Hydrogeochemical Framework and Factor Analysis of Fluoride Contamination in Groundwater within the Savelugu-Nanton District, Northern Ghana

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Abstract

Fluoride contamination of groundwater within the Savelugu-Nanton District was assessed using hydrogeochemical framework and multivariate statistical approach. Eighty-one (No) boreholes were sampled for quality assessment in May and June 2008. The main objective of this study was to assess the fluoride levels in groundwater and delineate areas of low fluoride and high fluoride within the district. The study show that, 41.9% of the boreholes are within the safe limits of 0.5 –1.5 mg/L of fluoride for the protection of bones and teeth, 43.2% of the boreholes have fluoride levels below the lower safe limit (< 0.5 mg/L) and therefore vulnerable to dental caries, 10.8% of the boreholes have fluoride levels between 1.5 and 3.0 mg/L and therefore vulnerable to dental fluorosis and 4.1% of the boreholes have fluoride levels between 3.0 and 10 mg/L and therefore vulnerable to skeletal fluorosis. The results further show that, 14.9% of groundwater requires defluoridation, while, 43.2% of groundwater requires fluoride addition to the groundwaters. PCA using Varimax with Kaiser Normalization results in the extraction of three main principal components which delineates the factors that influence the principal components of the physico-chemical parameters. The three principal components have accounted for approximately 83% of the total variance. Component 1 delineates the main natural processes through which groundwater within the basin acquire its chemical characteristics. Component 2 delineates pollution sources principally fluoride and nitrate. Component 3 suggests mineralogical influence of fluoride with some major ions on the chemistry of groundwater. The loadings and score plots of the first two PCs which explains 71.52% of the total variance show grouping pattern which indicates the strength of the mutual relation amongst the hydrochemical variables. Biological defluoridation though not very well understood, is recommended as a best alternative to the conventional methods of defluoridation especially in developing countries due to its cost effectiveness.

Introduction

Within the framework of the provision of drinking water supply globally, groundwater plays a significant role as it continues to provide a reliable source of the drinking water budget to the populations worldwide. The quality of groundwater therefore is paramount to the health needs and socio-economic development of a country. Generally, the quality of groundwater gives an indication of the mineral composition of the rocks with which the water is in contact (Hounslow, 1995). The sluggish movement of water in the subsurface environment results in the gradual alteration of its composition, thereby, reflecting the increasing end products of various water-rock interactions or the saturation of some ions (Hounslow, 1995).Thus, groundwater contamination is the result of the geochemical and biochemical processes taking place within the aquifer during water-rock interactions.

One of the globally widespread groundwater contamination challenges is low or high levels of fluoride in groundwater. Low fluoride concentrations (< 0.5 mg/L) in drinking water is known to cause dental caries, while, high fluoride concentrations (> 1.5 mg/L) causes dental and skeletal fluorosis (BIS, 2003; WHO, 2004).Consequently, according to the World Health Organization (WHO, 2004), the acceptable range of fluoride concentration in drinking water is 0.5–1.5 mg/L. Thus, waters with fluoride concentrations below 0.5 mg/L and above 1.5 mg/L are considered unsuitable for drinking purposes. Accordingly, Ayoob and Gupta (2006) have reported that, approximately two hundred (200) million people in twenty-five (25) nations across the world are exposed to health risks due to high fluoride levels in groundwater.

Earlier studies on fluoride contamination around the world include: periodic occurrence of high fluoride from India, Sri Lanka, China, West Indies, Spain, Holland, Italy, Mexico, Ethiopia and North and South American countries (Suma *et al.,* 1998). The weathering of rocks and evaporation of groundwater for instance, were reportedly responsible for high fluoride concentration in groundwater in the Nalgonda District of Andhra Pradesh in India (Brindha *et al.,* 2011). Widespread fluoride occurrence in top aquifer systems as against the critical limits of 1.5 mg/L in drinking water set by the Bureau of Indian Standards, Drinking water specifications (First Revision) IS 10500 in 1991 have also been reported in many parts of Andhra Pradesh, Tamil, Nadu, Karnataka, Gujarat, Rajasthan, Punjab, Haryana, Bihar and Kerala in India (Suma *et al.,* 1998).

Other reported cases of fluorosis worldwide include; increased incidence of dental and skeletal fluorosis due to high fluoride concentration in drinking water in India with about sixty-two (62) million people at risks (Andezhath *et al.,* 1999), widespread dental fluorosis in fourteen (14) states and one hundred and fifty thousand (150,000) villages in India especially in the Andhra Pradesh, Gujarat, Rajasthan, Madhya Pradesh, Punjab, Bihar, Tamil, Uttar Pradesh and Nadu states (Pillai and Stanley, 2002). Fluoride contamination in groundwater therefore, is a widespread endemic health problem associated with groundwater geochemistry.

Fluoride contamination of groundwater through natural geochemical processes can cause irreparable damage to plant and human health. Excessive oral intake of fluoride results in kidney damage, thyroxine changes, physiological disorders and skeletal and dental fluorosis in humans (Grandjean *et al.,* 1992). Acceptable levels of fluoride in humans, is capable of preventing tooth decay. In view of this, in the developed countries, fluoride is sometimes added to drinking water with fluoride levels below 0.5 mg/L in order to prevent dental fluorosis. However, excessive fluoride in drinking water can result in serious health problems including malformed bones and neurological disease.

The application of multivariate statistical methods to geo-environmental datasets have aided the disclosure of hidden structures in the datasets and assisted in solving key geo-environmental problems at various scales (Sandaw *et al,* 2012). Despite the fact that, statistical associations do not ascertain cause-and effect relationships, they provide useful associations from which such relationships can be deduced. Previous classical applications of multivariate statistical approaches in the Earth Sciences are contained in Güler *et al.* (2002); Cluotier *et al.* (2008); Jiang *et al.* (2009) and Kim *et al.* (2009). With the aim of unearthing the hidden processes responsible for high nitrate concentrations in groundwater, Jiang *et al.* (2009) applied multivariate methods to the major physico-chemical parameters in groundwater from Yunan, China and subsequently, assigned anthropogenic contributions to groundwater contamination in the area. In their study, the researchers combined factor analysis with geospatial methods to ascertain the spatial distribution of the major causes of variation in groundwater quality within the area.

Access to groundwater within the Upper Region especially in the Bolgatanga and Bongo Districts and some parts of the Northern Regions in Ghana presents serious health problems with respect to dental and skeletal fluorosis (Apambire *et al.,* 1997). According to the statistics obtained from the Community Water and Sanitation Agency (CWSA), out of a total population of about one million nine hundred thousand (1,900,000) in eighteen (18) districts of the Northern Region of Ghana, only 59% of the population has access to potable water.

To further worsen the problem of non-availability of potable water to these districts, groundwater supplies to the 59 % of the populations in these districts are potentially exposed to fluoride contamination. According to Apambire *et al.* (1997), in a few cases, high levels of fluoride in groundwater within the granitic terrain of the Northern Region of Ghana is attributable to groundwater contact with rocks that have particularly high fluorine contents. However, most fluoride-rich waters are found in sandy aquifers where, the rocks contain fluorine levels typical of background levels (Apambire *et al.,* 1997).

Assessment of water supply systems especially in groundwater within the Northern Region, including the Savelugu-Nanton District to ascertain areas of low and high fluoride levels and their sources is therefore, of outmost importance to the health needs and socio-economic development of the consuming public.

Earlier studies on groundwater by the CSIR-Water Research Institute in the area include; Borehole inventory, numbering and functionality survey- final district specific functionality report (2006); Borehole inventory, numbering and functionality survey- final district specific preliminary hydrogeological report (2006) and hydrochemistry of groundwater in the Savelugu-Nanton District, Northern Ghana (Tay, 2012). Elsewhere in the Upper Regions of Ghana, Apambire *et al.* (1997) conducted a study on the geochemistry, genesis, and health implications of fluoriferous groundwaters. The study showed that, 49 % of consumers within the area are potentially exposed to dental caries as fluoride concentrations in the wells were below the WHO (2004) minimum acceptable limit of 0.5 mg/L, 28% of the wells were within the WHO optimum interval for good dental health of 0.5–1.5 mg/L, while, 23% of consumers were susceptible to dental and skeletal fluorosis as fluoride concentrations in the wells were above the WHO maximum acceptable limit of 1.5 mg/L. Yidana *et al.* (2012), conducted a study on a factor model to explain the hydrochemistry and causes of fluoride enrichment in groundwater from the middle Voltaian sedimentary aquifers in the Northern Region of Ghana and concluded that, fluoride enrichment in the study area is related to the weathering of silicate minerals. However, the literature do not indicate detailed studies on possible dental caries or dental and skeletal fluorosis through drinking of groundwater supplies within the Savelugu- Nanton District.

It is against this background that, this study seeks to assess the fluoride levels in groundwater within the Savelugu-Nanton District to ascertain whether communities with access to groundwater from the district are vulnerable to low (< 0.5 mg/L) or high (> 1.5 mg/L) fluoride intake from groundwater and consequently, ascertain the health related problems (whether dental caries or dental and skeletal fluorosis) associated with fluoride intake from groundwater within the district. The study also seeks to employ multivariate statistical approach for the assessment of the physico-chemical parameters in order to uncover the hidden processes responsible for groundwater contamination within the district.

Study area

Location

The location of the Savelugu-Nanton District is between latitudes 9° 28’ N and 10° 08’ N, and longitudes 0° 39’ W and 1° 02’ W. The district’s boundary to the east and west are the Gushiegu/Karaga and Tolon-Kubugu Districts respectively, and to the north it is bounded by the West Mamprusi District and to the south by the Tamale metropolis. Fig. 1 presents the map of the Savelugu-Nanton District showing sampling communities.

Geomorphology

The district is extremely flat and gently rolling with topographic elevation which range 120–185 m above sea level (Dickson and Benneh, 2004). The Savelugu-Nanton District is characterized by several dams and streams such as the Zulabong and Peli, which flow into the White Volta River (Dickson and Benneh, 2004). Several marshy areas also exist, especially at the low-lying grounds and the confluence of the Mbuom and Peli streams, which join the Nabogo and Zulabong streams into the White Volta River (Dickson and Benneh, 2004).

Climate and Vegetation

The district lies within the Interior Savannah climatic or Tropical Continental zone and experiences a single rainfall season between May and October (Dickson and Benneh, 2004). Annual rainfall within the district ranges between 1005 and 1150 mm with the heaviest occurring in August (Dickson and Benneh, 2004). Daily temperatures are generally high (above 35° C) except during the

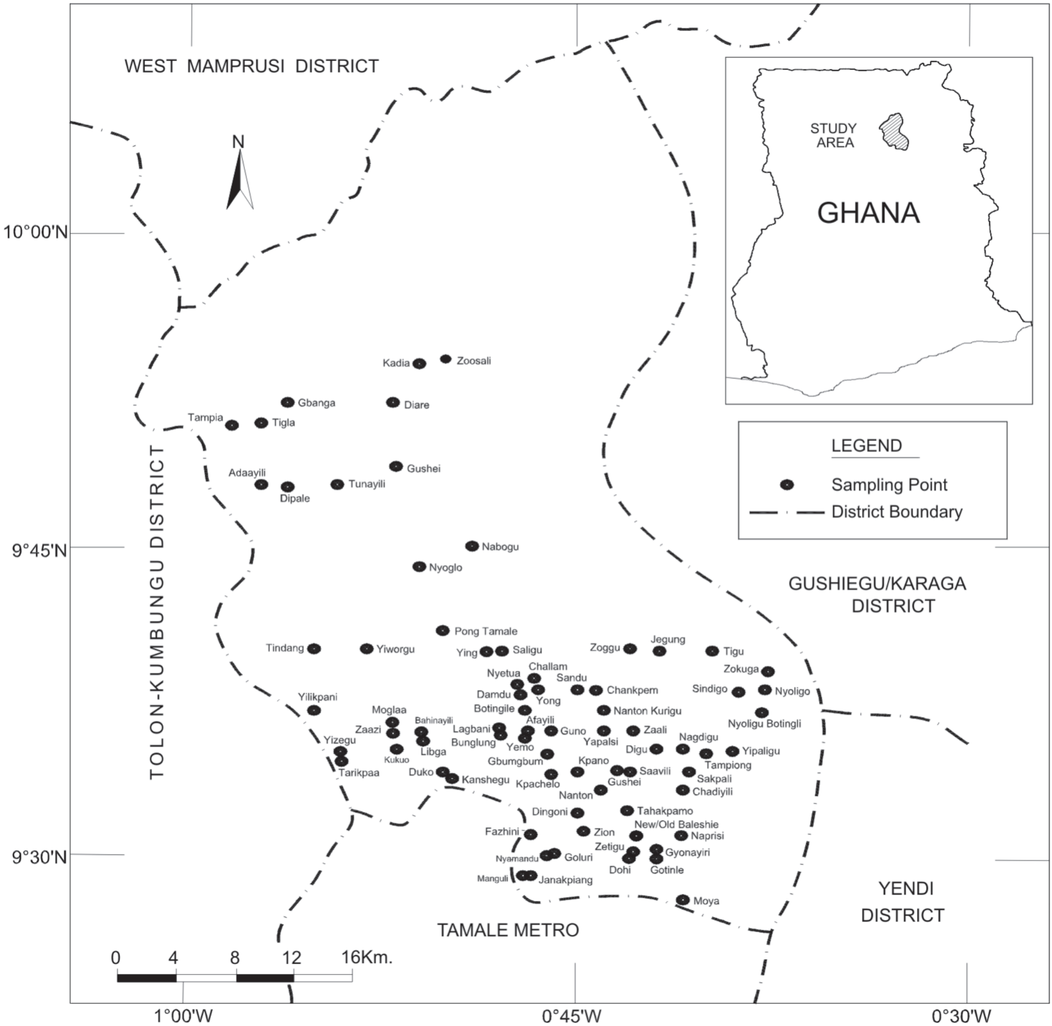

Fig. 1. Map of the Savelugu-Nanton District showing sampling communities.

harmattan season (November-February) when temperatures fall to 20 °C and below especially during the night (Dickson and Benneh, 2004). Mean monthly temperatures vary between 36° C in March/April to 27 °C in August (Dickson and Benneh, 2004). Relative humidity is high during the rainy season (65–85%) but may fall to as low as 20% during the dry season (Dickson & Benneh, 2004). The district lies in the Savannah vegetation zone characterized by tall grasses, which grow in tussocks, and widely scattered trees such as baobab, dawa-dawa, acacia and shea (Dickson & Benneh, 2004).

Geology and soil

According to Kesse (1985) the rock types of the district is homogeneous, with sandstone, mudstone, shale and conglomerates of the Oti and Obosum beds of the Middle Voltaian System principally forming the only basement rocks that underlie the district. The Upper Voltaian sandstone and quartzite occur at a small section at the extreme southeast. The Middle and Upper Voltaian Sedimentary formations characterize the geology of the Savelugu-Nanton District (Kesse,1985). The Middle Voltaian covers the northern part of the district and comprises of sandstone, shale and siltstone. The Upper Voltaian covers the southern part of the district and consists of shale and mudstone (Kesse, 1985).

Groundwater occurrence

Hydrologically, the characteristics of the Palaeozoic Voltaian Sedimentary rocks are similar to that of hard rocks (Gill, 1969). The sandstones contain openings along joints and fractures, bedding and cleavage planes and are mainly impervious (Gill, 1969). In sandstones in which these openings are extensive and are not filled with impervious material, groundwater reservoirs are formed through considerable percolation of water into the regolith (Gill, 1969). Gill (1969) also reported that, lateritic cover renders the shale poor in groundwater and areas underlain by mudstone are generally impermeable. Water is tapped in wells located in the fractures or fracture zones with saturated regolith rather than from extensive aquifers (Gill, 1969). The regolith or weathered layer developed on the fractures and rocks within the bedrock constitutes the principal sources of groundwater supply to the rocks (Gill, 1969). Wherever the saturated regolith is thin or absent, ample permeability has to be identified in the fractured rock such that local drawdown interacts with storage in the overlying regolith to provide continued yield (Gill, 1969). Depending on factors such as topography, the regional climatic conditions, the degree of fracturing, as well as vegetation cover the thickness, extent and physical character of the weathered layer differ from one weathered layer to another (Gill, 1969). During the wet seasons, the water table generally gets higher, supplying water to a number of shallow wells (Gill, 1969). Additionally this permits the movement of fresh recharge water beyond the weathered zone into the fractured aquifer, particularly in places where there is hydraulic continuity between the weathered zone and the underlying fractures or fissures (Gill, 1969). Thus, the basement aquifers formed are typically phreatic to semi-confined in character, and structurally dependent and often discontinuous in occurrence (Gill, 1969). Due to the fact that, water is tapped in wells located in the fractures or fractured zones with saturated regolith rather than from extensive aquifers, boreholes drilled in the predominantly hard rock environment have a wide range of yields, with a high failure rate. Borehole depths within the study area ranged 27.7–72.6 m and mean 41.7 m, with varied yield which ranged 6–302 l/min and mean 47.7 l/min.

Previous study by the CSIR-WRI (2006) showed that a plot of yield against depth showed no apparent correlation between yield and depth. However, it was clear that beyond 60 m depths, yields decrease. Generally, groundwater potential is determined by the Middle Voltaian sedimentary formation, which has varying potential for groundwater compared to the Upper Voltaian formation.

Materials and methods

Sampling and analysis

Eighty-one (81) water samples were collected from boreholes between May and June 2008. Sampling protocols described by Claasen (1982) and Barcelona *et al*. (1985) were strictly observed during sample collection. Samples were collected using 4–1 acid-washed high-density linear polyethylene (HPDE) containers to avoid unpredictable changes in sample characteristic as per standard procedures (APHA, 1998). The polyethylene bottles were soaked in water with 10% HNO_3 washed and pre-rinsed with distilled water. The samples were collected into 1 litre polyethylene bottles without preservation.

All samples were stored on ice in an ice-chest and transported to the Potable Water Section of the Environmental Chemistry and Sanitation Engineering Division of the CSIR–Water Research Institute laboratories in Accra, stored in a refrigerator at a temperature of 4 °C and analyzed within 1 week. Temperature, pH, and electrical conductivity were measured on-site using Hach Sens ion 156 Meter.

Chemical analyses of the samples were carried out using appropriate certified and acceptable international procedures outlined in the Standard Methods for the Examination of Water and Wastewater (APHA, 1998); sodium (Na) and potassium (K) were analysed by flame photometric method; calcium (Ca) by EDTA titration; Magnesium (Mg) by calculation after EDTA titration of calcium and total hardness; chloride (Cl) by argentometric titration; fluoride was determined using SPANDS method. Standard concentrations of fluoride are prepared in the range of 0.1–10.0 mg F^- /L by diluting appropriate quantities of the standard fluoride solution to 50 ml with deionized water. 5ml each of SPANDS solution and zirconyl-acid reagent is pipetted and added to the standards and mixed well. The absorbance of the mixed solution is obtained using the spectrophotometer. A graph of the milligram fluoride- absorbance relationship is then plotted. A 50 ml of the sample to be measured is taken and a 5ml each of SPANDS solution and zirconyl-acid reagent are added. The solution is mixed well and the absorbance is read.

Fluoride concentration for each sample is then determined from the calibration curve.

Quality ontrol

For every batch of 5 samples a duplicate is prepared and run. A blank sample is also analyzed together with unknown sample to assess contamination of samples. A control standard of 1 mg/L F^- is prepared and run together with the samples. The values are plotted on the control chart. If the values fall outside the action limit of ± 3δ a fresh control standard is prepared.

Statistical analyses

Statistical analyses were performed using Statistical Programme for Social Sciences (SPSS) 16.0 for windows. PCA technique was used to reduce the dimensionality of the dataset, while, as much as possible, retaining the variability presented in a dataset. The Spearman correlation matrix was generated to determine any relationship between the observed parameters in order to explain factor loadings during PCA. In order to ensure normality of the data all hydrochemical data (except pH) were log-transformed prior to statistical analyses. The hydrochemical data was also auto-scaled by calculating the standard scores (z scores) and ensuring that all z scores are < ± 2.5. A probability value of $P < 0.05$ was considered as statistically significant in this study. An eigenvalue gives a measure of the significance of the factor and the factor with the highest eigenvalue as the most significant. Eigenvalues of 1.0 or greater are considered significant (Kim and Mueller 1978). Factor loadings are classified as 'strong', 'moderate' and 'weak' corresponding to absolute loading values of > 0.75, 0.75–0.50, 0.50–0.30 respectively (Liu *et al.,* 2003).

Results and discussions

Table 1 presents the summary statistics of the hydrochemistry of groundwater within the district, while, Table 2 presents fluoride doses and their effects on human health alongside with the percent (%) of population with access to groundwater and their potential exposure to fluoride contamination. Fluoride concentration within the district range 0.1–4.1 mg/L, with a mean value of 0.79 mg/L. From Table 2, 43.2% of groundwater within the district had fluoride concentration below the WHO lower limit of 0.5 mg/L, suggesting dental caries, 41.9% of groundwater within the district had fluoride concentration within the WHO guideline limit of 0.5–1.5 mg /L, while, 10.8% of groundwater had fluoride concentrations within 1.5–3.0 mg/L, suggesting dental fluorosis and 4.1% of groundwater had fluoride levels within 3.0–10.0 mg/L suggesting skeletal fluorosis. The results further show that, 14.9% of groundwater requires defluoridation, while, 43.% of groundwater requires fluoride addition to the groundwaters. Fig. 2 presents F^- concentrations against pH in groundwater within the district. Fig. 2 shows that, there is a weak positive correlation between F^- and pH in groundwater within the study area. Boyle (1992); Macfarine *et al.,*(1992); Queste *et al.* (2001); Saxena and Ahmed (2001) have shown a positive pH – fluoride correlation in areas with high fluoride in groundwater especially in

TABLE 1
Summary statistics of the hydrochemistry of groundwater within the Savelugu-Nanton District

Parameter	*Min*	*Max*	*Mean*	*Median*	*Stdev*	*WHO (2004) Guideline limit*
pH	6.1	8.3	7.4	7.5	0.4	6.5–8.5
Temp	25.6	32.8	28.4	28.1	0.9	
TDS	62	11900	942.2	405	1686	1000
Ca^{2+}	5.1	1156	99.6	45	165.7	200
Mg^{2+}	6.6	520	46.7	20.3	52.7	150
Na^{+}	6.2	754	71.1	26.9	121	200
K^{+}	0.1	70	7.4	3	13	30
HCO_3^-	31	4095	506.0	280	745	
SO_4^{2-}	0.4	947	38.6	5.2	106.3	250
F^-	0.1	4.1	0.79	0.72	0.82	0.5–1.5
Cl^-	1.3	1260	56.8	10.4	147.5	250

All parameters are measured in mg/L, except, EC(ìS/cm), pH (pH units), Temp (°C)

TABLE 2
Fluoride doses and their effects on human health alongside the percent (%) of population with access to groundwater and their potential exposure to fluoride contamination within the basin.

Fluoride dose	*Corresponding effects on human health*	*Percent (%) of consumers exposed to human health through drinking water within the study area*
< 0.5	Dental caries	43.2
0.5- 1.5	Protection against dental caries. Safe limit for bones and teeth	41.9
1.5 -3.0	Dental fluorosis	10.8
3.0 – 10.0	Skeletal fluorosis (adverse changes in bone structure)	4.1
> 10	Crippling skeletal fluorosis and severe osteoclerosis	-

geological formations with sandy aquifers such as the Upper Voltaian sand stone of the district. According to Hubner (1969); Deshmukh *et al.* (1995), fluoride is readily adsorbed in clay minerals under acidic conditions and desorbed in alkaline environments. The positive correlation between F^- and pH and HCO_3^- in the shallow aquifers within the area suggests the dissolution of F^- under alkaline conditions through the substitution of OH^- ion in groundwater. The pH of groundwater

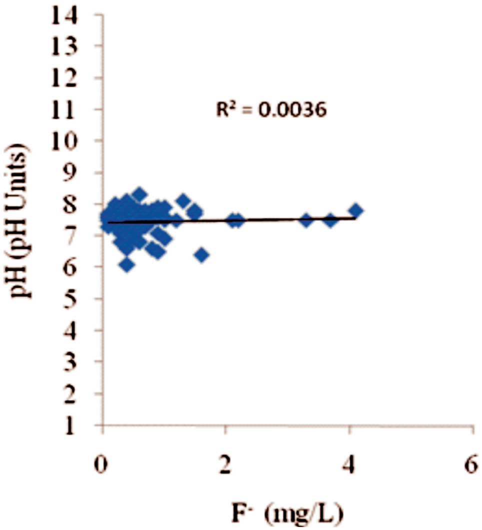

Fig. 2. Plot of F^- against pH

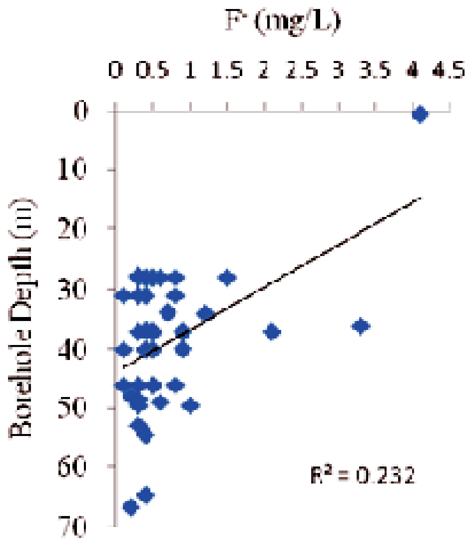

Fig 3: Plot of F^- against borehole depth

show slight increase with increasing fluoride (Fig. 2) suggesting that, fluoride content in groundwater within the district will vary as a result of variations in alkalinity- i.e, carbonate and bicarbonate content (Brindha *et al*., 2011). Several studies have shown that fluoride in groundwaters generally increases with depth to an extent where, water use authorities are required to control well drilling depths, particularly for municipal well supplies (Boyle and Chagnon, 1995). Fig. 3 presents a scatter plot of F^- against borehole depth for groundwater within the district. Fig. 3 shows that, there is no apparent relationship between F^- concentration and borehole depth. This suggests that, the structural entities controlling the hydrogeological properties of the rocks are distinct and therefore do not vary with depth (Yidana, 2012).

According to Madhnure *et al.* (2007), a positive correlation between F^- and pH and HCO_3^- in groundwaters suggests the dissolution of F^- under alkaline conditions through the substitution of OH^- ion and constitutes favourable conditions for the dissolution of CaF_2 in groundwater. Tay (2012), showed that, groundwater within the district is predominantly Ca-Mg-HCO_3 type, where the chemical properties of the water are dominated by alkaline earths and weak acids. Thus, the dissolution of CaF_2 in groundwater is probable. However, there is a weak positive correlation between Ca^{2+} and F^- (Fig. 4). This suggests that, there are no Na-HCO_3 type groundwaters which are associated with base-exchange (Ca and Mg for Na) processes which often results in highly fluoriferous, high-pH, Na-HCO_3 waters in other regions of the world (Boyle, 1992). This is consistent with the results from the current study where only 9.5% of groundwater had fluoride concentrations

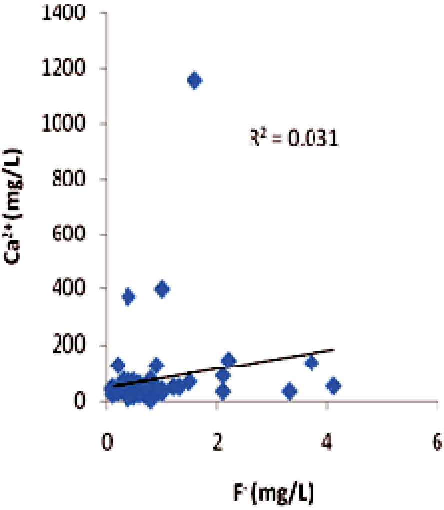

Fig. 4. Plot of F^- against Ca^{2+}

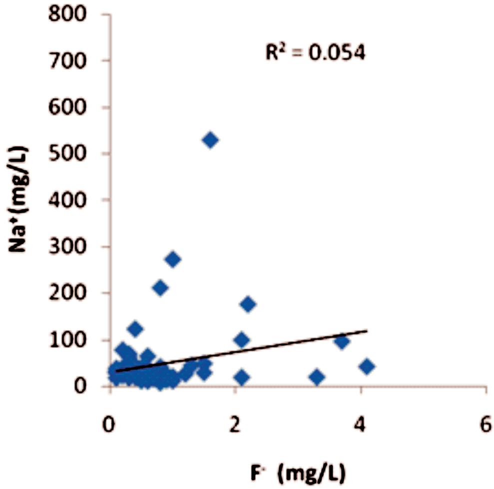

Fig. 5. Plot of F^- against Na^+

exceeding the WHO (2004) upper guideline limit of 1.5 mg/L. Fig. 5 presents a weak positive correlation (R^2 = 0.052) between F^- and Na^+ suggesting a weak chemical relationship between these ions. According to Apambire *et al*., (1997), Na^+ shows positive correlation with F^- in several groundwater types.

According to Brindha, *et al.,* (2011), fluoride content in groundwater will vary as a result of alkalinity variations (i.e, carbonate and bicarbonate content) with increasing pH. This is consistent with the slight increase in fluoride content of groundwater within the study area with increasing bicarbonate concentration (Fig. 6).

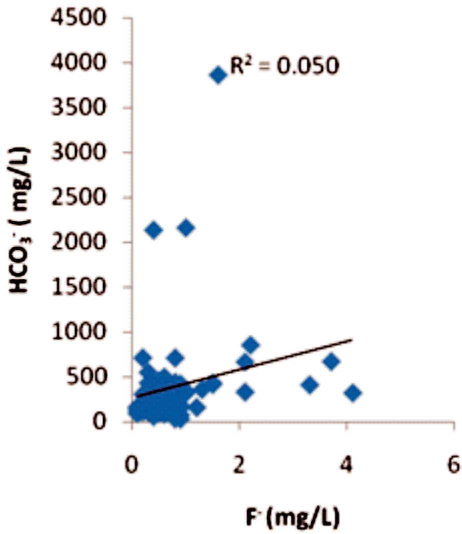

Fig 6: Plot of F^- against HCO_3^-

Health effects of Fluoride through drinking water consumption within the Savelugu-Nanton District

Fluoride is an essential element, which is good for the teeth enamel and helps to prevent dental caries (BIS, 2003). However, excessive doses of fluoride results in dental and skeletal fluorosis, while, low doses results in dental caries (BIS, 2003). Both conditions, whether low or excessive fluoride in drinking water results in chronic fluoride poisoning (WHO, 2004). The effects of fluoride on human health can be very severe depending on the amount of fluoride that has been ingested (WHO, 2004). This is because fluorine is very electronegative and thus easily binds to the positively charged calcium ions in teeth and bone (WHO, 2004). In large quantities fluoride can also affect the kidneys and the thyroid gland and in the most extreme cases it can lead to death (WHO, 2004). WHO (2004) recommends that drinking water should ideally contain 0.5–1.5 mg/L fluoride for the prevention of dental caries as well as dental and skeletal fluorosis. Osteoporosis is a condition that affects the bones in which the bones of the victims become very fragile and breaks very easily (Lundell and Rennel, 1996). Fluoride can be used to treat that condition as it affects the enzyme that controls the production and degradation of bone (Lundell and Rennel, 1996). This result into a faster production than degradation and the bones will become less fragile (Lundell and Rennel, 1996). Low fluoride concentration provides protection against dental caries, especially in children. This protective effect increases with fluoride concentration up to 2 mg/l of fluoride in drinking water. The minimum concentration of fluoride in drinking water required to produce the effect is approximately 0.6 mg/l. High fluoride concentrations exert a negative effect on the course of metabolic processes and consequently individuals may suffer from dental fluorosis, skeletal fluorosis (capable of causing joint pain, restriction of mobility, and possibly increase the risk of some bone fractures) and non-skeletal manifestations. Table 2 presents the health situation within the Savelugu-Nanton District in respect of fluoride ingestion through access to drinking water. From Table 2 only 41.9% of the boreholes are within the safe limits (0.5–1.5 mg/L for fluoride) for the protection of bones and teeth. 43.2% of the boreholes have fluoride levels below the lower safe limit (< 0.5 mg/L) and therefore exposed to dental caries, 10.8% of the boreholes have fluoride levels between 1.5 and 3.0 mg/L and therefore exposed to dental fluorosis and 4.1% of the boreholes have fluoride levels between 3.0 and 10 mg/L and therefore exposed to skeletal fluorosis, with the highest fluoride level in drinking water within the district as 4.1 mg/L though. Higher levels of fluoride have been reported in other regions of the world such as 5.2 mg/L in Medak District, Andhra Pradesh (Srikanth *et al*., 1994), 15 mg/L in Nawabganj Block, Uttar Pradesh (Mukherjee *et al*., 1995), and 18 mg/L in Jaipur, Rajasthan (Agrawal *et al.,* 1997).

Spatial distribution of fluoride in groundwater within the Savelugu-Nanton District

The spatial distribution of fluoride in groundwater within the district has been expressed as a symbol plot (Fig. 7). The WHO (2004) guideline limit of fluoride has been adopted in presenting the spatial distribution plot. Clearly from Fig 7, the northern part of the district towards the middle belt from Zoosali to Nyoglo, with the exception of Tampia, Tigla and Dipale with fluoride levels < 0.5 mg/L, > 3.0

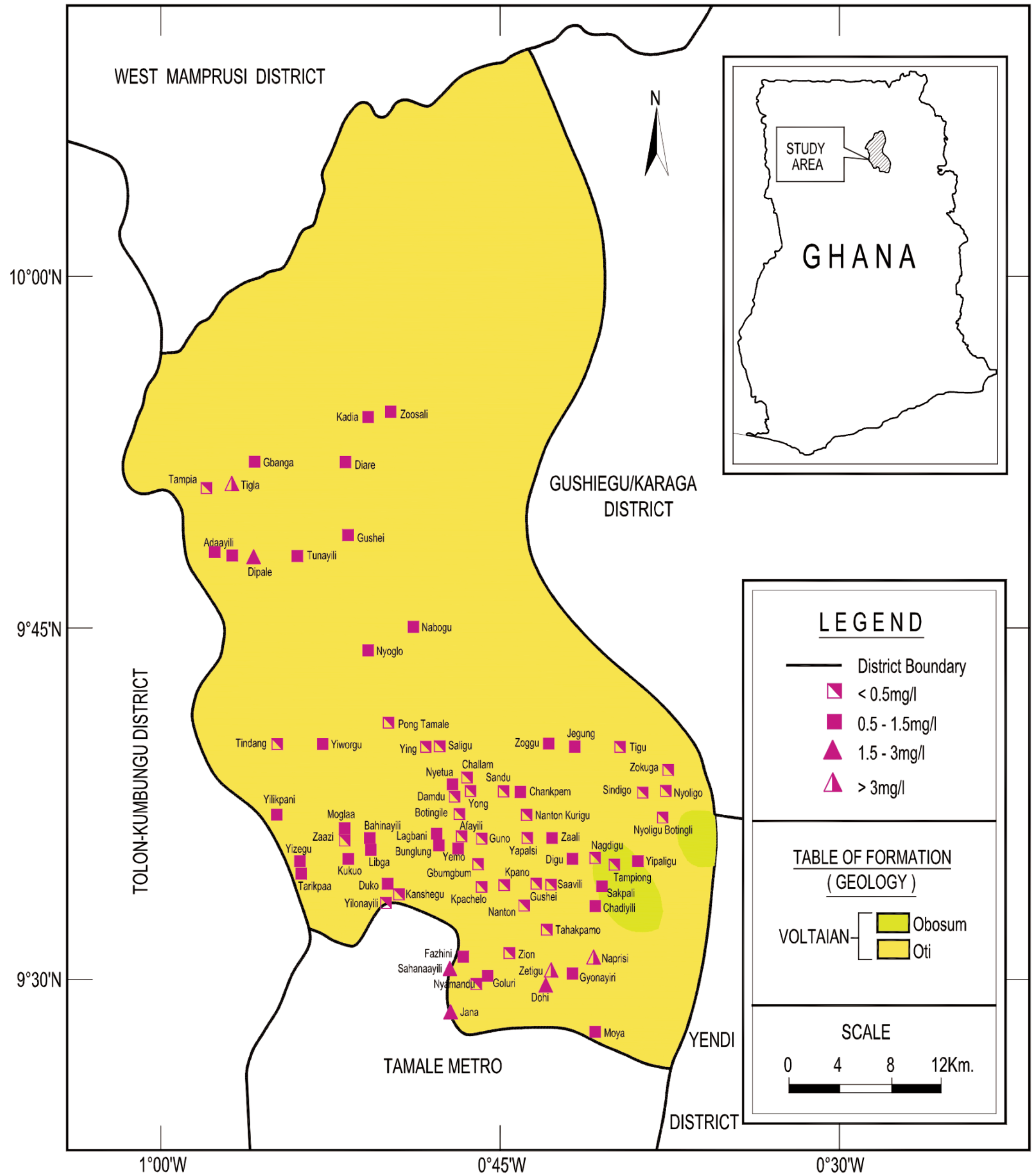

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Fig. 7. Spatial distribution of fluoride in groundwater within the Savelugu-Nanton District

mg/L and 1.5–3.0 mg/L respectively, had fluoride levels within safe limits (0.5–1.5 mg/L) set by WHO. Majority of groundwater in the south-eastern part of the district from Pong Tamale, to Zeligu, with the exception of Zoggu, Jegung, Chankpem, Zaali, Digu, Sakpali, Chadiyili, Yapaligu, Moya, Gontile, Ligba and Kukuo with fluoride concentration within safe limit (0.5–1.5 mg/L) set by WHO (2004), had fluoride levels below the lower limit of < 0.5 mg/L and therefore, consumers in these communities are exposed to dental caries. However, Dohi, Manguli and Fazhini had fluoride levels between 1.5–3.0 mg/L and therefore, consumers of the groundwaters in these communities are exposed to dental fluorosis. Zetigu and Naprisi also within the south-eastern part of the district had fluoride levels in groundwater > 3.0 mg/L and therefore consumers of the groundwaters in these communities are exposed to skeletal fluorosis. Fluoride levels in groundwater within the south-western parts of the district are generally within the safe limits set by the WHO (2004).

Hydrogeochemical framework of F^- concentration in shallow aquifers within the Savelugu-Nanton District

According to Apambire *et al.,* (1997), the fluoride content in "hard" groundwaters (low Na concentration) is generally within the range 0.02–3.0 mg/L. Results from this study show that, 95.9% of groundwater within the district had fluoride levels within 0.02–3.0 mg/L. Tay (2012) also delineated Ca-Mg-HCO_3 as the major water type within the district. This suggest that, groundwater within the district could be regarded as "hard" with low Na concentration (Table 1) and therefore the generally low fluoride content in groundwater within the district is expected. Apambire *et al.,* (1997) reported that, elevated fluoride in the granitic terrain of the Northern Region of Ghana in a few cases is attributable to groundwater contact with rocks that have particularly high fluorine contents, however, most fluoride-rich waters are found in sandy aquifers where the rocks contain fluorine levels typical of background levels. Kesse (1985), reported that, the rock types of the district is homogeneous, with sandstone, mudstone, shale and conglomerates of the Oti and Obosum beds of the Middle Voltaian System, principally forming the only basement rocks that underlie the district. This is consistent with the generally low fluoride levels in groundwater within the district. Saxena and Ahmed (2001) have shown a positive pH – fluoride correlation in areas with high fluoride in groundwater especially in geological formations with sandy aquifers such as the Upper Voltaian sandstone of the district. According to Hubner (1969); Deshmukh *et al.,* (1995), fluoride is readily adsorbed in clay minerals under acidic conditions and desorbed in alkaline environments. The positive correlation between F^- and pH and HCO_3 in the shallow aquifers within the study area suggests the dissolution of F^- under alkaline conditions through the substitution of OH^- ion in groundwater.

Spearman's Correlation matrix analyses

Correlation analyses of major ions as

published earlier in Tay (2012) and reviewed in Table 3, revealed expected processes- based relationships derived primarily from the geochemical and biochemical processes within the aquifer. These process-based relationships between the observed parameters may be due to mineralogical influence which would be explicitly explained by factor loadings during principal component analysis (PCA). The weak positive correlations between fluoride and the major ions (Table 3) confirms the results from the scatter plots of fluoride and the major ions in Figs. 2, 4, 5 and 6 and suggests weak chemical relationships amongst these ions in groundwater within the district. Table 3 is also consistent with findings by Shivanna and Mohokar (2003); Madhnure *et al.,* (2007) that, a positive correlation between F^- and pH and HCO_3 in groundwaters suggests the dissolution of F^- under alkaline conditions through the substitution of OH^- ion and constitutes favourable conditions for the dissolution of CaF_2 in groundwater. However, the major water type within the district according to Tay (2012) is Ca-Mg-HCO_3, suggesting that, there are no Na-HCO_3 type groundwaters which are associated with base-exchange (Ca and Mg for Na) processes which often results in highly fluoriferous, high-pH, Na-HCO_3 waters in other regions of the world (Boyle, 1992).

TABLE 3

Spearman's Correlation Matrix for groundwater within the Savelugu-Nanton District.

	pH	EC	Sal	TDS	Ca	Mg	Na	K	HCO_3	SO_4	Cl	F	NO_3N	SiO_2
pH	1													
EC	-0.34	1.00												
Sal	-0.29	**0.85**	1.00											
TDS	-0.34	1.00	**0.85**	1.00										
Ca	-0.36	**0.98**	**0.83**	**0.99**	1.00									
Mg	-0.38	**0.97**	**0.83**	**0.97**	**0.97**	1.00								
Na	-0.33	**0.88**	**0.73**	**0.87**	**0.89**	**0.89**	1.00							
K	-0.10	0.44	0.36	0.42	0.43	0.44	**0.67**	1.00						
HCO_3	-0.31	**0.95**	**0.80**	**0.94**	**0.92**	**0.95**	**0.93**	0.53	1.00					
SO_4	-0.31	**0.77**	**0.66**	**0.78**	**0.77**	**0.78**	0.52	0.08	0.58	1.00				
Cl	-0.32	0.79	**0.68**	**0.80**	**0.80**	**0.82**	0.57	0.15	**0.62**	**0.98**	1.00			
F	0.08	0.08	0.10	0.08	0.06	0.11	-0.01	0.19	0.04	0.16	0.20	1.00		
NO_3N	0.05	0.18	0.12	0.16	0.15	0.18	0.22	0.55	0.18	0.15	0.21	0.46	1.00	
SiO_2	-0.23	**0.74**	**0.60**	**0.72**	**0.68**	**0.72**	**0.64**	0.43	**0.71**	**0.61**	**0.62**	0.22	0.41	1.00

PCA using Varimax with Kaiser Normalization resulted in the extraction of three main principal components which delineates the factors that influence the principal components of the physico-chemical parameters. The three principal components have accounted for approximately 83% of the total variance in the hydrochemical data (Table 4).

Component 1 explains approximately, 54.3% of the total variance (Table 6) and has strong positive loadings(i.e > 0.75) for EC (0.984), TDS (0.981), Ca^{2+}(0.0.973), Mg^{2+}(0.983), Na^{+} (0.894), HCO_3^- (0.936), Cl^- (0.829), SO_4^{2-} (0.798) and SiO_2 (0.782); suggesting that, the major ions contribute positively to the total dissolved solids of the groundwater, reflecting a common source and can be accounted for by major geochemical processes within the aquifer. The positive loading of SiO_2 in Component 1 is consistent with results by Tay (2012) that, silicate weathering processes is one of the main geochemical processes responsible for the water chemistry within the district.

TABLE 4

Component matrix of the physico-chemical parameters of groundwater within the district.

Physico-chemical parameters	*Component* 1	2	3
pH	–0.383	0.313	0.061
EC	0.984	–0.079	–0.040
Sal	0.858	–0.100	–0.005
TDS	0.981	–0.101	–0.017
Ca	0.973	–0.113	–0.039
Mg	0.983	–0.081	–0.011
Na	0.894	0.050	–0.382
K	0.498	0.605	–0.519
HCO_3	0.936	–0.016	–0.249
SO_4	0.798	–0.190	0.502
Cl	0.829	–0.128	0.469
F	0.142	0.649	0.528
NO_3-N	0.269	0.838	0.108
SiO_2	0.782	0.232	0.092

Extraction Method: Principal Component Analysis.

Component 2 explains approximately 17.2% of the total variance (Table 6) and has strong positive loading for NO_3-N (0.838), moderate positive loadings (i.e 7.5–0.5) for K^+(0.605) and F^-(0.649) and weak (0.5-0.3) positive loading for pH (0.313) (Table 4). Clearly, this suggests contamination sources by fluoride and NO_3-N. Thus, in addition to fluoride contamination, Component 2 depicts the oxidation of organic matter by nitrate in the unsaturated zone. Nitrate is a powerful oxidizing agent besides oxygen. In cases where the oxygen content in groundwater is low, nitrate is used in the oxidation of organic matter present in the unsaturated zone of the aquifer. The dissolved oxygen content of groundwater was not measured in this study, however, the correlation matrix (Table 3) and the component matrix of the physico-chemical parameters (Table 4) both show weak positive relationships between HCO_3 and NO_3-N, suggesting that the two parameters are not linearly related to each other in the groundwater system. This observation however, does not preclude the oxidation of organic matter by nitrate since the HCO_3^- concentration is affected by several other processes such as incongruent silicate weathering in the aquifers. The positive loadings of pH and fluoride in Component 2 is consistent with results from Boyle (1992); Macfarine *et al.,* (1992); Queste *et al.,* (2001); Saxena and Ahmed (2001) that, areas with high fluoride in groundwater especially in geological formations with sandy aquifers such as the Upper Voltaian sandstone of the district show positive pH – fluoride characteristics.

Component 3 explains approximately 11.9% of the total variance (Table 6) and has moderate positive loadings for K^+(-0.519), SO_4^{2-} (0.502) and F^- (0.528), a weak positive loading for Cl^- (0.469) and a weak negative loading for Na^+(-0.382) (Table 4). Component 3 suggests mineralogical influence of fluoride with some major ions on the chemistry of groundwater within the district.

Table 5 presents the rotated component matrix of the main physico-chemical parameters.The component plot in rotated space is presented in Fig 8. Component 1 explains nearly 54.3% of the total variance (Table 6) and has strong positive loadings (> 0.75) for EC (0.920), TDS (0.930), Mg^{2+}(0.927), Ca^{2+} (0.920), Cl^-(0.921), SO_4^{2-} (0.919), Salinity (0.819), HCO_3^- (0.804) and a moderate positive loading for Na^+ (0.711) and SiO_2 (0.676) (Table 5), suggesting that, the major ions contribute positively to the total dissolved solids of the groundwater and can be accounted for by major geochemical processes within the aquifer. The strong positive loading of salinity in component 1 is consistent with results by Tay (2012) that, 23.5% of groundwater within the district are either brackish (1,500–5,000 µS/cm) or saline (> 5,000 µS/cm) and therefore, unsuitable for potable purposes. Component 2 explains nearly 17.2% of the total variance (Table 6) and has strong positive loading for K^+(0.892), moderate positive loadings Na^+ (0.659), HCO_3^-(O.537), and weak positive loadings for NO_3N (0.429), SiO_2 (0.335), EC (0.360), TDS (0.330), Ca^{2+}(0.338) and Mg^{2+} (0.336), suggesting mineralogical influence. Component 3 explains nearly 11.9% of the total variance (Table 6) and has strong positive loadings for F^- (0.844) and NO_3N (0.775) and a weak positive loading for SiO_2 (0.322), clearly suggesting a common source of contamination.

TABLE 5

Rotated Component Matrix of the physico-chemical parameters

Rotated Component Matrix[a]			
	Component		
Physico-chemical parameters	*1*	*2*	*3*
pH	-0.429	-0.036	0.251
EC	0.920	0.360	0.014
Sal	0.819	0.275	0.004
TDS	0.930	0.330	0.009
Ca	0.920	0.338	–0.015
Mg	0.927	0.336	0.028
Na	0.711	0.659	–0.082
K	0.150	0.892	0.255
HCO_3	0.804	0.537	–0.056
SO_4	0.919	–0.189	0.210
Cl	0.921	–0.121	0.245
F	0.076	–0.041	0.844
NO_3N	0.031	0.429	0.775
SiO_2	0.676	0.335	0.322

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

The loadings and score plots of the first two PCs which explain 71.52% of the total variance is presented in Fig 9. Fig 9 shows grouping and relationship between the variables. The major ions, EC and TDS are visible in the first and second quadrants and have been shown to group together indicating their close relations. Fluoride loaded in the first quadrant together with the major ions indicating

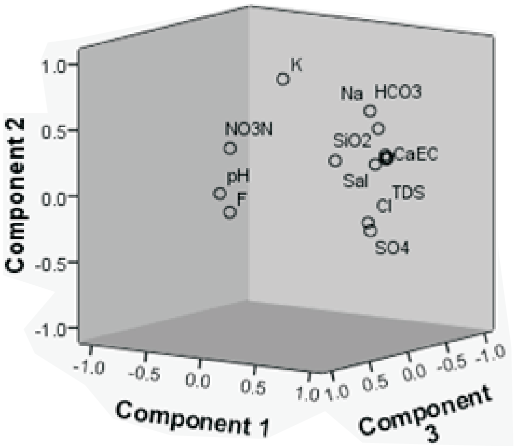

Fig. 8. Component plot in rotated space for groundwater within the District

their close relations, while, pH loaded in the third quadrant. This grouping pattern shows the strength of the mutual relation amongst the hydrochemical variables.

Thus, from the PCA, it can be deduced that, Component 1 delineates the main natural processes (water-soil-rock interactions) through which groundwater within the basin acquire its chemical characteristics. Component 2 delineates pollution sources principally fluoride and nitrate. The sources of nitrate pollution perhaps is input from anthropogenic activities possibly, agriculture. Component 3 suggests mineralogical influence of fluoride with some major ions on the chemistry of groundwater within the district. The loadings and score plots of the first two PCs which explain 71.52 % of the total variance show grouping pattern which indicates the strength of the mutual relation amongst the hydrochemical variables.

Defluoridation in groundwater

Several methods of fluoride removal in groundwater such as synthetic ion exchange and precipitation processes, activated alumina filters, bone char and reverse osmosis have been employed in the developed world (Feenstra *et al*., 2007). Another widely known fluoride removal technique is the Nalgonda technique. The Nalgonda technique employs hydrated aluminum sulfate ($Al_2(SO_4)_3 18H_2O$) and lime for the flocculation, sedimentation, and filtration of fluoride in groundwater. However, there is no universally accepted or routinely used defluoridation techniques in the developing world. This is due to the social, financial, cultural, and environmental factors that come into play in determining the best options to be adopted in a region.

Biological defluoridation can serve as a best alternative to the conventional methods of defluoridation since such methods may be cost effective and material employed are considered to be biodegradable. The mechanism of fluoride uptake with biological materials such as strains of fungi, bacteria, and algae can serve as a best alternative to the conventional methods of defluoridation though, relatively unknown (Lakshmaiah *et al.* 1997). Studies have been conducted using biological option for defluoridation by creating activated carbon from water Hyacinths (*Eichhornia crassipes*) by Amir Haider *et al.,* (2001). Amir Haider *et al.,* (2001) charred the water hyacinths at 600°C and observed fluoride capacities as high as 4.4 mg/g of carbon.

TABLE 6

Total Variance explained

Component	*Initial eigenvalues* Total	% of variance	Cumulative %	*Total Variance Explained* *Extraction sums of squared loadings* Total	% of variance	Cumulative %	*Rotation sums of squared loadings* Total	% of variance	Cumulative %
1.	8.677	61.982	61.982	8.677	61.982	61.982	7.603	54.304	54.304
2.	1.743	12.449	74.431	1.743	12.449	74.431	2.411	17.218	71.523
3.	1.254	8.956	83.387	1.254	8.956	83.387	1.661	11.865	83.387
4.	.821	5.863	89.251						
5.	.539	3.853	93.103						
6.	.365	2.609	95.713						
7.	.263	1.880	97.592						
8.	.195	1.395	98.987						
9.	.062	.444	99.431						
10.	.041	.293	99.724						
11.	.022	.158	99.881						
12.	.013	.091	99.973						
13.	.003	.021	99.994						
14.	.001	.006	100.000						

Extraction Method: Principal Component Analysis.

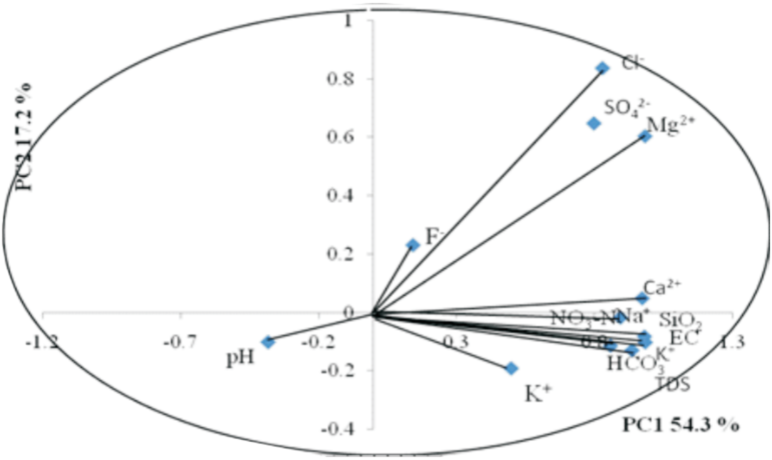

Fig. 9. loadings and score plot for the first two PCs

Conclusions and recommendations

The study shows that, 41.9% of the boreholes are within the safe limits of 0.5 - 1.5 mg/L of fluoride for the protection of bones and teeth, 43.2% of the boreholes have fluoride levels below the lower safe limit (< 0.5 mg/L) and therefore exposed to dental caries, 10.8% of the boreholes have fluoride levels between 1.5 and 3.0 mg/L and therefore exposed to dental fluorosis and 4.1% of the boreholes have fluoride levels between 3.0 and 10 mg/L and therefore exposed to skeletal fluorosis, with the highest fluoride level in drinking water within the district as 4.1 mg/L. From the results, 14.9% of groundwater requires defluoridation, while, 43.2% of groundwater requires fluoride addition to the groundwaters as is often the case in developed countries. PCA using Varimax with Kaiser Normalization resulted in the extraction of three main principal components which delineates the factors that influence the principal components of the physico-chemical parameters. The three principal components have accounted for approximately 83% of the total variance in the hydrochemical data. Results show that, Component 1 delineates the main natural processes (water-soil-rock interactions) through which groundwater within the basin acquire its chemical characteristics. Component 2 delineates pollution sources principally fluoride and nitrate. The sources of nitrate pollution perhaps is input from anthropogenic activities possibly, agriculture. Component 3 suggests mineralogical influence of fluoride with some major ions on the chemistry of groundwater within the district. The loadings and score plots of the first two PCs which explain 71.52% of the total variance show grouping pattern which indicates the strength of the mutual relation amongst the hydrochemical variables. Several physical and chemical defluoridation methods such as the addition of alum and lime in right proportions and the generation of residual aluminum in the treated water due to complexation reaction with the adsorbed fluoride have been designed to treat high fluoride waters. However, ion exchange and chemical treatments are cost intensive, while, physical defluoridation suffer limitations such as frequent change of defluoridants beds and inability to reduce fluoride to non-toxic levels. Biological defluoridation can serve as a best alternative to the conventional methods of defluoridation since such methods may be cost effective and material employed are considered to be biodegradable.

Acknowledgments

The author is grateful to the CSIR–Water Research Institute for its facilities and Mr Rex John Sappah, a Principal Draftsman and Head of Section, for the map of the study area.

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