Original Research Article

Spatial distribution of fluoride in groundwater of Narasinghpur block, Cuttack, Odisha, India

ABSTRACT

Aims: Fluoride-rich groundwater is common in granite aquifers throughout India and the world. The fluoride concentration of tube well water was investigated in this study. Also discussion was made on fluorides and their correlation with other water-quality indicators.

Place and Duration of Study: The research area i.e. Narasinghpur block fall in the western half of the Cuttack district of Odisha under lateritic uplands and hilly tract. Before the rainy season (January, 2020), fifty two groundwater samples from different places in Narasinghpur were collected.

Methodology: The strategies and procedures utilised for collecting, preserving, analysing, and interpreting several parameters of water samples were done according to [14, 1, 2].

Results: The content of fluoride ranged from 0.58 to 4.95 mg L^{-1}. Fluoride containing minerals released into groundwater due to the alkaline pH and high bicarbonate levels. The arid environment of the region, the predominance of granitic, khondalitic, and charnockitic rocks, the longer contact time with fluoride-bearing minerals, and the minimal freshwater exchange are responsible for the high concentration of fluorides in the groundwater. Positive correlations were found between F^- and pH (r= 0.681**), Na^+ (r= 0.690**), and HCO_3^- (r= 0.719**), and negative correlations with Ca^{2+} (r= -0.565**) and Mg^{2+} (r= -0.597**).

Conclusion: Majority of the groundwater samples collected from gram panchayats falling under the block contained fluoride level higher than that set by BIS/WHO standard, posing a hazard to various ecosystems. The people dependent on these groundwater resources are prone to several health hazards.

Keywords: [Groundwater, fluoride, Granite, water quality]

1. INTRODUCTION

Most rural communities in India rely heavily on groundwater for domestic need. Groundwater is widely regarded as a safe source of potable water because it is relatively free of microbiological and inorganic chemical contamination and requires little treatment. Contaminants in groundwater that reach toxic levels in the aquatic environment are a major source of concern due to their ill effects on plants, animals, and human life. These pollutants are typically discharged through both natural (weathering, bedrock erosion, ore deposits, and volcanic activities) and anthropogenic (mining, smelting, industrial inflow, and agricultural operations) sources. Fluoride is one of the most frequent inorganic pollutants impacting people's health worldwide. F is the most electronegative and chemically reactive halide element. It is generally consumed by humans through drinking water, food, and polluted air [9]. High levels of fluoride in drinking water are a major cause of dental and skeletal fluorosis. About 2.5 to 6 million people in India, mostly children, are reported to have fluorosis as a result of drinking F containing groundwater [13, 3, 18]. (Based on the harmful effects of high fluoride on human health, the World Health Organization (WHO) developed a fluoride limit for drinking water of 1.5 mg L^{-1} [21]. Fluoride availability and enrichment in groundwater are primarily determined by the dissolution of fluoride-bearing minerals such as fluorite (CaF_2), sellaite (MgF_2), fluorapatite [$Ca_5(PO_4)_3F$], amphiboles, cryolite (Na_3AlF_6), topaz [$Al_2SiO_4(F,OH)_2$] and micas, clays found in the igneous rocks (such as granite, gneisses and pegmatite) and sediments [11, 15, 20]. Only a small amount of water may dissolve fluoride minerals. Due to its instability and quick formation of fluoride compounds, free fluorine has little impact on toxicity. Only favourable physicochemical conditions and sufficiently long residence times make the presence of dissolved fluoride possible [8, 7]. The present study attempted, to delineate the distribution of fluoride concentrations in groundwater and to determine its relationship with other chemical components in water.

2. MATERIALS AND METHODS

The study region situated at latitude 21°24'29"N and longitude 81°40'19"E of Cuttack district of Odisha. It comprised of an area 3432 km^2. The research area *i.e.* Narasinghpur block fall in the western half of the Cuttack district under lateritic uplands and hilly tract. The Laterite highland surrounding the hilly area is characterized by gently undulating topography supporting some flora. The average altitude varies from 50 to 100m above msl with the maximum of 337m. The granitic rocks mostly create undulating plain while the Khondalite and Charnockites constitute mostly the hills. The granitic rocks and charnokite-Khondalite rocks cover more or less fifty -fifty geographical area, in hard rock terrain [5]. 2013). Red soils are found in the hilly terrain while younger alluvial soil is located along the course of Mahanadi River. Bore wells and tube wells are the main sources of water supply for domestic and agricultural use. From 26 gram panchayat s of the Narsinghpur block, 52 groundwater samples were collected in polyethylene containers from tube wells. The water samples were refrigerated following collection. Fluoride was measured using an ion-selective electrode [19]. Other water quality measures including pH, electrical conductivity, total dissolved solids, total hardness, total alkalinity, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride, and sulphate were detected. The strategies and procedures utilised for collecting, preserving, analysing, and interpreting was done according to [14, 1, 2]. Geo-referenced ground water fluoride concentration data for Cuttack district was put in GIS software (Arc GIS 10.3) and map was developed. Descriptive statistics and Pearson correlation coefficient of physico-chemical parameters were accessed following the procedures of Snedecor and Cochran [17] using IBM SPSS Statistics 22.

3. RESULTS & DISCUSSION

Physical examination of the samples revealed that they are colourless and odourless. The examined parameters are explained briefly with reference to the range, the causes for the variations at different sites, the variation of fluoride and its link to other chemical parameters, etc. The descriptive statistics of the 52 water samples from the Narasinghpur region that illustrate the current situation of groundwater quality are depicted in Tables 1 and the Pearson correlation between many physico-chemical parameters is displayed in Table 2.

3.1 pH and Electrical Conductivity

The pH of groundwater varied from 7.32 to 8.67, which was related to the carbonates and bicarbonates present (r=0.492**, r=0.722**) (Table 1 & 2). The electrical conductivity (EC) of water samples varied between 0.33 and 1.63 dSm^{-1}, with a mean of 0.87 dSm^{-1} (Table 1). Some of the samples' high conductivity was presumably the result of extended and extensive agricultural operations, such as irrigation, and the natural geological conditions that result in large concentrations of dissolved minerals.

3.2 Calcium, Magnesium, Sodium, and Potassium

Calcium values ranged from 28.45 to 105.23 mg L^{-1}, with an average of 62.76 mg L^{-1} (Table 1). Its behavior in natural aqueous environments is typically determined by the presence of more soluble calcium compounds, solution–gas phase equilibria involving carbon dioxide species, or the presence of sulphur in the form of sulphate. In these groundwaters, calcium concentrations are noted to be low compared to other cations such as sodium. These reduced calcium and sulphate concentrations may be the result of calcium's interaction with sulphates (r=0.379**) and subsequent precipitation.

With a mean value of 38.71 mg L^{-1}, the Mg values ranged from 13.18 to 98.32 mg L^{-1} (Table 1). Magnesium exhibits cation exchange behaviour that is comparable to calcium's. Clay minerals and other surfaces with exchange sites strongly absorb both ions. Magnesium concentrations are higher than calcium concentrations because more magnesium is dissolved in water once calcium precipitates during super saturation.

Sodium values ranged from 19.34 to 102.93 mg L^{-1}, with an average of 52.10 mg L^{-1}. With a mean value of 24.44 mg L^{-1}, potassium values ranged from 1.76 to 51.56 mg L^{-1} (Table 1).

3.3 Carbonates, Bicarbonates and Total Alkalinity

The average carbonate content was 107.48 mg L^{-1}, with values ranging from 45.27 to 187.46 mg L^{-1}. Bicarbonate concentrations range from 213.37 to 1118.11 mg L^{-1}, with a mean value of 528.45 mg L^{-1}. With a mean value of 119.27 mg L^{-1}, alkalinity varied from 54 to 221 mg L^{-1} (Table 1). Carbonates and bicarbonates contribute to water alkalinity and hardness. Weathering of country rocks under semiarid climate of the region favoured production of CO_2 which combines with H_2O to form carbonic acid. The enhanced dissolution of carbonates by carbonic acid in the aquifers may explain the higher bicarbonate concentrations than the carbonate concentrations. Bicarbonate and carbonate levels depend on pH of water (r=0.722**, r= 0.492**) (Table 2). Bicarbonate increases to roughly 100 mg L^{-1} as pH rises from 7.0 to 8.0. Most natural waters (7.0–8.0) have more bicarbonates than carbonates [4].

The high prevalence of fluoride is mostly due to the alkalinity of the flowing water (r=0.631**) (Table 2). The extended residence time of water in the aquifer region, caused by a high incidence of evapotranspiration and a weathered zone with poor hydraulic conductivity, accelerates the dissolution of fluorine-bearing minerals, elevating F concentration in groundwater even more. Higher alkalinity of groundwater stimulates fluoride leaching, hence influencing fluoride concentration in groundwater [15].

3.4 Chloride and Sulfate

The chloride concentration ranged from 18.44 to 103.64 mg L^{-1}, with a mean of 53.04 mg L^{-1} (Table 1). This small levels of chlorides are essential for plant and animal cells to function normally. The sulphate concentration of the samples ranged from 23.17 to 96.21 mg L^{-1}, with an average of 45.51 mg L^{-1} (Table 1). Sulfates are related to the types of soil and bedrock minerals. Sulfur in the form of sulphate is an essential plant nutrient that, at low quantities, is not considered hazardous to plants or animals. Additionally, sulphate ions are engaged in complexing and precipitation reactions, which influence the solubility of metals and other compounds. These may be the causes of the reduced soluble sulphate amounts in these groundwater.

3.5 Fluoride

The average level of fluoride was 1.79 mg L^{-1}, with a range of 0.58 to 4.95 mg L^{-1} (Table 1). Fluoride concentrations in drinkable water should not exceed 1.5 mg L^{-1} [21]. Fluorides are dissolved from granitic or fluoride-bearing rocks in aquifers due to alkaline pH of the water. Additionally, OH^- readily replaces the F^- adsorbed on the clay surface, enriching F^- in an alkaline environment. Due to the comparable ionic radii of hydroxyl (OH^-) and fluoride (F^-) at alkaline conditions, F^- can be substituted with hydroxyl (OH^-) ion and transported from fluoride-bearing rocks and clay minerals into groundwater by ion exchange [10].

Fluoride concentrations in the environment can have a negative impact on human health. Water and food fluoride levels in fluoride rock regions are the primary means of fluoride exposure to the general populace [6]. Fluorosis can develop endemic in some locations due to a combination of geological processes, weathering of fluoride-bearing minerals, and hydrogeological conditions. Some areas of the region have varying levels of fluoride in their groundwater. Fluorine-bearing minerals may be present in different concentrations in the circulating water, but it could also be a result of weathering and leaching.

3.6 Total Dissolved Solids (TDS) and Hardness

TDS varied from 209.92 to 1,045.76 mg L^{-1} with an average value of 554.18 mg L^{-1}. Hardness ranged between 125.31 and 641.27 mg L^{-1} with a mean value of 316.14 mg L^{-1} (Table 1). Hardness in groundwater is mainly attributable to the presence of calcium and magnesium ions (r=0.823**, r=0.935**) (Table 2). Excess hardness is undesirable largely for economic or aesthetic reasons [12].

Table 1. Descriptive statistical analysis of the studied physico-geochemical parameters in groundwater (N = 52)

Parameters	Minimum	Maximum	Mean	Std. Deviation	Std. Error of Mean	Variance	BIS, 2012	WHO, 2011
pH	7.32	8.67	7.89	0.34	0.05	0.12	6.5-8.5	7.0-8.0
EC (dSm^{-1})	0.33	1.63	0.87	0.29	0.04	0.08	-	-
Ca^{2+} (mg L^{-1})	28.45	105.23	62.76	19.01	2.64	361.39	75.00	75.00
Mg^{2+} (mg L^{-1})	13.18	98.32	38.71	18.52	2.57	342.81	30.00	30.00
Na^{+} (mg L^{-1})	19.34	102.93	52.10	19.03	2.64	362.03	200.00	200.00
K^{+} (mg L^{-1})	1.76	51.56	24.44	11.63	1.61	135.19	12.00	12.00
CO_3^{-} (mg L^{-1})	45.27	187.46	107.48	39.13	5.43	1530.91	-	-
HCO_3^{-} (mg L^{-1})	213.37	1118.11	528.45	229.47	31.82	52656.38	497.00	500.00
Cl^{-} (mg L^{-1})	18.44	103.64	53.04	23.75	3.29	564.01	250.00	250.00
SO_4^{2-} (mg L^{-1})	23.17	96.21	45.51	15.56	2.16	242.09	200.00	250.00
F^{-} (mg L^{-1})	0.58	4.95	1.79	1.04	0.14	1.07	1.00	1.50
TDS (mg L^{-1})	209.92	1045.76	554.18	185.53	25.73	34420.20	500.00	1000.00
Alkalinity as $CaCO_3$ (mg L^{-1})	54.00	221.00	119.27	39.49	5.48	1559.69	200.00	-
Hardnessas $CaCO_3$ (mg L^{-1})	125.31	641.27	316.14	110.36	15.30	12179.92	200.00	-

3.7 Mutual Relationships between Fluoride and other Ions

It has been demonstrated that correlation coefficients are effective for determining the linear strength and direct link between fluoride and other ions. According to Table 2, a positive association (r=0.681**) exists between pH value and F^-. The pH level of groundwater plays a crucial effect in fluorine's presence. Numerous forms of fluorine, such as F, CaF^+, MgF^+, etc., exist in neutral and alkaline groundwater. As the pH level rises, soluble F acquires the dominant position. The activity of

Ca^{2+} decreases in alkaline groundwater (r=-0.619**) (Table 2), hence weakening the F^- aggregation ability and facilitating the enrichment of F^- in groundwater. The association between F^- content and Ca^{2+} content is negative (r=-0.565**) (Table 2). This can be explained by the interaction between calcium ion and fluorine ion, which leads to the development of insoluble apatite (Ca_5 $(PO_4)_3F$), fluorite (CaF_2) and other solid minerals when Ca^{2+} concentration increases [22]. According to Table 2, there is a positive association between F^- concentration and total dissolved solids (TDS) in water (r=0.685**), indicating that F^- concentration in groundwater rises as TDS increases. Evaporation gradually concentrates groundwater and increases the total dissolved solids (TDS). Minerals having a low solubility readily attain saturation and precipitate. Fluoride in groundwater is mostly derived from water-soluble fluorine ion in the study area, which continually increases with groundwater evaporation. As the TDS concentration rises, the total number of ions in water also rises, which promotes the dissolution of F in groundwater.

Table 2. Correlation co-efficient matrix of the physico-chemical parameters of the groundwater samples based on Pearson correlation coefficient method

Parameters	pH	EC (dSm^{-1})	Ca^{2+} ($mg\ L^{-1}$)	Mg^{2+} ($mg\ L^{-1}$)	Na^+ ($mg\ L^{-1}$)	K^+ ($mg\ L^{-1}$)	CO_3^- ($mg\ L^{-1}$)	HCO_3^- ($mg\ L^{-1}$)	Cl^- ($mg\ L^{-1}$)	SO_4^{2-} ($mg\ L^{-1}$)	F^- ($mg\ L^{-1}$)	TDS (mg /lit)	Alkalinity as $CaCO_3$ ($mg\ L^{-1}$)	Hardnessas $CaCO_3$ ($mg\ L^{-1}$)
pH	1													
EC (dSm^{-1})	0.587**	1												
Ca^{2+} ($mg\ L^{-1}$)	-0.558**	-0.372**	1											
Mg^{2+} ($mg\ L^{-1}$)	-0.482**	-0.429**	0.568**	1										
Na^+ ($mg\ L^{-1}$)	0.637**	0.659**	-0.358**	-0.454**	1									
K^+ ($mg\ L^{-1}$)	0.597**	0.566**	-0.460**	-0.542**	0.708**	1								
CO_3^- ($mg\ L^{-1}$)	0.492**	0.387**	-0.24	-0.246	0.308*	0.412**	1							
HCO_3^- ($mg\ L^{-1}$)	0.722**	0.730**	-0.364**	-0.462**	0.660**	0.673**	0.668**	1						

Cl^- (mg L^{-1})	0.12	-0.017	0.086	0.052	0.09	0.174	-0.033	0.004	1					
SO_4^{2-} (mg L^{-1})	-0.076	-0.048	0.379**	0.309*	0.02	-0.238	-0.233	-0.113	0.059	1				
F^- (mg L^{-1})	0.681**	0.685**	-0.565**	-0.597**	0.690**	0.652**	0.414**	0.719**	0.085	-0.234	1			
TDS (mg L^{-1})	0.587**	1.000**	-0.372**	-0.429**	0.659**	0.566**	0.387**	0.730**	-0.017	-0.048	0.685**	1		
Alkalinity as $CaCO_3$ (mg L^{-1})	0.604**	0.473**	-0.427**	-0.485**	0.523**	0.519**	0.369**	0.536**	0.078	-0.057	0.631**	0.473**	1	
Hardness as $CaCO_3$ (mg L^{-1})	-0.573**	-0.457**	0.823**	0.935**	-0.467**	-0.572**	-0.273**	-0.476**	0.073	0.376**	-0.656**	-0.457**	-0.519**	1

*** Correlation is significant at the 0.01 level (2-tailed).*

** Correlation is significant at the 0.05 level (2-tailed).*

3.9 Distribution Characteristic of Fluoride

There appears to be little uniformity in the horizontal distribution of groundwater fluoride concentration (Figs. 1, 2). The quantity of fluoride in groundwater increases from the west to the east of the block (Figure 2), and in nearly all gram panchayats, the F^- concentration in groundwater was higher than the permitted level set by BIS or WHO [2, 21]. Basantapur (P7), Chakamunda (P8), Jodum (P13), Kamaladihi (P15), Nizigarh (P19), Regeda (P23), and Saradhapur (P25) are some of the most severely afflicted regions with F^-. Since groundwater is the primary source of industrial and agricultural production, it is vital to evaluate the human health risk associated with groundwater in the research region.

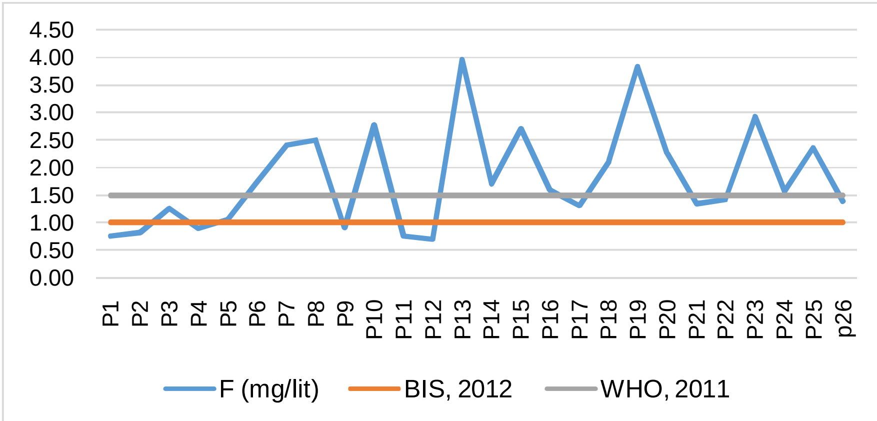

Fig.1. Comparison of mean fluoride concentrations in groundwater of 26 gram panchayats with WHO and BIS guideline of fluoride in drinking water

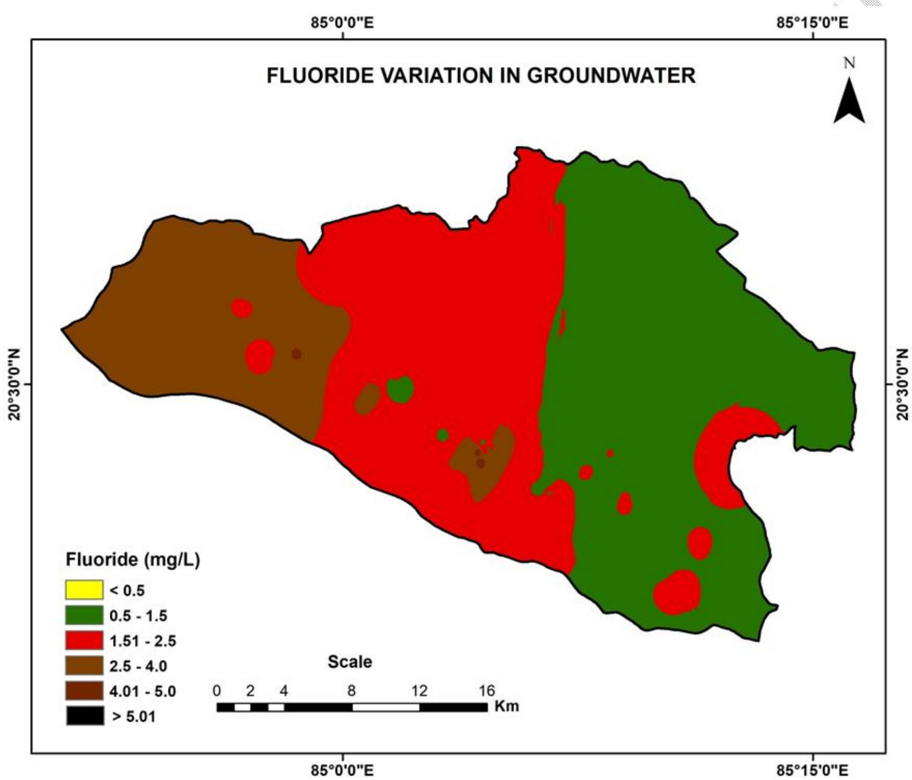

Figure 2. Map of fluoride concentrations in groundwater of Narasinghpur block (generated with ArcGIS desktop 10.3 programme)

4. CONCLUSION

The water samples in the research area are enriched in sodium, magnesium, and calcium among cations and bicarbonate, flouride among anions. The detected incidence of fluoride in the regions of Narasinghpur block is worrisome. In general, a significant proportion of groundwater samples had fluoride contents greater than 1.5 mg L^{-1}. Based on fluoride concentrations, the tubewell water is unfit for consumption. Lithology and soil are the primary elements that determine the quality of water. Fluoride levels in ground water are influenced by high ambient temperature, alkalinity, calcium, and magnesium. In fractured granitic, khondalitic and charnockitic rocks, fluoride concentrations in water are ubiquitous [16]. Due to extended contact time with fluoride-bearing minerals, ground water often contains a higher concentration of fluoride than surface water. The incidence of fluoride concentration is always localised, as demonstrated in Narasinghpur block, where the fluoride concentration in the villages varies considerably. Educating the public about the mechanisms necessary to enhance the health status of the population and emphasising public knowledge on the detrimental effects of excessive F^- concentrations in drinking water on human health are crucial. To remediate the impacted area, practical and cost-effective methods must be implemented. In addition, rainwater harvesting must be implemented to combat this fluoride danger.

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