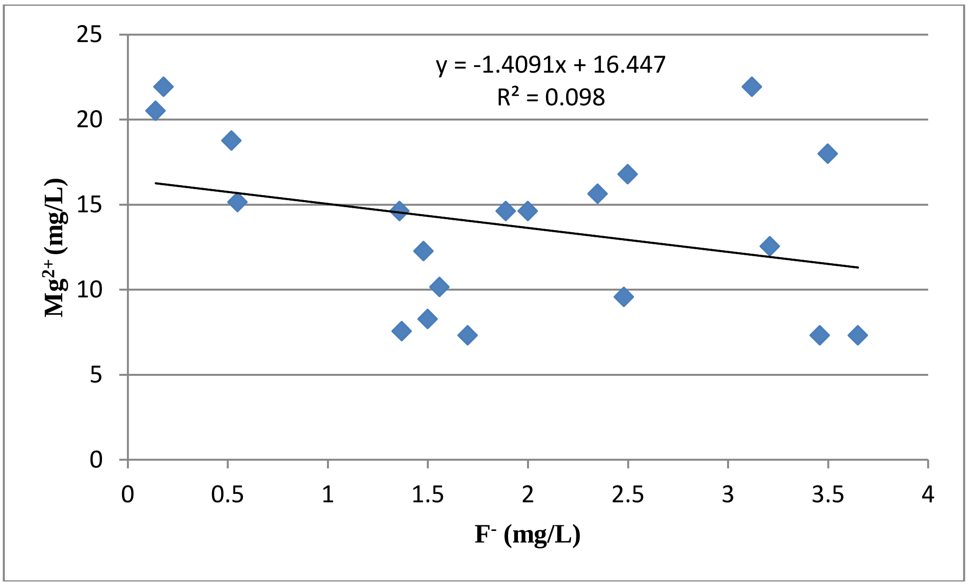

Figure 3: Correlation of Mg^{2+} vs F^- in the samples.

The alkali metal ions, Na^+ and K^+ showed positive correlation with fluoride (fig.4,5). During ion exchange process, Ca^{2+} and Mg^{2+} ions present in groundwater can react with clay minerals such as Na montmorillonite to release Na^+ ions which can increase their concentration in groundwater [11].

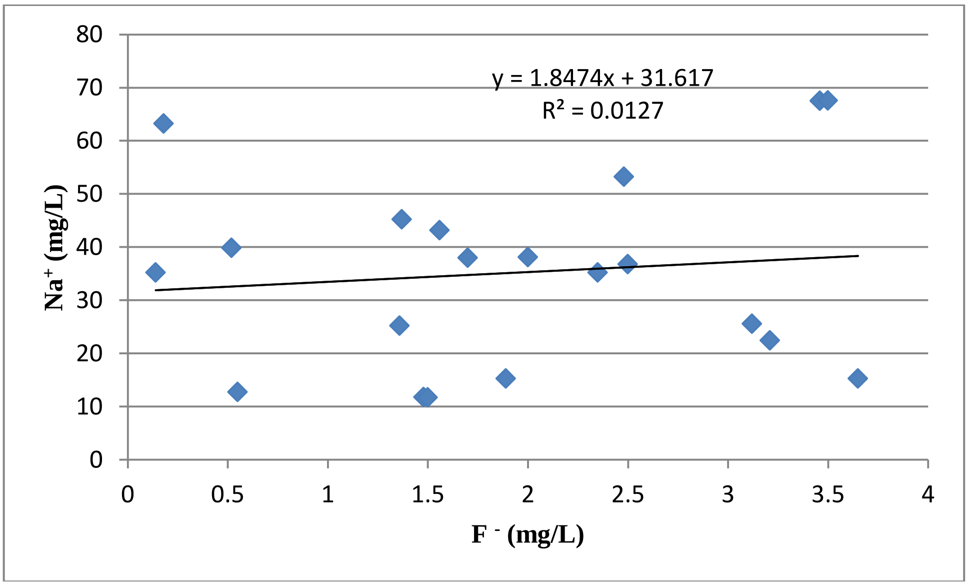

Figure 4: Correlation of Na^+ vs F^- in the samples.

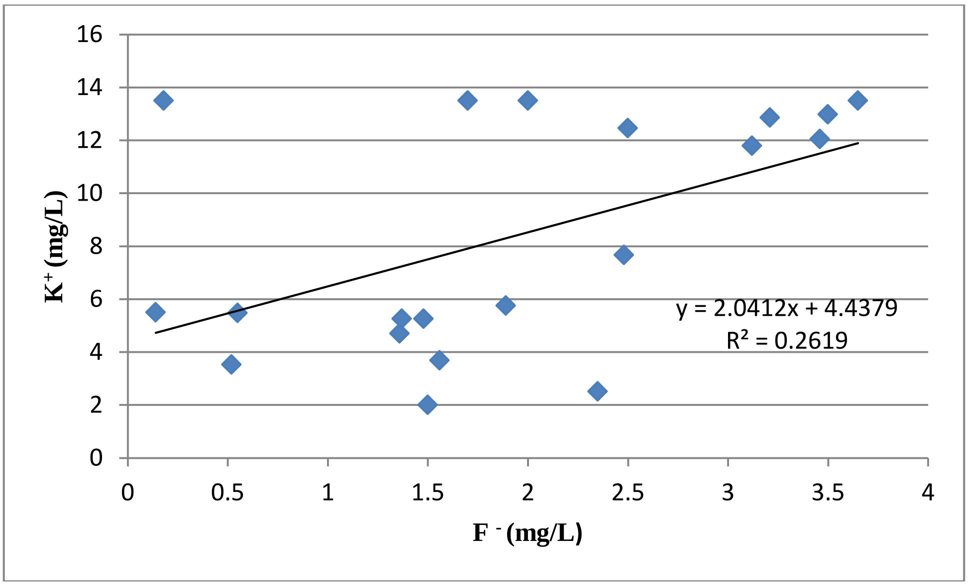

Figure 5: Correlation of K^+ vs F^- in the samples.

A strong positive correlation of fluoride with NO_3^- was observed (fig.6), which may be due to the geo diversity of the area. This may also be attributed to the nitrate contamination through fertilizers [7].

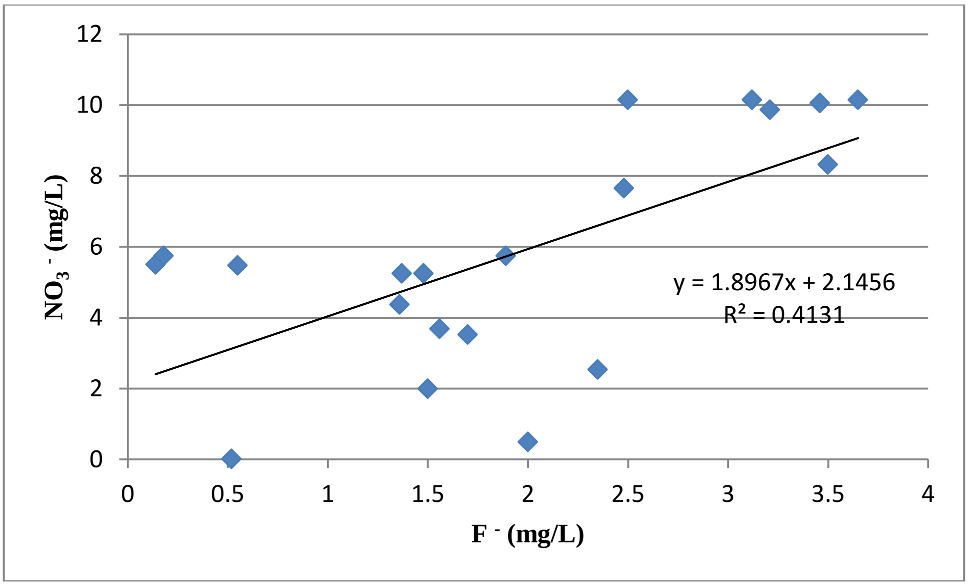

Figure 6: Correlation of NO_3^- vs F^- in the samples.

The anions SO_4^{2-} and Cl^- did not show any correlation with fluoride (fig.7,8), which rules out evaporation as a reason for the high fluoride content [13].

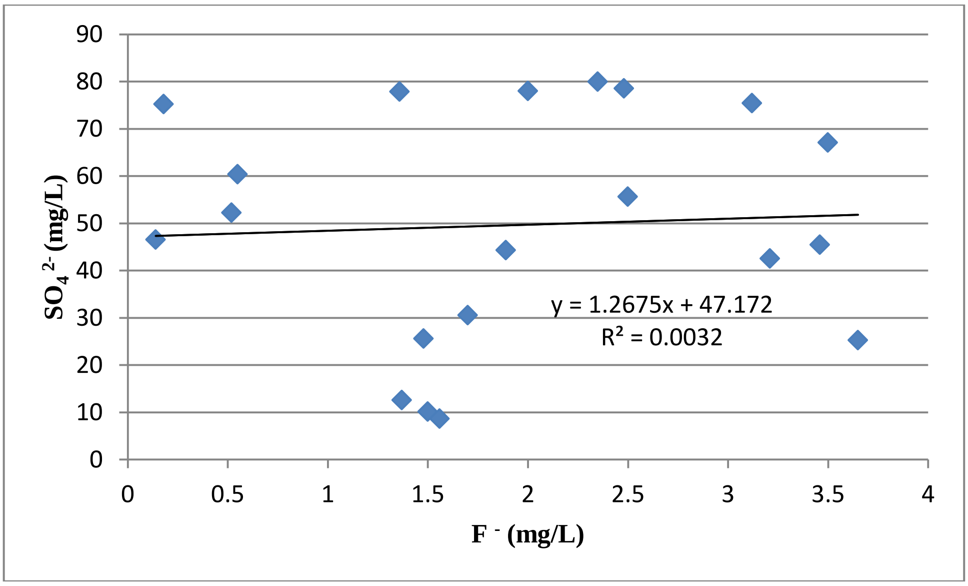

Figure 7: Correlation of SO_4^{2-} vs F^- in the samples.

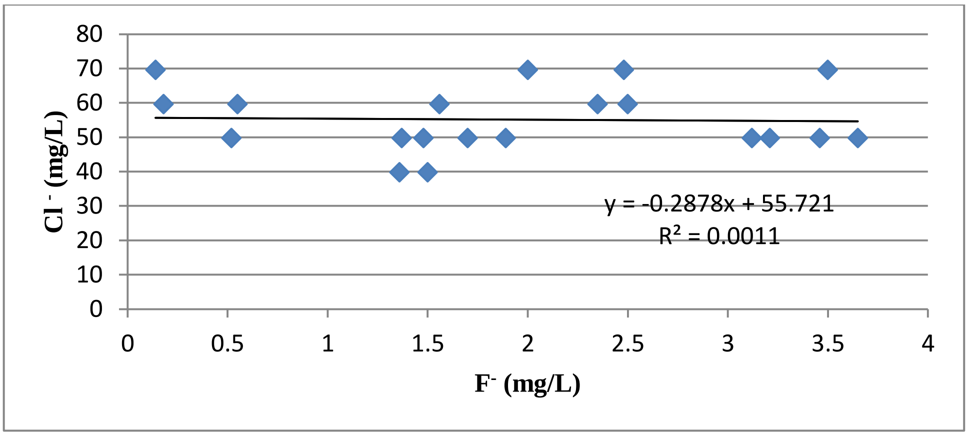

Figure 8: Correlation of Cl^- vs F^- in the samples.

A moderately positive correlation between fluoride and pH was observed (fig.9). A positive corrrelation with pH indicates a possible leaching of fluoride under high alkaline conditions of the groundwater [14]. This is because of the similarity between the ionic radius of fluoride and OH^- ion thereby replacing each other at higher pH.

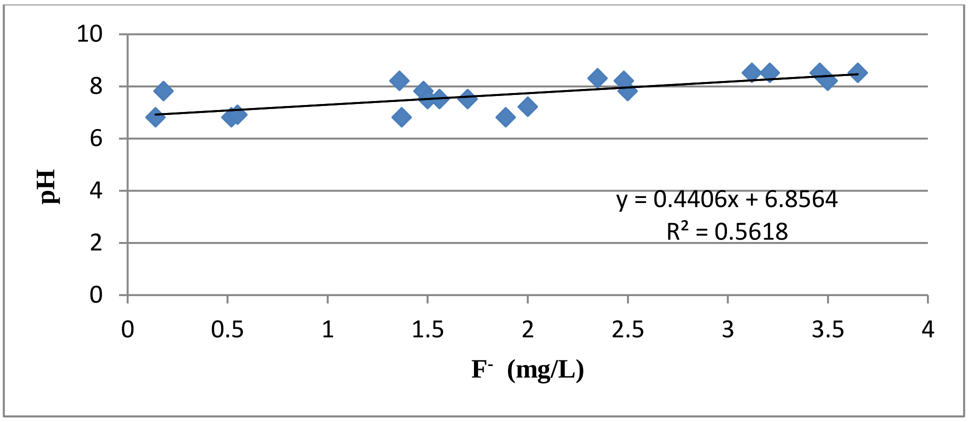

Figure 9: Correlation of pH vs F^- in the samples.

Only about 25% of the analysed samples had fluoride within the permissible limits. The underground basement of the study area is of Precambrian metamorphic rock complex origin; hence the minerals may be fluorite and/or apatite and the geological formation in the area seems to be the basic cause for the excess concentration of fluoride in most sampling sites. The chemical characteristic of the groundwater study shows that the cationic chemistry is dominated by Ca^{2+} and Na^+ while anionic chemistry is primarily dominated by chloride. Weathering processes and anthropogenic inputs are usually two main contributors for changing the geochemical composition of the groundwater [15,16]. However, in the absence of any significant anthropogenic sources in the study area, the basic cause for the excess fluoride content seems to be geogenic in origin. Climate and tectonic factors may also play some part in affecting the fluoride concentration of the groundwater. The interaction of the fluoride-bearing minerals with water and aquifer is likely to be an important factor [17]; since the decomposition, dissociation and dissolution are the main chemical processes for the occurrence of fluoride in groundwater. During rock–water interaction, concentration of fluoride in the host rocks, aqueous ionic species and residence time of interaction, etc. may also be important parameters [18].

Conclusion: About 60% of the groundwater samples in the study area had F^- content higher than the recommended maximum permissible level of 1.5 mg/L, while about 10% samples had it below the recommended level of 0.6 mg/L. About 25% of the samples had fluoride within the permissible limits. The geological formation in the area seems to be the basic cause for the excess concentration of fluoride in its groundwater. Since groundwater seems to be the only reliable source of drinking water for the people residing in the area, the excess fluoride concentration implies that there is an urgent need to implement suitable measures for remediation, also since significant number of cases of dental and skeletal fluorosis have already been reported from the area again and again.

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References:

[1] A new danger confronts Assam, The Independent, fluoridealert.org., February 14th, 2002,
[2] N. Kundu, M.K. Panigrahi, S. Tripathy, S. Munshi, M.A. Powell and B.R.Hart, Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa, India, Environmental Geology, 2001.
[3] M. M. Saikia and H. P. Sarma, Hydro-geochemical characterization of groundwater of Nagaon district of Assam, India, Journal of Environmental Research and Development Vol. 6, No. 1, 2011.
[4] R. Brunt, L. Vasak and J. Griffioen, Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale, International Groundwater Resources Assessment Centre, Report nr. SP 2004-2, 2004.
[5] (17th ed.), Standard Methods for the Examination of Water and Waste Water, APHA, American Public Health Association, Washington DC, 1989.
[6] (2nd ed.), Guideline for Drinking Water Quality, Health Criteria and Other Supporting Information Vol. 2, World Health Organization, Geneva, 1997.
[7] Babulal Das, Jitu Talukdar, Surashree Sarma, Biren Gohain, Robin K. Dutta, Himangshu B. Das and Subhash C. Das, Fluoride and other inorganic constituents in groundwater of Guwahati, Assam, India, Current Science Vol. 85, No. 5, 2003.
[8] M. Taher and P. Ahmed, (2nd ed.), Geography of North-East India, pp. 12–40, Manik Prakash, Guwahati, 2001.
[9] D. Chakraborti *et al.*, Current Science 78, 1421–1423, 2001.
[10] Mukut. M. Saikia and H.P. Sarma, Fluoride geochemistry of Kollong river basin, Assam, India, Archives of Applied Science Research 3 (3), 367-372, 2011.
[11] A.W. Hounslow, Water Quality Data: Analysis and Interpretation, CRC, p. 54, 1995.
[12] B.K. Handa, Ground Water 13, 275–281, 1975.
[13] P.L. Smedley and D.G. Kinningburgh, Applied Geochem, 17, 517-568, 2002.
[14] S. Gupta, S. Banerjee, R. Saha, J.K. Datta and N. Mondal, Fluoride Geochemistry of Groundwater in Nalhati-1 Block of the Birbhum District, West Bengal, India, Fluoride 39(4), 318-320, 2006.
[15] C.H. Jeong, Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea, J. Hydrol. 253, 194–210, 2001.
[16] Pallavi Sharma and Hari Prasad Sarma, Groundwater quality assessment of Pachim Nalbari block of Nalbari district, Assam based on major ion chemistry, International Journal of ChemTech Research Vol. 3, No.4, pp 1914-1917, CODEN(USA), 2011.
[17] Joydev Dutta, Manoranjan Nath, Mridul Chetia and Abani Kr.Misra, Monitoring of Fluoride Concentration In Ground Water of Small Tea Gardens in Sonitpur District, Assam, India: Correlation with physico-chemical Parameters, International Journal of ChemTech Research Vol.2, No.2, pp 1199-1208, CODEN(USA), 2010.
[18] X.B.Gaoa, F.C.Zhangb, C.Wangb and Y.X.Wanga, Coexistence of high fluoride fresh and saline groundwaters in the Yuncheng Basin, northern China, Procedia Earth and Planetary Science, Elsevier 7, 280 – 283, 2013.