

## Study on groundwater quality and status of Amas Block in Gaya District of Bihar with special reference to fluoride contamination

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### ABSTRACT /RESUME

**Abstract:** The study was carried out to investigate the groundwater quality and to establish its relationship with fluoride in Amas Block of Gaya District, Bihar (India). The samples were collected from One hundred ninety-nine bore wells from different locations which were extensively used for drinking and other domestic purposes. Then, samples were analyzed according to standard methods (APHA) procedure. The study revealed that the total dissolved solids in 39%, total alkalinity in 93%, total hardness in 10%, calcium in 64% and magnesium in 19% samples but in case of chloride only one sample exceeded the BIS acceptable limit. In the case of nitrate and sulfate, none of the samples exceeded the BIS acceptable limit. Iron concentration was found high with a mean of 0.7 mg/l. The groundwater was severely affected by fluoride, varied from 0.2 mg/l to 5 mg/l and 63% samples were exceeded the permissible limit of BIS.

Fluoride has a significant positive correlation with pH and sulfate as well as a significant negative correlation with calcium, magnesium, alkalinity and total hardness. Additionally, fluoride has a negative but poor correlation with electrical conductivity, total dissolved solids, chloride, nitrate, and iron.

### I. Introduction

Worldwide, for millions of rural and urban families, the major source of drinking water is groundwater. Groundwater contamination with excess iron, fluoride, arsenic, and nitrates, etc. is a major problem in many parts of the world including India and fluoride stands first among them. The range of fluoride concentration in groundwater is 0.01 to 48 mg/l, which causes fluorosis and has an adverse impact on teeth, and bones. Fluoride contaminated drinking water imposing a serious threat to human health as one of the major problems worldwide. From among 25 nations, around 200 million people are under the frightful fate of fluorosis. The two worst affected countries of the world are India, and China [1].

In India, 80% of the rural domestic water needs and 50% of the urban water needs are fulfilled by

groundwater. Here groundwater is also intensively used for irrigation and industrial purposes. In 19 states of India, approximately 65 million of the populations are affected by fluorosis, out of which 6 million are children. Bihar is of the fluorosis endemic states. Gaya District of Bihar is among 6-7 district of the state which has had cases of fluorosis, as per the report of Ministry of Environment, Forests and Climate Change (MoEF&CC), Government of India (2009). It is, therefore, a matter of high concern from the point of view of public health and welfare.

In the same perspective, primary reasons behind the fluoride occurrence in groundwater are natural or geogenic contamination but its source is over and over again unknown [2]. Geogenic contamination of groundwater depends primarily on the geological setting of the area. Rainwater dissolves partly certain components of bedrock as it reaches the

water table by infiltration. The dissolution of fluorine bearing minerals in the bedrock originates fluoride content of groundwater [3]. The functions of fluoride contamination in groundwater are temperature, pH, availability and solubility of fluorine bearing minerals, and the concentration of calcium and bicarbonate ions [4]. Geogenic contamination of groundwater is intricate to detect and even more difficult to control in compared to anthropogenic contamination of surface water. The occurrence of excessive concentration of fluoride in groundwater can reach the food system and may persist for a long time even for centuries. The main source of fluoride intake is groundwater but not only food items and also contributes to it [5]. The presence of fluoride in drinking water has both positive and negative effects on human health.

Fluoride mainly affects the skeletal systems, teeth and also the structure and function of skeletal muscle, brain, and spinal cord [6]. Long term exposure to fluoride through water and other products leads to the development of fluorosis. It is also known as a crippling and painful disease. Dental fluorosis occurs during the period of enamel formation. It is associated with excessive absorption of fluoride into dental enamel and dentine, which prevents normal maturation of enamel. Skeletal fluorosis is a pathological condition which includes inhibition of bone hardening, causing the bones to become brittle and their tensile strength may be reduced [7]. Symptoms include limited movement of joints, skeletal deformities, and intense calcification of ligaments, muscle wasting and neurological deficits [8]. The objective of this study was to investigate the detailed physicochemical characteristics of Amas Block groundwater and to establish their relationship with fluoride, toxic elements for human health.

## II. Materials and methods

### II.1. Study Area

Amas is a Block in Gaya District of Bihar State, India (Figure 1). An Amas Block headquarter is Amas town. It belongs to Magadh Division. It is located 40 km towards west from District head quarters Gaya and 140 km from state capital Patna towards the north. Amas Block consists of 84 villages and 9 panchayats. It is at an elevation of 102 m. This place is at the border of the Gaya and Aurangabad district. The total population of Amas Block is 81,640 living in 12,079 houses including 42,710 males and 38,930 females.

### II.2. Groundwater sampling and chemical analysis

One hundred ninety-nine groundwater samples were collected from 199 different locations of the study area which includes Amas Block of Gaya

District, Bihar. The samples were collected from bore wells which were extensively used for drinking and other domestic purposes. The samples were collected in pre-cleaned and sterilized polyethylene bottles of two-litre capacity. Then, samples were analyzed according to standard methods (APHA, 2000) [9] procedure, and suggested precautions were taken to avoid contamination. The various parameters like pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca), magnesium (Mg), chloride (Cl), alkalinity (ALK), Sulfate (SO<sub>4</sub>), Nitrate (NO<sub>3</sub>), Fluoride (F) and iron (Fe).



Figure 1. Location map of the study area

pH, electrical conductivity and total dissolved solids were determined by pH meter, conductivity meter, and TDS meter respectively during on-site sampling. The other parameters like total hardness and alkalinity were analysed also by titrating the sample with EDTA and sulphuric acid respectively. The titrimetric analysis was also used to analyze chloride, calcium and magnesium concentrations. In addition to this the sulfate, nitrate, fluoride as well as iron were determined by using a spectrophotometer.

To evaluate the potential relationship between various physicochemical parameters, Statistical analysis like maximum, minimum, mean, median, standard deviation and correlation coefficients were carried out by using "Statistical Package of Microsoft Office - Excel, version-10".

## III. Results and discussion

### III.1. Groundwater quality

In groundwater quality assessment the estimation of the physical and chemical characteristic of

groundwater is essential as it is an important factor which determines its suitability for drinking purposes. As such the appropriateness of groundwater for potable uses with regard to its physicochemical characteristic has to be deciphered and defined on the basis of some essential characteristics of the water. Bureau of Indian Standards (BIS, 2012) [10], has recommended the quality standards for drinking water and these have been used for finding the suitability of groundwater. The summarized physicochemical parameters of groundwater samples are presented in Table 1. The groundwater quality of the Amas block is evaluated by comparing the range of values of different physicochemical parameters of drinking water with Bureau of Indian Standards (BIS, 2012) as presented in Table 2.

The logarithm of the reciprocal of the hydrogen ion concentration (pH) in the groundwater samples varied from 6.4 to 7.9 with a mean value of 7.1. All the samples, except three, are found within the recommended limits for human consumption. For drinking water, the pH value must be within the range of 6.5 – 8.5, as per the BIS (2012). The electrical conductivity (EC) values are found to be within the range of 282  $\mu\text{S}/\text{cm}$  to 3919  $\mu\text{S}/\text{cm}$  with a mean value of 899.48  $\mu\text{S}/\text{cm}$ .

In groundwater, total dissolved solids mainly consist of carbonates, bicarbonates, chlorides, sulfates, phosphates, and nitrates of calcium, magnesium, sodium, and potassium with traces of iron, manganese and other minerals. In trace amount, various dissolved gases and organic matter are also present [11]. Total Dissolved Solids (TDS) value varied from 169 mg/l – 2406 mg/l with a mean value of 549.22 mg/l and a standard deviation of 334.34 mg/l. About 39% of samples exceeded the BIS acceptable limit of 500 mg/l (BIS, 2012). Water having more than 500 mg/l TDS values if

used for drinking purposes may induce an unfavorable physiological reaction in the transient consumer and gastrointestinal irritation [12].

Alkalinity in natural waters is a result of the dissolution of  $\text{CO}_2$  in water. Carbonates and bicarbonates thus formed are dissociated to yield hydroxyl ions. After analyzing the samples total alkalinity was found in the range of 130 mg/l – 953 mg/l with a mean value of 348.92 mg/l and a standard deviation of 140.47 mg/l. About 93% of samples were exceeded the acceptable limit of 200 mg/l but only 7% of samples exceeded the BIS permissible limit of 600 mg/l (BIS, 2012). The alkalinity of the drinking water has little public health significance.

The principal natural sources of the total hardness in water are dissolved polyvalent metallic cations from sedimentary rocks, seepage, and runoff from the soil. The total hardness values ranged from 113 mg/l – 833 mg/l with mean and median values of 316.90 mg/l and 288 mg/l respectively and standard deviation of 130.44 mg/l. Only 10% of samples exceed the acceptable limit of 200 mg/l BIS (2012). Calcium (Ca) ion concentrations in groundwater samples show a wide variation from a minimum of 34 mg/l to as high as 256 mg/l with a standard deviation of 38.37 mg/l. About 64% of samples exceeded the acceptable limit of 75 mg/l but only 3% of samples exceeded the BIS permissible limit of 200 mg/l (BIS, 2012). The magnesium (Mg) concentration varied from 3 mg/l to 88 mg/l with mean and median values of 21.58 mg/l and 18 mg/l respectively. All the samples from Amas Block, are found within the permissible limit of 75 mg/l but only 19% of samples exceeded the acceptable limit of 30 mg/l. Generally, the calcium ion concentrations in groundwater exceeded the magnesium ion concentrations according to their relative abundance in rocks [11].

*Table 1. Summarized physicochemical parameters of groundwater samples.*

Parameter	Minimum	Maximum	Mean	Median	Standard Deviation
pH value	6.4	7.9	7.1	7.1	0.25
Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	282	3919	899.5	719.0	541.09
Total dissolved solids (mg/l)	169	2406	549.2	445.0	334.34
Calcium (as Ca) (mg/l)	34	256	91.0	81.0	38.37
Chloride (as Cl) (mg/l)	2.0	267	48.7	29.0	47.93
Fluoride (as F) (mg/l)	0.2	5.0	2.2	2.0	1.29
Iron (as Fe) (mg/l)	0.1	6.1	0.7	0.5	0.80
Magnesium (as Mg) (mg/l)	3.0	88	21.6	18.0	13.76
Nitrate (as $\text{NO}_3$ ) (mg/l)	0.2	40.78	6.4	5.4	5.80
Sulphate (as $\text{SO}_4$ ) (mg/l)	4.0	94	22.6	17.0	20.28
Total alkalinity (as $\text{CaCO}_3$ ) (mg/l)	130	953	348.9	313.0	140.48
Total hardness (as $\text{CaCO}_3$ ) (mg/l)	113	833	316.9	288.0	130.44

**Table2.** Comparison of groundwater quality with Bureau of Indian Standards (2012).

Parameter	Minimum	Maximum	Indian Standard (BIS, 2012)	
			Requirement (Acceptable Limit)	Permissible Limit in the Absence of Alter Source
pH value	6.4	7.9	6.5-8.5	No Relaxation
Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	282	3919	--	--
Total dissolved solids (mg/l)	169	2406	500	1500
Calcium (as Ca) (mg/l)	34	256	75	200
Chloride (as Cl) (mg/l)	2	267	250	1000
Fluoride (as F) (mg/l)	0.2	5	1.0	1.5
Iron (as Fe) (mg/l)	0.1	6.1	0.3	No Relaxation
Magnesium (as Mg) (mg/l)	3	88	30	100
Nitrate (as $\text{NO}_3$ ) (mg/l)	0.2	40.78	45	No relaxation
Sulfate (as $\text{SO}_4$ ) (mg/l)	4	94	200	400
Total alkalinity (as $\text{CaCO}_3$ ) (mg/l)	130	953	200	600
Total hardness (as $\text{CaCO}_3$ ) (mg/l)	113	833	200	600

The range of chloride (Cl) concentration was found between 2 mg/l to 267 mg/l and only one groundwater sample in the study area was exceeded the BIS acceptable limit of chloride i.e. 250 mg/l. Primarily from taste viewpoint, the chloride limits have been laid down. Water having high chloride concentrations has no adverse health effects on human being [11].

Generally, sulfate presents as calcium, magnesium, and sodium soluble salts in groundwater. A significant change in the sulfate concentration takes place with time during rainfall infiltration and groundwater recharge [11]. The concentrations in the samples varied from 4 mg/l to 94 mg/l. None of the samples exceeded sulfate BIS acceptable limit of 100 mg/l (BIS, 2012). Sulfate, when present alone may not cause any adverse health effects while greater than 400 mg/l of sulfate with sodium or magnesium may lead to gastrointestinal irritations [12].

Nitrate ( $\text{NO}_3$ ) concentration greater than 45 mg/l in drinking water has adverse health effects on human resulting methemoglobinemia commonly known as a blue baby syndrome which generally affects the infants [11] and gastric carcinoma [13]. The nitrate concentrations ranged from 0.2 mg/l to 40.78 mg/l in all the samples indicates within the BIS acceptable limit of 45 mg/l.

The iron (Fe) concentration in groundwater samples varied from 0.1 mg/l to 6.1 mg/l with a standard deviation of 0.8 mg/l. Approximately 69% of the groundwater samples in the study area exceeded the iron BIS permissible limit of 0.3 mg/l. The higher concentration of iron causes an inky flavor, turbidity, bitter and astringent taste. Water having soluble iron remains clear while pumped out. Exposure to air causes precipitation of iron resulting in rusty color and turbidity [11].

### III.2. Correlation of fluoride with other physicochemical parameters

For establishing the relationship of fluoride with other physicochemical parameters correlation matrix (Table 3) and scatter plots have been drawn. The statistical analysis of the correlation matrix showed that electrical conductivity has a positive and significant correlation with total dissolved solids, total hardness, calcium, magnesium, and alkalinity. Calcium, magnesium, and alkalinity are positively and significantly correlated with total hardness. The alkaline nature of water is shown by the positive correlation between pH and fluoride that probably promotes the dissolution of fluoride and hence the causes of the concentration of fluoride in groundwater.

The analysis of the correlation matrix of fluoride and other physicochemical parameters showed that fluoride has a significant positive correlation with sulfate and significant negative correlation with calcium, magnesium, alkalinity and total hardness. Additionally, fluoride has a negative but poor correlation with electrical conductivity, total dissolved solids, chloride, nitrate, and iron.

The low calcium concentration favours the presence of high fluoride concentration in groundwater [14]. The negative correlation between calcium and fluoride found in the present study also support this view. The association of high fluoride zone with feldspathic sandstones and a negative correlation between fluoride and total hardness indicate that dissolution of feldspars, cation/base exchange are most likely to be the hydrogeochemical processes operating in the area leading to decrease in calcium concentrations with an increase in the concentration of fluoride in groundwater.

Generally, high alkalinity concentration favours the occurrence of high fluoride concentration in the groundwater [15] [16]. In the present study, a

negative correlation has been found between fluoride and alkalinity. Such a negative relation was also found by Tiwari et al. [17] in deeper aquifers of basaltic terrain which they attributed to the low partial pressure of CO<sub>2</sub> in deeper zones. The same

reason may also be attributed to the negative correlation between fluoride and alkalinity found in the present study as the high Fluoride zone is mainly associated with deeper wells.

Table 3. Comparison of groundwater quality with Bureau of Indian Standards (2012).

	pH	EC	TDS	TH	Ca	Mg	F	Fe	Cl	SO <sub>4</sub>	NO <sub>3</sub>	ALK
<b>pH</b>	1											
<b>EC</b>	-0.28	1										
<b>TDS</b>	-0.27	0.99	1									
<b>TH</b>	-0.24	0.89	0.89	1								
<b>Ca</b>	-0.26	0.80	0.80	0.92	1							
<b>Mg</b>	-0.12	0.68	0.68	0.74	0.42	1						
<b>F</b>	0.07	-0.07	-0.08	-0.04	-0.07	0.02	1					
<b>Fe</b>	0.08	0.01	-0.01	0.04	0.03	0.03	-0.16	1				
<b>Cl</b>	-0.29	0.74	0.75	0.58	0.53	0.45	-0.05	-0.1	1			
<b>SO<sub>4</sub></b>	-0.23	0.65	0.64	0.51	0.49	0.33	0.51	-0.0	0.50	1		
<b>NO<sub>3</sub></b>	-0.15	0.27	0.27	0.18	0.22	0.05	-0.01	0.0	0.26	0.23	1	
<b>ALK</b>	-0.22	0.86	0.85	0.96	0.87	0.72	-0.04	0.0	0.56	0.43	0.14	1

The correlation between fluoride and other physicochemical parameters (pH, TDS, total hardness, Ca, Mg, Cl, alkalinity, SO<sub>4</sub>, NO<sub>3</sub>, and Fe) are shown as scattered plot, in the figure 2-11. Fluoride is positively and significantly related to SO<sub>4</sub> and negatively related to Ca concentration (Figure 2 and Figure 3). Fluoride has a positive relation with pH (Figure 4). According to Chae et al. [3], a hydrogeochemical process that increases the fluoride concentration is closely related to a process that sinks for calcium. Fluoride is also negatively correlated with Mg (Figure 5). Due to precipitation of calcium carbonate, high fluoride, low Ca and Mg concentration is found in groundwater.

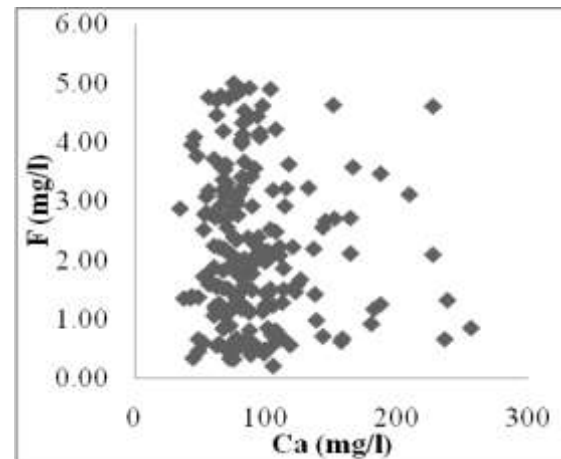


Figure 3. Correlation between F & Ca

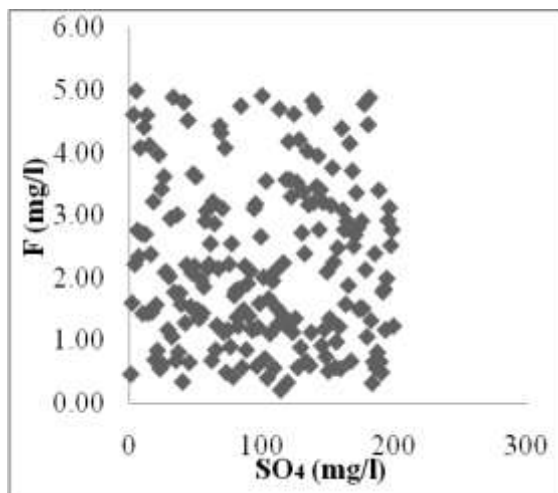


Figure 2. Correlation between F & SO<sub>4</sub>

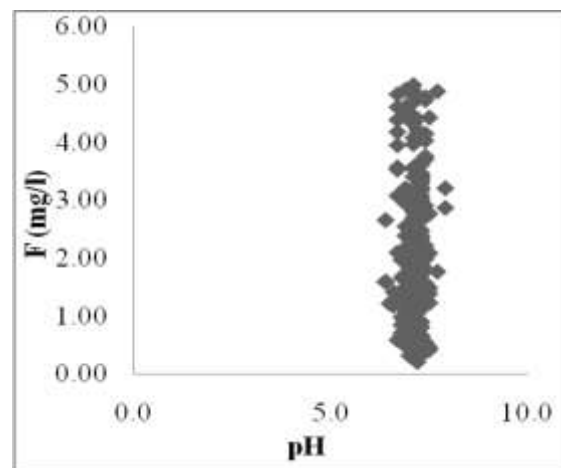


Figure 4. Correlation between F & pH

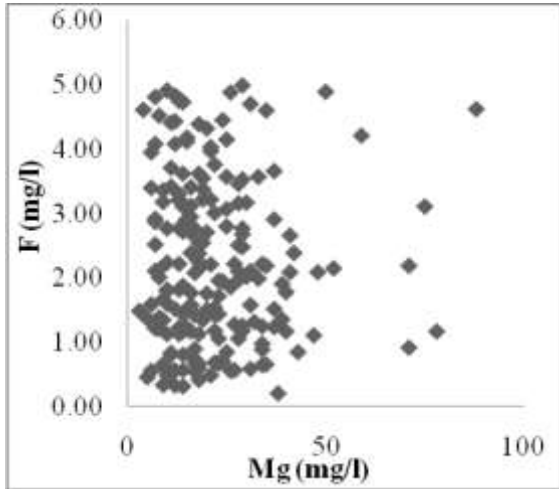


Figure 5. Correlation between F & Mg

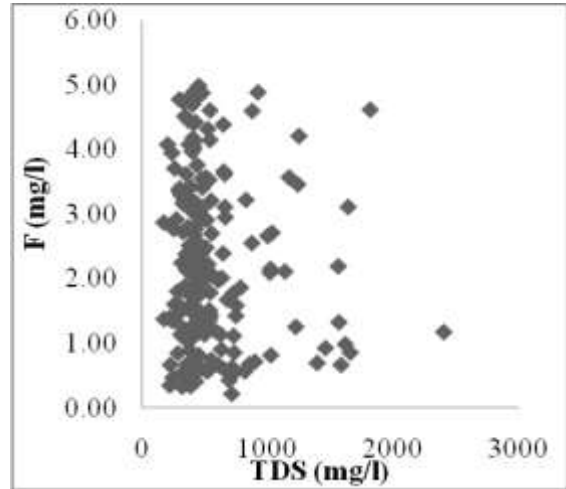


Figure 8. Correlation between F & TDS

The negative relation of fluoride with total hardness (Figure 6) is because of its precipitation as carbonates [18]. Fluoride shows a negative relation with alkalinity (Figure 7). As observed in water samples fluoride has a negative but poor correlation with electrical conductivity, total dissolved solids, chloride, nitrate, and iron (Figure 8-11).

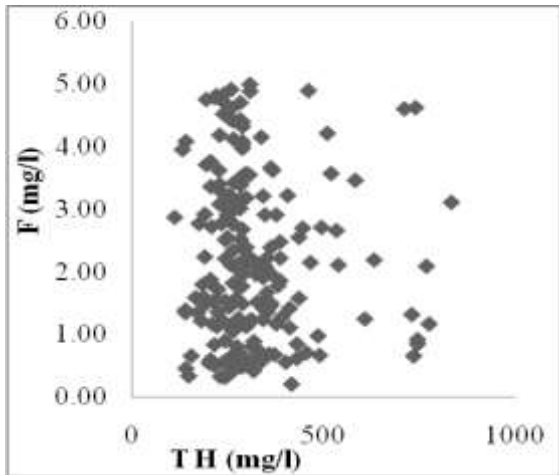


Figure 6. Correlation between F & TH

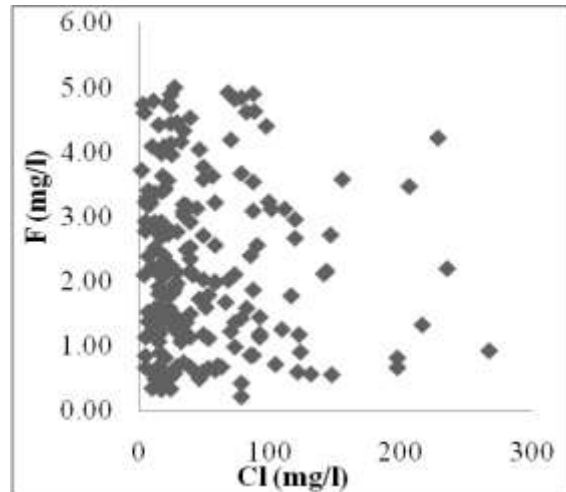


Figure 9. Correlation between F & Cl

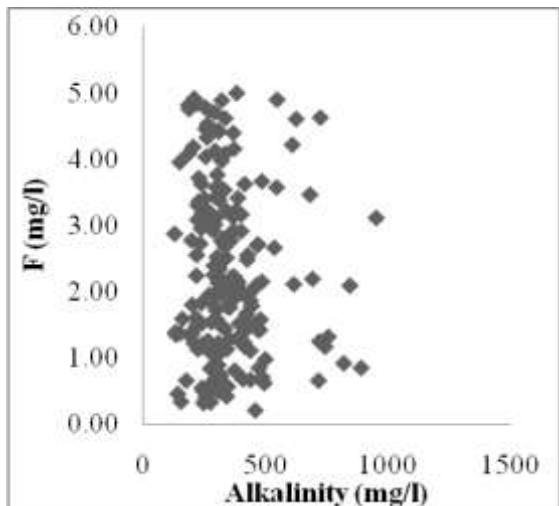


Figure 7. Correlation between F & Alkalinity

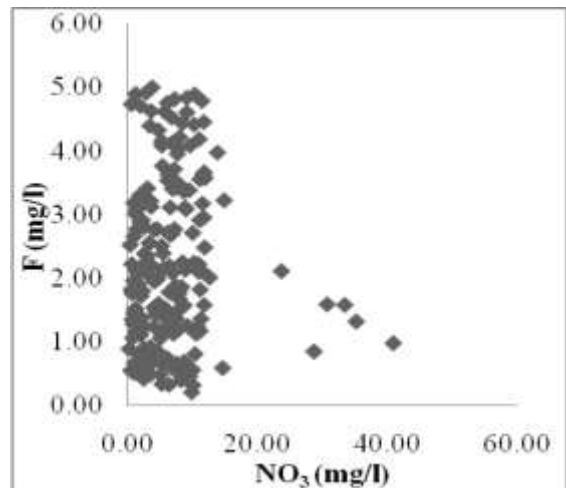


Figure 10. Correlation between F & NO<sub>3</sub>

#### IV. Conclusion

The groundwater is the main source of drinking water for the people of Amas Block of Gaya District, Bihar and the study revealed that the total dissolved solids in 39%, total alkalinity in 93%, total hardness in 10%, calcium in 64% and



magnesium in 19% samples exceeded the BIS acceptable limit but in case of chloride only one sample exceeded the BIS acceptable limit. In the case of nitrate and sulfate, none of the samples exceeded the BIS acceptable limit. Iron concentration was found high and samples exceeded the BIS permissible limit.

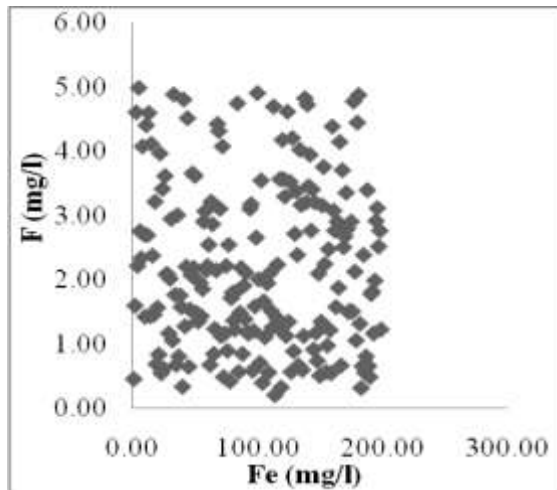


Figure 11. Correlation between F & Fe

The correlation matrix showed that electrical conductivity has a positive and significant correlation with total dissolved solids, total hardness, calcium, magnesium, and alkalinity. The total hardness was positively and significantly correlated with calcium, magnesium, and alkalinity. Fluoride has a significant positive correlation with pH and sulfate as well as a significant negative correlation with calcium, magnesium, alkalinity and total hardness. Additionally, fluoride has a negative correlation with electrical conductivity, total dissolved solids, chloride, nitrate, and iron whereas a negative correlation has been found between fluoride and alkalinity.

The groundwater was severely affected by fluoride contamination in the study area. Only 20% of samples were observed within the acceptable limit whereas 63% of samples exceeded the permissible limit as recommended by BIS (2012).

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