A STUDY OF FLUORIDE OCCURRENCE AND SOME HEAVY METALS IN GROUNDWATER FROM SHALLOW AQUIFERS NEAR OGBOMOSHO, SOUTHWEST NIGERIA

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ABSTRACT

The present study evaluates the presence of fluoride and some heavy metals in groundwater from shallow aquifers around Ogbomosho, Southwest Nigeria. The fluoride concentration ranged from 1.35 mg/l to 2.75 mg/l with a mean value of 1.58 mg/l as against the recommended value of 1.50 mg/l by World Health Organization and Nigerian Standard for Drinking Water Quality. Continuous use of water from this area may result to colouration of the teeth (dental fluorosis) and deformation of the bone and skeleton (skeletal fluorosis) especially in children below the age of five. The high fluoride content in groundwater from shallow aquifers in the area as well as the heavy metals may be attributed to water-rock interaction during the process of percolation with fluoride-bearing rocks under arid, low precipitation, and high evapotranspiration conditions leading to intensive chemical weathering and bedrock dissolution of the granite aquifers in the area. The heavy metal enrichment is in the increasing order of: Ni > Mn > Cr > Cd > Fe > Cu > Zn. These findings suggest that the enrichment of the groundwater system in the area is geogenic and is a function of the local geology. It is recommended that people living in the coarse grained porphyritic biotite granite dominated area should discontinue the use of groundwater from hand dug wells for domestic and drinking purposes in order to avoid the occurrence of fluorosis in future. Regular monitoring of the groundwater in the area is advocated. Furthermore, environmental friendly techniques such as phyto-remediation and bio-remediation should be employed to absorb the fluoride and heavy metal in the groundwater system.

Keywords: Groundwater Quality Assessment. Fluorosis, Heavy Metals Contamination, Shallow Aquifers, Ogbomosho and Southwest Nigeria

INTRODUCTION

According to UNICEF (1999), about 65 million people globally are affected by either skeletal or dental fluorosis. Fluorosis is an abnormal disease of the bone and teeth due to excessive intake of fluoride through water or food. Skeletal fluorosis is a crippling disease with major manifestation of overgrowth or distortion of the bones leading to total deformity of the individual. Dental fluorosis is the damage of the teeth in form of permanent dark-brown colouration. Both skeletal and dental fluorosis are as a result of consumption of water with fluoride concentration greater 1.5mg/l (NSDWQ, 2007; WHO, 2010) while fluoride content below or equal to 1.5mg/l in water is beneficial in building strong bones and tooth (Ahmad *et al.*, 2010).

Groundwater is one of the most important natural resources that when contaminated by either natural or anthropogenic means is difficult and expensive to clean-up. Fluorosis is a disease affecting the bone and teeth of humans due to excessive intake of fluoride either through water or food. Heavy metal pollution is a burning environmental issue due their toxic, persistent and bio-accumulative nature.

Waters with high levels of fluoride content are mostly found at the foot of high mountains and in areas where the sea has made geological deposits. The known fluoride belt on land include: one that stretches from Syria through Jordan, Egypt, Nigeria, Ghana, Libya, Algeria, Sudan and Kenya, and another that stretches from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China (Fig. 1). Long-term ingestion of large amounts of fluoride in the body can lead to potentially severe skeletal problems. The early symptoms of skeletal fluorosis include stiffness and pain in the joints. In severe case, the bone structure may change and ligaments may calcify, with resulting impairment of muscles and pain. Acute high-level exposure to fluoride causes immediate effects of abdominal pain, excessive saliva, nausea and vomiting. Seizures and muscle spasm may also occur (Chae *et al.*, 2007; Aminu and Amadi, 2014).

About 85% of all communicable diseases affecting human being are either water borne or water related. Fluoride in groundwater in primarily derived from decomposition/dissociation and dissolution of fluoride bearing minerals and secondly by the use of fertilizer containing fluoride impurities (Saxena and Ahmed, 2002). Fluoride contamination in groundwater in parts of northern Nigerian may be attributed to lithogenic interference arising from rock-water interaction as well as pro-longed application of phosphatic fertilizer containing fluorideas impurities (Aminu and Amadi, 2014). Amadi *et al.*, (2015) revealed that lithogenic contamination of groundwater depends on climate of the area, pH, flow pattern and frequency, ionic exchange, resident time, chemistry and mineralogy of the rock. High fluoride concentration in groundwater may persist for years, decades, centuries, and can contaminate the food chain (Chidambaram *et al.*, 2003; McAllister *et al.*, 2005; Chae *et al.*, 2007; Dan-Hassan *et al.*, 2012).

Minerals in rock that contain fluoride include: fluorite, apatite, fluomica, cryolite, epidote, topaz, phosphorite, tremolite, amphiboles, villaumite and clay (Boyle and Chagnon, 1995). The chemistry of groundwater are modifies as it migrates from one area to another due exchange of ions in the course of its movement. Studies have shown that hydrogeochemical processes such as dissolution, chemical weathering, decomposition, ionic exchange processes and resident time along flow path controls the chemistry of groundwater in shallow aquifers (Olasehinde et al., 2015; Amadi *et al.*, 2015).

Fig.1: Map of fluoride occurrence in groundwater across the World (After IGRAC, 2004)

MATERIALS and METHODS

Study Area Description

Ogbomoso town lies between $4^{0}10'$E to $4^{0}20'$E of the Greenwich Meridian and $8^{0}00'$N to $8^{0}15'$N of the Equator. The geology of this area (Fig. 2) has been studied by many workers (Oyawoye, 1964; Olarewaju, 2006). However some work has been done in recent past on the hydrogeophysics and hydrogeochemistry of the area (Olasehinde *et al.*, 2015). The study area lies within North-central Nigeria which is underlain by the Basement Complex terrain characterized by Migmatite-gneiss complex, low grade schist belt and the older granite suites. The study area is dominated by banded-gneiss, granite-gneiss and granites with some quartzite intrusion (Fig. 2).

The study area is characterized by two season's namely wet and dry seasons. Relative humidity can be as high as 72% during the beginning of the rainy season and could fall rapidly during the dry season. The highest amount of precipitation occurs during July and August. The highest monthly temperature is usually experienced during March with temperature of about 30 ^{0}C and the lowest occurring in August with a temperature of about 25°C. Vegetation type is of Guinea Savannah and the area is mostly dominated by shrubs and grasses while tree are sparsely populated.

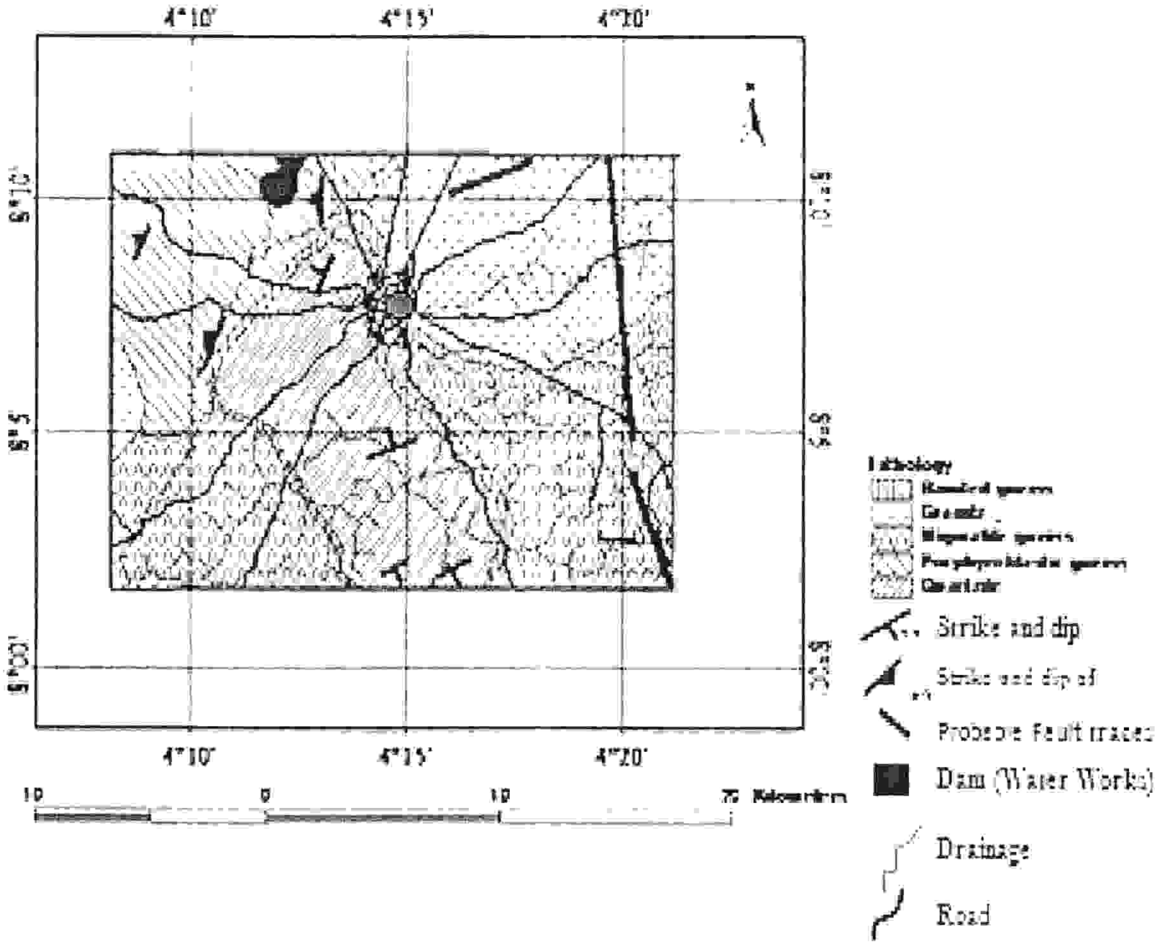

Fig. 2: Geology map of the study Area

Sampling

A total of 40 groundwater samples from shallow aquifers were collected and taking into account the direction of groundwater flow and the density of the population within the studied area. The sampling was carried out between April and August, 2014. Glassware and vessels were treated in 10% (v/v) nitric acid solution for 24 hours and were washed with distilled and deionized water. The samples for cation determination were collected in polypropylene containers, labeled and immediately few drops of HNO_3 (ultra-pure grade) to pH < 2 were added to prevent loss of metals, bacterial and fungal growth and then stored in a refrigerator while samples for anion analysis were collected in glass containers. The physical parameters were determined insitu in the field using appropriate instruments in accordance with APHA (2008) standard. The samples were stored on ice in cooler boxes and transported to the laboratory immediately after sampling was completed.

Laboratory Analysis

The physical parameters are measured in the field using martini MI 806 with sensitive probe. The cations and heavy metals were determined using ICP-OES method while fluoride was determined using Hana Hatch 83300 Multi-parameter Spectrophotometer. Sulphate was analyzed by colorimetric method while bicarbonate and chloride were determined by titrimetric method. Nitrate determination was by ultra violet visible Spectrophotometer.

Statistical Analysis of Hydrochemical data

Principal Component Analysis

The Principal Component Analysis (PCA) is a statistical technique that focused on data reduction in order to understand a small number of components that explain most of the variations observed in a much larger number of manifest variables (Abdullah and Aris, 2007; Amadi, *et al.*, 2010). It attempt to identify new underlying factors that give a better understanding the relationship within a set of data (Praus, 2005). Principal Component analysis is based more on explaining the covariance structure of the variables than with explaining the variances (Lambarkis, *et al.*, 2004). The purpose of principal component analysis is to interpret the structure within the variance-covariance matrix of a multivariate data collection. It uses the extraction of the eigenvalues and eigenvectors from the matrix of correlation or covariance. The information gained about the interdependencies between observed variables can be used later to reduce the set of variables in a dataset (Prasad and Narayana, 2004; Olobaniyi and Owoyemi, 2006). SPSS-window-16 version was the statistical software used to perform principal component analysis on the data set.

RESULTS and DISCUSSION

The results of the laboratory analyses are summarized in Table 1. The pH value ranged from 6.70 to 7.25 with a mean value of 6.96. The pH values fall within the acceptable limit of 6.50 to 8.50 postulated by Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). The pH is a good water quality parameter indicating the acidity or alkalinity of a medium. The conductivity values ranged between 6.88 µs/cm to 1710 µs/cm with an average value of 678.65 µs/cm. The conductivity values in most locations exceed the WHO acceptable limit of 1000.0 µs/cm. Electrical conductivity is an indication of dissolved materials in water as water in its pure state does not conduct electricity. The concentration of total dissolved solid (TDS) varied from 81.30 mg/l to 1108.05 mg/l with a mean value of 461.76 mg/l. The concentration of TDS in some locations was higher than the recommended value of 500.0 mg/l (WHO, 2010; NSDWQ, 2007).

The obtained TDS value in each location is directly proportional to the amount of dissolved ions in groundwater from that location and it is relative (Amadi *et al.*, 2014). Even though no direct health effects is known for TDS, certain components of TDS, such as chlorides, sulphates, bicarbonates, carbonates, magnesium, calcium, sodium and potassium affects corrosion or encrustation in water distribution systems. TDS level (> 500 mg/l) causes scaling in water pipes which can reduce the lifespan of water heaters, boilers, kettles, pots, and steam irons. Hardness of water is due to the presence of calcium and magnesium ions and it reduces lather formation as well as increases the boiling point of water (Lohani *et al.*, 2008). Hardness of water also leads to the formation of scales in sinks, pipe fittings and cooking utensils (Nwankwoala *et al.*, 2014).

The concentration of fluoride ranged between 1.35 mg/l to 2.75 mg/l with an average value of 1.58 mg/l. These values imply that the fluoride concentration in groundwater in most locations exceeds the permissible limit of 1.5 mg/l (WHO, 2010; NSDWQ, 2007). Since there was no known industry in the area that could have discharged fluoride rich-effluent into the soil or surface water, high fluoride concentration in groundwater of an area may be attributed to weathering and dissolution of rocks as well as irrigation processes which also accelerates weathering of rocks (Murthy *et al.*, 2003; Amadi *et al.*, 2015).

Table 1: Descriptive Summary of the Physico-chemical Parameters analyzed

Parameters	Minimum	Maximum	Mean	NSDWQ (2007)
pH	6.70	7.25	6.96	6.50-8.50
Conductivity	6.88	1710.00	678.65	1000.00
TDS	81.30	1108.00	466.75	500.00
Fluoride	1.35	2.75	1.58	1.50
Nickel	0.00	0.09	0.04	0.02
Chromium	0.01	1.00	0.06	0.05
Cadmium	0.00	0.01	0.003	0.003
Copper	0.10	1.06	0.42	1.00
Zinc	0.00	0.82	0.34	3.00
Iron	0.01	0.48	0.22	0.30
Manganese	0.00	0.07	0.03	0.02

Fluoride when consumed in inadequate quantities (< 0.5 mg/l) causes health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children (Fluhler *et al.*, 1982). Also, fluoride when consumed in excess (> 1.5 mg/l), it leads to several health complications such as skeletal and or dental fluorosis (Deshmukh *et al.*, 1995). Being a cumulative bone seeking mineral, the resultant skeletal and dental changes/ metabolic processes are progressively affected negatively. Fluoride is a typical lithophile element under terrestrial conditions and studies have revealed their association with granitic rocks. It is a major constituent in silicate rocks especially those of late magmatic stages typified in apatite, Fluorspar, Cryolite and Fluorapatite as well as villiaumite and syenites (Aminu and Amadi, 2015). According to Omueti (1977), the fixation of the bulk of fluoride as complex hydroxy-silicates and hydroxyalumino-silicates, in which the hydroxyl ions (OH) are largely replaced by fluoride are common in amphiboles and minerals of the mica family (biotite and muscovite).

A substantial amount of this fluoride is retained in subsoil horizons, where it complexes with Aluminium that is associated with phyllosilicates (Vaish and Vaish, 2002). The result of XRD analyses of the soil/rock sample (Fig. 3) from the area revealed the presence of nacaphite, a fluoride rich mineral and the geochemical processes described above may have been responsible for their high concentration in the groundwater system in the area. The concentration of fluoride in most of the location were observed to be higher than the recommended maximum permissible limit of 1.5 mg/l (NSDWQ, 2007; WHO, 2010). A mean fluoride value of 1.58 mg/l (Table 1) calls for urgent attention in terms of remediation before the situation becomes endemic as we have in Zango, Katsina State (Aminu and Amadi, 2014) and Hong in Adamawa State (Maspalma, 2014).

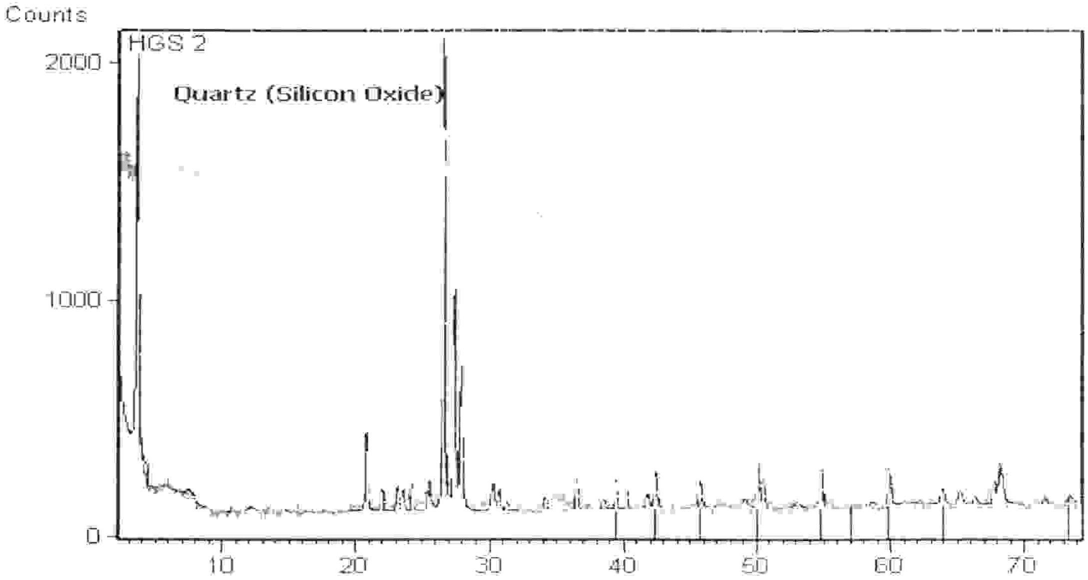

Fig. 3: XRD Chart indicating the presence of Necaphite

The concentration of iron varied between 0.01 mg/l to 0.48 mg/l and an average value of 0.25 mg/l as against the permissible limit of 0.30 mg/l (WHO, 2010; NSDWQ, 2007). Iron is essential to the human body and its deficiency causes goiter while high intake has no known health effect except reasons of taste and avoidance of staining of sinks and laundered textiles (Amadi *et al.*, 2013). The concentration range of manganese is 0.07 mg/l and a mean value of 0.03 mg/l. The mean concentration is slightly above the recommended WHO guideline value of 0.02 mg/l. Manganese is an important micronutrient for both plants and animals and also plays an important role in enzyme catalysis. However, it can cause damage the liver and other organs at relatively high concentration (Karbassi *et al.*, 2008). Cadmium is a toxic element with no known essential biological function and can travel for long distance from the source of emission by atmospheric transport (WHO, 2007). The average concentration of cadmium is 0.003 mg/l from the groundwater analysis. The concentration of zinc in the water sample was below the permissible level of 3.00 mg/l (WHO, 2010; NSDWQ, 2007). Zinc is an essential growth element for plants and animals and also plays useful role in a variety of enzyme systems which contribute to energy metabolism, transcription and translation.

The concentration of nickel varied from 0.00-0.09 mg/l with a mean value of 0.041 mg/l as against the approved limit of 0.02 mg/l (WHO, 2010; NSDWQ, 2007). Nickel may be present in groundwater due to chemical weathering and dissolution from nickel ore-bearing rocks. The mean concentration of chromium and copper in the groundwater are 0.04 mg/l and 0.42 mg/l while their respective permissible limits are 1.00 mg/l and 0.05 mg/l (WHO, 2010; NSDWQ, 2007). Copper unlike chromium has nutritional value for plants and animals and plays key role in body metabolic processes. Similarly, the presence of these metals in the groundwater system in the area is due to dissolution processes occasioned by rock-water interaction and other favourable geochemical conditions prevalent in area over a period of geological time.

A strong positive correlation with Cu and Ni as well as Cu and Zn as noted at <0.01 level (Table 2) while a low correlation of Cr with Mn and Ni was noted. An excellent relationship of Cu and Fe was established in the study (Table 2). This implies that these metals are released into the groundwater by the same geochemical processes. Also a good relationship exists between TDS and conductivity as well as fluoride and pH. The fluoride and heavy metal are released into the groundwater system at slightly low pH and elevated temperature and their presence in water contribute to TDS content and these makes groundwater conductive.

Table 2: Overall Pearson's correlation coefficient of the Analyzed Parameters

	Cd	Cr	Cu	Fe	Mn	Ni	Zn	F	pH	TDS	Cond.
Cd	1.000										
Cr	0.505*	1.000									
Cu	0.207	0.090	1.000								
Fe	0.064	-0.271	0.567*	1.000							
Mn	0.089	0.585*	0.213	0.291	1.000						
Ni	0.012	0.502*	0.623**	0.077	0.231	1.000					
Zn	0.036	0.558*	0.611**	0.342	0.098	0.405	1.000				
F	-0.018	0.095	0.498	0.028	0.122	0.082	0.052	1.000			
pH	0.169	0.380	0.089	0.365	0.206	0.216	0.278	0.385	1.000		
TDS	0.256	0.065	0.221	0.045	0.235	0.346	0.353	0.227	0.335	1.000	
E.Cond	0.167	0.234	0.163	0.202	0.124	0.128	0.054	0.189	0.301	0.652**	1.000

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

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

Table 3: Principal Component Analysis of the Groundwater System in the Area

Parameters	PC1	PC2	PC3	PC4
Cr	-0.046	-0.120	-0.109	**0.524**
Ni	**0.828**	0.301	-0.214	0.088
Fe	0.124	-0.190	**0.607**	0.224
Mn	0.135	**0.818**	0.247	0.125
Zn	- 0.061	**0.623**	0.312	0.174
Cu	0.214	0.145	**0.525**	0.283
Cd	-0.164	**0.739**	0.183	0.234
F	**0.780**	**0.505**	0.250	0.052
Ph	**0.589**	0.141	-0.324	0.213
TDS	**0.654**	0.222	0.175	**0.518**
E Cond	**0.710**	0.198	**0.582**	0.234
Eigenvalue	2.846	2.214	1.852	1.386
Total variance (%)	26.428	20.350	16.922	11.680
Cummulative (%	26.428	46.778	63.700	75.380

Principal component analysis was applied to dataset and it generated four significant factors (Eigenvalues >1) which explained 75.38% of the variance in datasets and it is an indication of four possible sources of groundwater contamination. The first factor consists of nickel, fluoride, pH, electrical conductivity (EC) and total dissolved solid (TDS) which accounts for 26.43% of the total variance (Table 3). The enrichment of nickel and fluoride in the groundwater may be attributed to the weathering and subsequent dissolution of nickel-rich and fluoride-rich minerals in the host-rock in the course of rock-water interaction. A slightly acidic environment favours chemical weathering and mineral dissolution. The dissolution of ions in water enhances the TDS and also makes water conductive.

Factor 2 accounts for 20.35% of the total variance and it includes manganese, zinc, cadmium and fluoride while Factor 3 has a high loading from iron, copper and electrical conductivity and constitutes 16.92% of the total variance (Table 3). Factor 4 has the moderate loading of 11.68% of the total variance and comprises of chromium and TDS. The occurrence of these trace elements in the groundwater system is as a result of lithologic influence arising from rock-water interaction processes. There are no industries located in the area and as a result no effluents are generated in the area that could be the possible source of these metals, hence they are most likely from the host-rock. The occurrence of Flouride in Factors (1 and 2), Electrical conductivity in factors (1and 3), total dissolved solids in factors (1 and 4) and the heavy metals (Ni, Mn, Zn, Cd, Cr and Cu) are indication that these parameters contribute significantly to the observed variance in the groundwater chemistry in the area (Table 3).

CONCLUSION and RECOMMENDATION

The presence of fluoride and trace elements such as copper, zinc, nickel, manganese, chromium, cadmium, and iron in groundwater around Ogbomosho was investigated in the study and their presence are no longer in doubt. The quality of groundwater depends on the nature of surface run-offs, weathered products and mineralogical composition of the underlying rocks. The geology of an area has a strong influence on the chemistry of groundwater. The natural processes of weathering and dissolution may be responsible for release of fluoride-bearing minerals as well as heavy metals into groundwater system. The enrichment order of the heavy metal are: Ni > Mn > Cr > Cd > Fe > Cu > Zn. People living in the granite dominated region should discontinue the use of groundwater from the area for domestic and drinking purposes in order to avert the problem of fluorosis in the near future. The findings of the present study agreed with the global fluoride distribution (fig. 1). which ranks the study area as medium (intermediate) with respect to fluoride content in groundwater, since the mean fluoride concentration (1.58 mg/l) exceeds the maximum permissible limit (1.5 mg/l) recommended by the Nigerian Standard for Drinking Water Quality and World Health Organization. It is suggested that Phyto-remediation, bio-monitoring, bio-mining and bio-remediation techniques be employed to monitor and control the fluoride and heavy metal in the groundwater system at the observed early stage before dental and subsequently skeletal fluorosis occurs in the area.

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