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Comparative Geological study and physico-chemical parameters of Groundwater in Hong and Zango Settlements in Northern Nigeria

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Abstract
This present study examined the impact of geology on the quality of groundwater in Hong and Zango communities in northern Nigeria with a view of establishing the source and extent of pollution of the groundwater systems in these areas. The geological mapping of Hong and Zango communities revealed that the area is partly underlain by granitic rock as well as other rock types. Petrographic study of the granitic rock domiciled in Hong and Zango areas showed quartz, feldspar, mica and some accessory minerals while the laboratory analysis using XRD indicated the presence of nacaphite (Na_2CaPO_4F) in the granite sample. Interestingly, the nacaphite, which is a fluoride bearing mineral was conspicuously absent in the other rock samples analyzed. The concentration of other parameters investigated was below the maximum permissible limits except electrical conductivity and total dissolved solid. Groundwater samples from Zango area had higher concentration compared to Hong area. This may be attributed to the age of the rocks, Zango are underlain by the older granites while Hong is domiciled by the younger granites. The older granites had more resident time for rock-water interaction than younger granites. An integration of the results of laboratory analysis from Hong and Zango areas against the respective geology further revealed that water samples collected from areas underlain by granitic rock showed higher concentration of fluoride (> 2.0 mg/L) compared to those underlain by other rock types. The paper has established the source of fluoride in groundwater as a possible cause of fluorosis in the study areas. Gibbs plot also confirmed that rock-water interaction and precipitation are the geochemical processes responsible for groundwater evolution and composition in these areas. Conclusively, the use of water in the granite dominated zone for domestic purposes especially drinking in Hong and Zango communities should be discontinued and alternative source of water provided for inhabitants until remediation processes targeted at extracting the fluoride from the groundwater systems in these settlements are executed.

Keyword: Geology, Groundwater, Quality, Hong, Zango, Northern Nigeria

Introduction
There is an increasing awareness that water will be one of the most critical natural resources in future due to the fact that about 80% of all communicable diseases such as typhoid, dysentery, cholera, meningitis and diarrhoea affecting human beings are either water borne or water related [1]. Studies have revealed that about 65 million people from 25 countries of the world including Nigeria are affected by fluorosis as a result of high fluoride concentration from water consumption [2-3]. The chemical composition of groundwater provides information about the environment through which water has migrated. Fluoride is a lithophile element occurring in association with granitic rocks under terrestrial conditions [4-6]. Fluoride in concentrations less than 1.0 mg/L, causes dental caries, non-formation of dental enamel and deficiency of mineralization of bones especially among children below the age of 5, when equal to 1.5 mg/L, it is essential for normal mineralization of bones and formation of dental enamel while in excess of 1.5 mg/L, leads to dental enamel to lose its luster thereby resulting to dental fluorosis [7]. Excessive fluoride intake results in slow, progressive crippling scourge known as skeletal fluorosis. Fluorosis is a disease caused by deposition of

fluorides in the hard and soft tissues of the body and is usually characterized by dark-brown discoloration of teeth and crippling disorders [8]. Crippling skeletal fluorosis, which is associated with the higher levels of exposure, can result from osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity [9,10].

Teeth impacted by fluorosis have visible discolouration from white spots to brown and black stains. [11] suggested one of the most accepted classifications of dental fluorosis is based on the level of the damage of tooth. He classified dental fluorosis into very mild, mild, moderate, severe and very severe categories while [7], categorized dental fluorosis into three viz: low, moderate and high based on the degree of tooth colouration in Zango area. Unlike other water borne diseases, dental fluorosis is an irreversible process as the victims have to live with the symptoms for the rest of their life. It was observed that the teeth of many people from Hong and Zango communities were dark-brown instead of the normal colour. It therefore becomes imperative to know the cause of the brownish teeth ravaging they people of the area as many of young people have abandoned school due to the psychological effect. The occurrence of dental fluorosis among communities in Hong, Adamawa State and Zango, Katsina State, Nigeria is the driving force for the present study. The need to ascertain the source and pollution level by fluoride in the water system in these communities led to this investigation. Prior to this study, no geospatial comparative assessment has been conducted on groundwater system with respect to fluorosis in two regions from different states in Nigeria.

Study Area Location

Hong Settlement lies between longitude $12^{\circ}50'$E to $13^{\circ}00'$E and latitude $10^{\circ}05'$N to $10^{\circ}22'$N, in Hong Local Government Area of Adamawa State, Northeastern Nigeria (Figure 1). The area covers about 60 km^2 and is accessible through major and minor roads, within Adamawa highlands [12]. Zango lies between longitudes $8^{\circ}26'$E and $8^{\circ}44'$E and latitudes $12^{\circ}50'$N and $13^{\circ}04'$N, within Zango Local Government Area of Katsina State, Northwestern Nigeria (Figure 1). It is located about 100 km east of Katsina town and is accessible through a network of both tarred and untarred roads [13].

Fig.1: Map of Nigeria showing the Study Locations

Materials and Methods

Physical parameters such as temperature, electric conductivity, pH and total dissolved solid were determined insitu using portable Martini MI 806 with sensitive probe. Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Model- Optima 200, by Perkin Elmer was employed to determine calcium. Hana Hatch 83300 Multi-parameter spectrophotometeric method was used for Fluoride determination, the colorimetry method was used for sulphate determination, titrimetry method for bicarbonates determination while Ultra Violet (UV) visible spectrophotometer was used for nitrate determination. The analyses were carried out in accordance with the American Public Health Association standards [14]. Rock samples were pulverized, homogenized and average bulk composition determined. The powdered sample was prepared using sample preparation block and compressed in the flat sample holder to create a flat surface, smooth surface was mounted on the sample stage in the XRD cabinet. The sample was analyzed using XRD Empyrean Diffractometer, employing the reflection-transmission spinner stage mounted on the Theta-Theta settings. The results are presented as peak positions at 2θ and X-ray counts in form of as x-y plots. The peaks obtained from the analysis were matched with the minerals from powdered Diffraction File (PDF) of International Center for Diffraction Data (ICDD) database. The rock and water analyses for Hong were carried out at the National Geosciences Research Laboratory, Kaduna while water analysis for Zango was done at National Research Institute for Chemical Technology Laboratory Zaria, Nigeria.

Results and Discussion

The result of selected physico-chemical analysis of groundwater samples from Hong and Zango communities are summarized in Table 1. The pH values in Hong ranged from 5.5 to 7.38 with a mean value of 6.55 while in Zango, it varied from 5.15 to 7.85 with an average value of 6.50 (Table 1). A pH value of 6.50 to 8.50 is within the acceptable limit recommended by Nigerian Standard for Drinking Water Quality [15]. The results of the pH values within the granites dominated area for Hong and Zango settlements were found to be slightly lower than the pH values from the other rock types. Low pH enhances chemical weathering, bedrock dissolution and rock-water interaction processes. The electrical conductivity (EC) ranged between 70.04 to 2670.10 µs/cm with a mean value of 778.60 µs/cm and 22.70 to 3200.01 µs/cm with an average value 980.80 µs/cm for Hong and Zango respectively (Table 1). The values in many locations exceeded the permissible limit of 1000.00 µs/cm for potable water [15]. High electrical conductivity is an indication of the presence of dissolved solutes in the groundwater system. The concentrations of total dissolved solids (TDS) for Hong are between 10.50 to 1320.80 mg/L with an average value of 498.70 as against 15.65 to 1502.32 mg/L with a mean concentration of 521.75 mg/L for Zango area (Table 1). Studies have shown that pH, electrical conductivity and total dissolved solid are good indicators of groundwater pollution [16-18]. Water in its pure form does not conduct both heat and electricity. However, the more solutes dissolved in water, the more conductive it becomes. The temperature values varied from 25.20 to 30.50 °C with a mean value of 27.95 °C for Hong and between 28.10 34.50 °C with an average value of 32.32 °C for Zango. High temperature and low pH encourages groundwater geochemical reactions leading to elevated concentration of electrical conductivity and total dissolved solid [19-20].

Table 1: Summary of Analyzed Physico-chemical Parameters

Parameters	Hong			Zango			NSDWQ, 2007
Mg/L	Min.	Max.	Mean	Min.	Max.	Mean	
pH	5.50	7.38	6.55	5.15	7.85	6.48	6.50-8.50
EC (µs/cm)	70.04	2670.10	778.60	22.70	3200.01	980.80	1000.00
TDS	10.50	1320.80	498.70	15.65	1504.32	521.75	500.00
Temp. (°C)	25.20	30.50	27.95	28.10	34.50	32.32	30.00
Fluoride	0.06	2.58	1.33	0.10	3.16	0.95	1.50
Calcium	23.45	134.35	58.92	0.06	167.82	25.82	200.00
Bicarbonate	21.50	122.30	60.05	6.05	135.68	57.44	150.00
Nitrate	0.20	5.86	4.07	0.06	19.40	7.30	50.00
Sulphate	2.30	18.15	9.20	1.08	110.72	28.45	200.00
Phosphate	0.01	2.05	0.46	0.01	7.6	1.72	10.00

NSDWQ-Nigerian Standard for Drinking Water Quality

Fluoride concentration in Hong ranged from 0.06 mg/L to 2.58 mg/L while in Zango, it varied from 0.01 mg/L to 3.16 mg/L (Table 1) as against the maximum allowable value of 1.50 mg/L (NSDWQ, 2007). The area underlain by granitic rocks in Hong and Zango showed high fluoride concentration while the sector occupied by other rock types had low fluoride concentration. This striking revelation suggest that the granitic rock contains a fluoride bearing mineral, and possibly during geochemical processes such chemical weathering, bedrock dissolution and rock-water interaction, the fluoride is released into the groundwater system. The geological mapping of Hong revealed that the area consists of predominantly Granites and Migmatites-Gneiss

(Figure 2) while Zango geology comprises of Granites, Rhyolites, Gundumi Formation and Chad Formation (Figure 3). The geology of Zango is unique because it is the only Local Government Area in Nigeria with four different lithologies. In order to unravel the conspicuous concentration of fluoride in groundwater system from Hong and Zango settlements, the rock samples from these areas were subjected to XRD analysis and the result identified the presence of sodium calcium phosphate fluoride (Na_2CaPO_4F) mineral called nacaphite, a fluoride bearing mineral in the granite dominated area. Interestingly, the nacaphite was completely absent in the area occupied by the other rocks in both Hong and Zango. The present study has established the influence of lithology on groundwater chemistry. High fluoride concentration in were found in areas underlain by granites in Hong and Zango communities. However, the concentration of fluoride was lower in areas dominated by other rock types, an indication that the fluoride is coming from the granitic rocks in these areas. It also implies that due to rock-water interaction and other hydrogeochemical processes, the groundwater within the granitic rock are enriched by fluoride from the nacaphite mineral contained in the granitic rock.

A representative granite samples with high nacaphite content is shown in Plate I while Plate II indicate magmatic-gneiss with no nacaphite content. It is also believed that the tectonic and or metamorphic process leading to the alteration of granite into migmatite-gneiss could have transformed the nacaphite mineral into another mineral. The result of the rock analysis has confirmed that fluoride enrichment in groundwater in Hong and Zango settlements are purely geogenic due to the presence of nacaphite in the granitic rocks. The concentration of major ions (bicarbonate, calcium, nitrate, phosphate and sulphate) in Hong and Zango areas are far below their respective maximum permissible limit as postulated by Nigerian Standard for Drinking Water Quality. Studies have shown a positive relation between fluoride, sodium, calcium and phosphate resulting in the formation of the nacaphite mineral [12]. The observed high EC and TDS values are due to fluoride enrichment in the groundwater system within the granite rich area. High nitrate and sulphate concentration are indicators of urban pollution by anthropogenic signatures such as fertilizer application, market wastes and dumpsite leachate [21,22]. According to [23], groundwater pollution by fluoride can be anthropogenic due to fertilizer application or natural as a result of bedrock dissolution processes. Hong and Zango communities are predominantly farmers and fertilizers were applied in the granitic (endemic zone) and non-granitic (non-endemic zone) for the cultivation of cash crops. The absence of nacaphite (fluoride rich mineral) in areas not dominated by granitic rock in both Hong and Zango settlements testify to the fact that the fluoride enrichment in the groundwater system in these settlements are through natural means such as bedrock dissolution/weathering processes and not anthropogenic means such as fertilizer application [24,25,26].

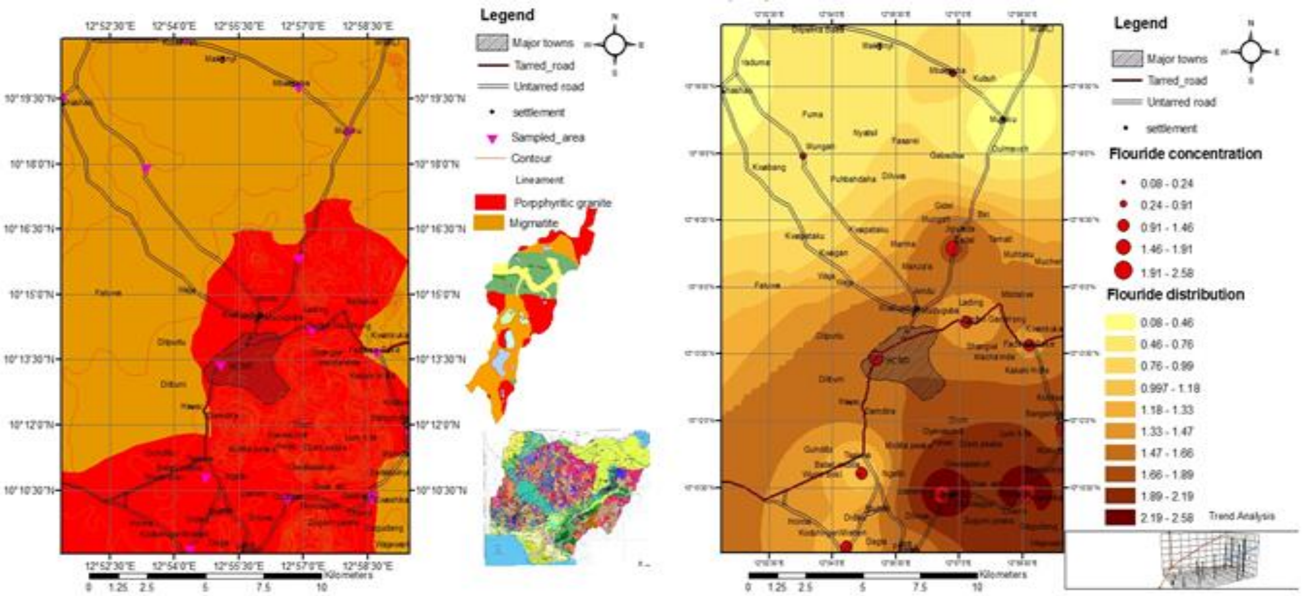


Fig. 2: Comparison of the Geology and Fluoride Concentration in Hong Area

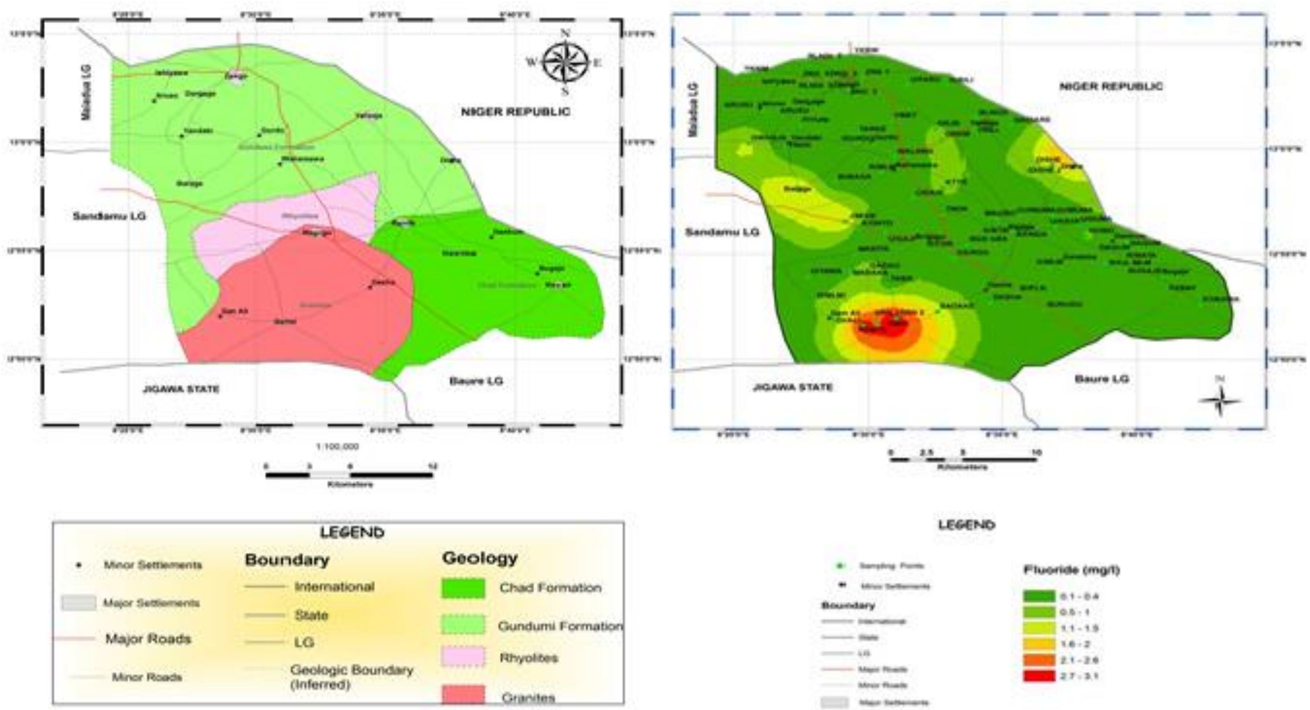
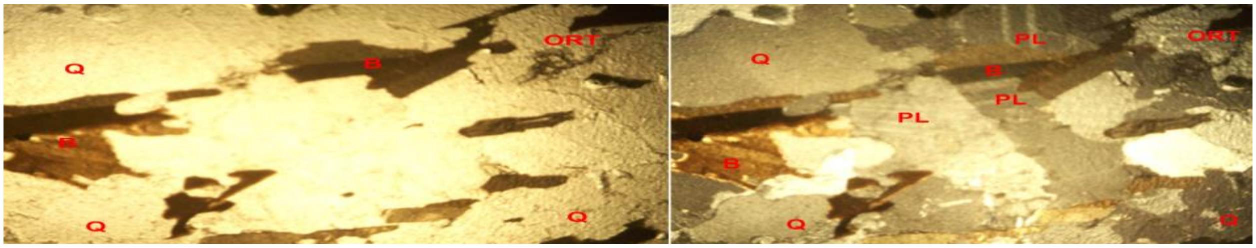


Fig. 3: Comparison of the Geology and Fluoride Concentration in Zango Area


Plate 1: Granite Sample


Plate 2: Migmatite-Gneiss Sample

Petrography is the study of rock under thin-section using petrological microscope. The following minerals were observed on the granitic rock sample: quartz (Q), biotite (B), plagioclase (PL) and orthoclase (ORT). They are the major constituents of granitic rock and it further confirmed the rock within the fluoride endemic zone is actually granite. From Bowen's Reaction Series, low temperature minerals such as biotite, feldspar and quartz are characteristics of granitic rock.



Plane Polar Cross Polar

Plate 3: Photomicrography of a Granitic Sample

Rock-water interaction allows infiltration of nacaphite minerals into the underlying the groundwater systems thereby resulting in fluoride enrichment in the groundwater. Studies have shown that the concentration of fluoride in groundwater is proportional to the degree of water-rock interaction, because the Fluoride originates from bedrock [27]. The fluorosis in both Hong (Plate 4) and Zango (Plate 5) are more of dental than skeletal at the moment and the damage done to the teeth of these villagers may be difficult to reverse.

Pella Dzumah Hong

Plate 4: Dental fluorosis in Pella, Dzumah and Hong communities in Adamawa State

Zango Garni Kasuwayal Jama'ar Malam Sani

Plate 5: Dental fluorosis in Zango Garni, Kasuwayal and Jama'ar Malam Sani communities in Katsina State

The concentrations of the parameters investigated were higher in Zango area compared to Hong area (Figure 4; Table 1). Although the granitic rocks in these communities have similar composition based on the XRD and petrographic analyses, Zango is underlain by the older granites while Hong is outcropped by the younger granites. The older granites are Pre-Cambrian while the younger granites are Jurassic in age. The older granites have more resident time for rock-water interaction and by implication has witnessed more geochemical processes resulting in the release of more ions in groundwater system in Zango area than Hong area, as resident time is a major factor in groundwater quality studies [19, 27,28].

Furthermore, Gibb's Plot (Figure 5) provides useful information on the major natural mechanisms controlling groundwater chemistry. The processes include but not limited to precipitation, evaporation, weathering and bedrock dissolution. It suggests that chemical weathering of rock-forming minerals is the main factor responsible for the evolution and chemical composition of groundwater in Hong and Zango settlements. The fluoride in groundwater in the area is primarily derived from decomposition, dissociation and dissolution of fluoride bearing minerals in the local geology and precipitation aids its infiltration into the groundwater system.

It may also be linked to presence of calcium fluorite (CaF_2) and weathering of alkaline granitic rocks with Feldspars, biotite and quartz as the constituent minerals (Plate 3). Detailed correlation analysis fluoride with pH and groundwater depth was carried out and the outcome of the result revealed that fluoride content increase with a decrease in pH, which implies that more fluoride is released into the groundwater system under slightly lower pH. This implies decomposition, dissociation and dissolution of fluoride bearing minerals are precipitated under slightly acidic condition. On the reverse, fluoride content increases as the depth increases. This implies that deeper well or boreholes are richer in fluoride than shallow wells and this can be explained due to resident time arising from rock-water interaction. Also the dilution effect arising from precipitation has no significant impact on deep wells unlike shallow wells [29,30]. The longer the resident time the high the fluoride content.

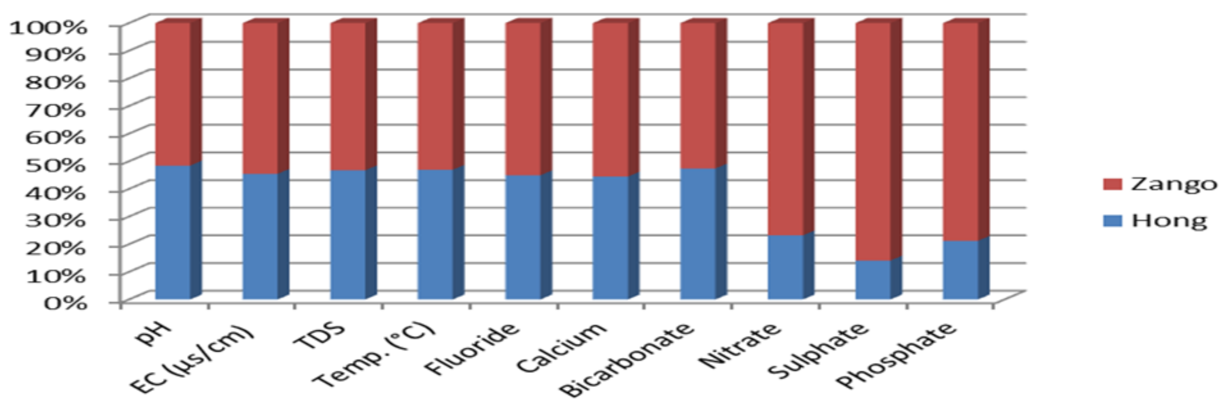


Fig. 4: Comparing the concentration of analyzed parameters in Hong and Zango Communities

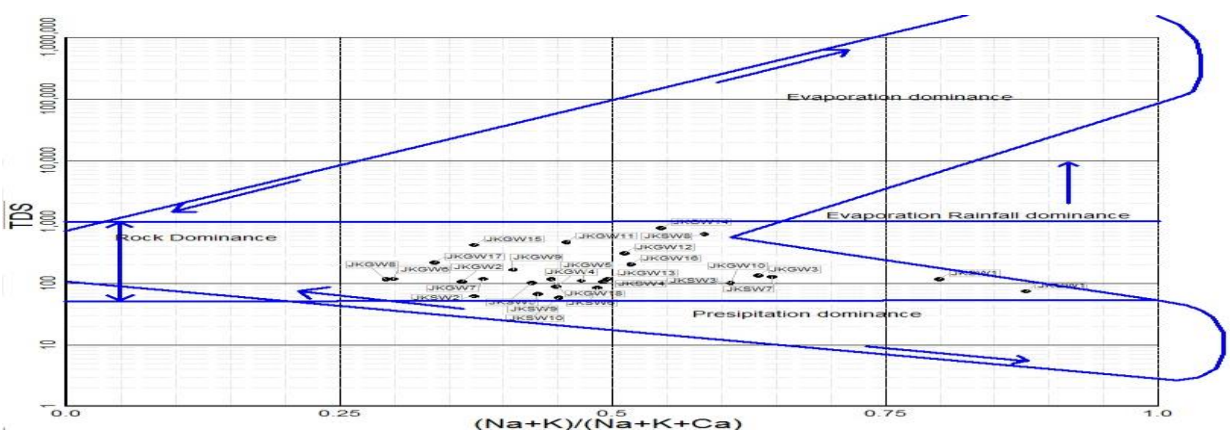


Fig. 5: A representative Gibbs Plot for Hong and Zango communities

Conclusion

The present study evaluates the concentrations of fluoride in groundwater in Hong and Zango settlements. This research was born out of the dental fluorosis observed by the people in the communities. High concentration of fluoride (>

2.0) was found only in the areas occupied by granites in both Hong and Zango communities while non-granitic zones showed low concentration of fluoride (< 1.0). This study established that high fluoride in the groundwater in Hong and Zango areas are clearly geogenic due to rock-water interaction and chemical weathering which led to subsequent decomposition, dissociation and dissolution of fluoride bearing minerals (nacaphite) contained in the granitic rock and the process is enhanced by the prevalent slightly acidic condition of the groundwater system. The high content of fluoride in the groundwater contributed to the high concentration of electrical conductivity and total dissolved solid. It is recommended that the government should provide an alternative source of drinking water in the fluoride endemic zone in Hong and Zango settlements. Remediation targeted at extracting the fluoride from the groundwater system is advocated.

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