Assessment of Groundwater Quality in Nagaon District of Assam, India, with Special Reference to Fluoride

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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. 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 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. Linear correlation studies between fluoride and some select ions showed positive correlation of* Ca^{2+}, Na^+, K^+ *and* NO_3^- *with fluoride, while* Mg^{2+} *showed negative correlation with fluoride. A moderately positive correlation of pH with fluoride was observed. The cationic chemistry is dominated by* Ca^{2+} *and* Na^+ *while anionic chemistry is primarily dominated by* Cl^-*.*

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 the world over. Presence of high levels of fluoride in groundwater of India too poses a great threat to the health of the people. India is one of the worst fluorosis affected countries in the world today. Fluorosis was first reported in the country as early as in 1937 in Andhra Pradesh. Assam also faces this grave issue of 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]. Cases of fluorosis and other harmful effects due to fluoride in drinking water have been reported from these two districts.

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 [2].

2. MATERIALS AND METHODS

2.1 Sampling Methodology

The groundwater samples were collected from shallow tube wells, deep tube wells, dug wells and hand pumps from various locations of the district based on their GPS co ordinates, twice a year during the wet and dry seasons. Pre-washed polythene bottles were used for sample collection, and the samples were then pretreated and stored following standard procedures. One part was acidified with conc. HNO_3 for cation analysis, and the unacidified part was used for analyzing the dissolved anions.

Following is a table showing the various methods used for sample preservation:

Table 1: Sample preservation methods:

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 HNO3 to pH < 2, analyzed within 30 days

Sodium, Potassium	Glass, rinsed with 1+15 HNO3 and deionized water	None required, analyzed within 7 days

2.2. Sample Analysis

The samples were analyzed for pH, major cations and anions following standard methods (APHA 1989, 17th edition) [3]. 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. 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.

3. RESULTS AND DISCUSSION

The results of analysis of the ions and other parameters of some selected samples (mostly having high fluoride concentrations) are given in Table 2. 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 [4]. 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).

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

Chemical parameter	Minimum value	Maximum value	WHO permissible limit
pH	6.8	8.5	9.2
F- (mg/L)	0.14	3.65	1.5
Cl- (mg/L)	39.76	69.58	600
SO42- (mg/L)	8.67	80	600
NO3- (mg/L)	0.02	10.15	_
Ca2+ (mg/L)	8.016	32.064	200
Mg2+ (mg/L)	7.308	21.92	150
Na+ (mg/L)	11.75	67.62	200
K+ (mg/L)	2	13.50	12

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, i.e. 0.6-1.5 mg/L [4].

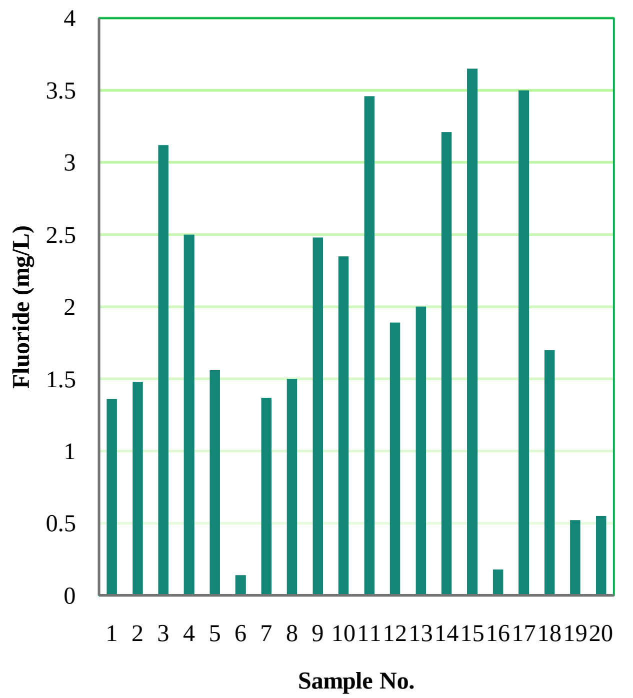

Fig. 1: Fluoride concentration in the collected samples

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 [5, 6]. Chakraborti *et al* also reported positive correlation of fluoride with Ca^{2+} in groundwater in parts of Nagaon and Karbi Anglong districts of Assam [7]. 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 [8].

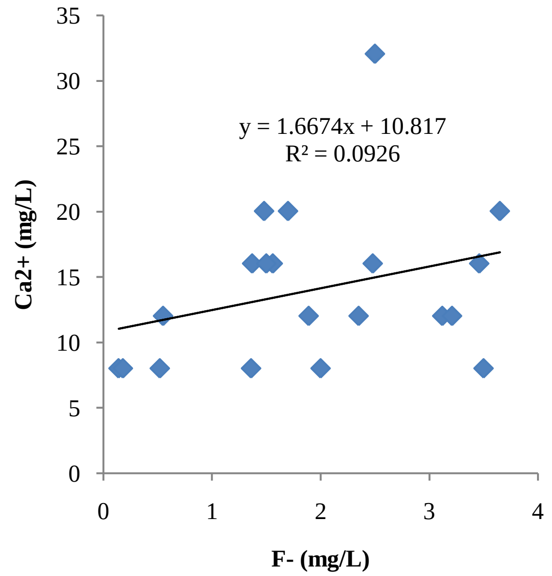

Fig. 2: Correlation of Ca^{2+} with F^-

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 [9, 10].

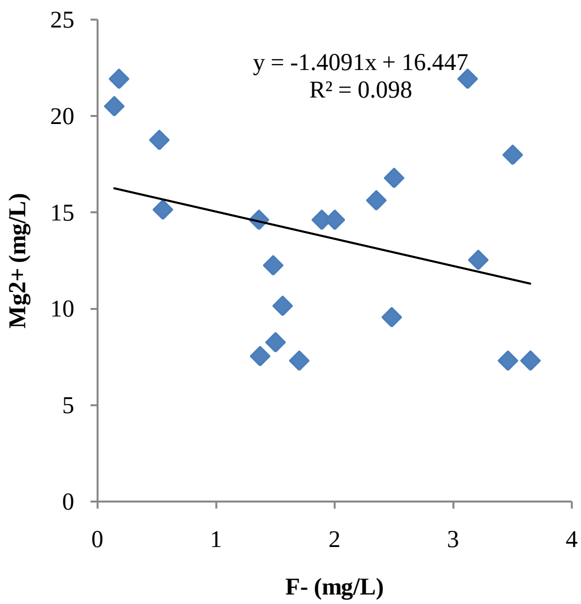

Fig. 3: Correlation of Mg^{2+} with F^-

The alkali metal ions, Na^+ and K^+ showed positive correlation with fluoride (Figures 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[9].

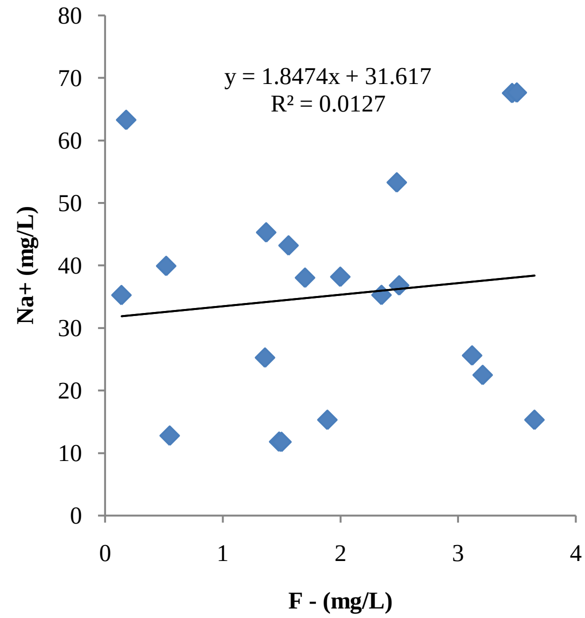

Fig. 4: Correlation of Na^+ with F^-

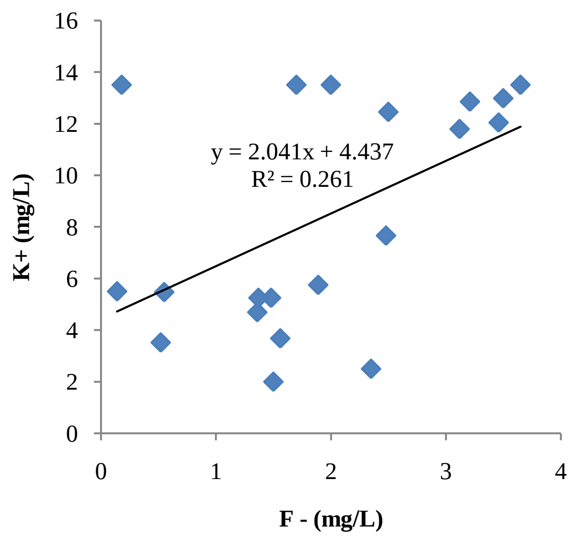

Fig. 5: Correlation of K^+ with F^-

A strong positive correlation of fluoride with NO_3^- was observed (Fig. 6) which may be due to the geodiversity of the area. This may also be attributed to the nitrate contamination through fertilizers [5].

The anions SO_4^{2-} and Cl^- did not show any correlation with fluoride (Figures 7, 8), which rules out evaporation as a reason for the high fluoride content [11].

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 [12]. This is because of the similarity between the ionic radius of fluoride and OH^- ion thereby replacing each other at higher pH.

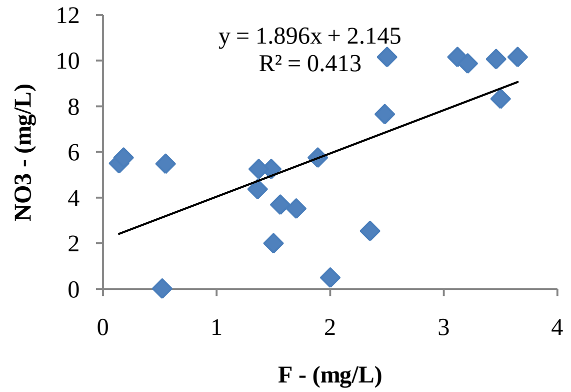

Fig. 6: Correlation of NO_3^- with F^-

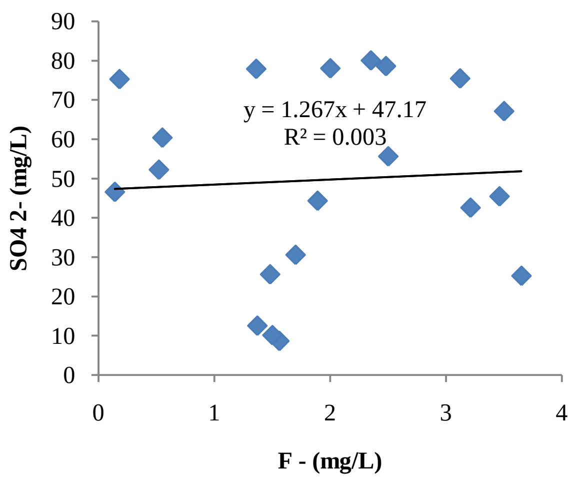

Fig. 7: Correlation of SO_4^{2-} with F^-

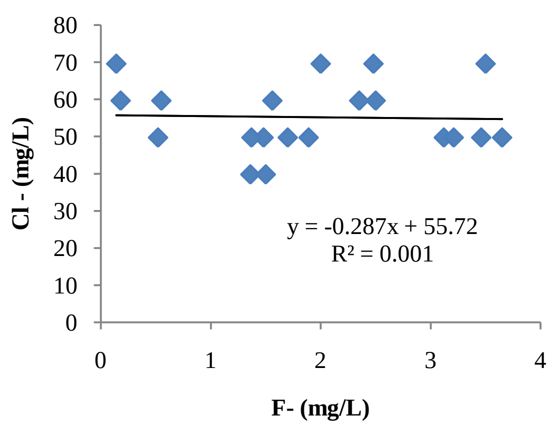

Fig. 8: Correlation of Cl^- with F^-

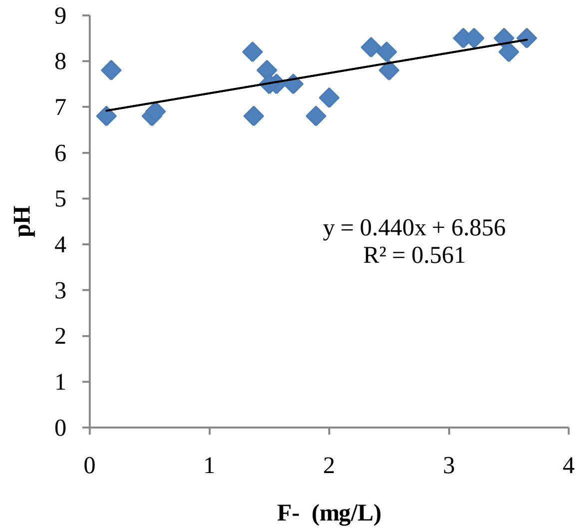

Fig. 9: Correlation of pH with F^-

4. CONCLUSIONS

About 60% of the groundwater samples in the study area had F^- content higher than the recommended maximum permissible level, while about 10% samples had it below the recommended level. Only about 25% of the 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. 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 [13]; 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 [14]. Since groundwater seems to be the only reliable source of drinking water for the people residing in the study area, the excess fluoride concentration implies that there is an urgent need to implement suitable measures for remediation.

5. ACKNOWLEDGEMENTS

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