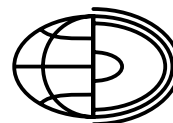


Geogenic Contamination: Hydrogeochemical processes and relationships in Shallow Aquifers of Ibadan, South-West Nigeria



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Abstract. The result of the spatial analysis as applied to the hydrogeochemical data set in the shallow aquifer of Ibadan provides an insight into the underlying factors controlling hydrogeochemical processes in the area. A total of thirty drinking water samples (six samples each from the five major lithologic formations of the study area) were collected from shallow aquifers during the rainy and dry season. Atomic Absorption Spectrophotometry (AAS) and the Beckan DU-7500 single beam spectrophotometer were used to determine concentrations of arsenic, iron and fluoride in drinking water samples and the concentrations of other chemical parameters that could affect the concentrations of the geogenic contaminants including Ca, Mg, Na and SO_4^{2-} were also analysed. pH and TDS were also determined. The Pearson Correlation and Factor Analysis were used to examine the relationship between the geogenic contaminants and concentration of other hydrogeochemical parameters while isopleth maps were drawn to ascertain lines of equal geogenic concentration (Isogeogenic lines). Factor analysis reduced the dataset into three major components representing the different sources of the contaminant. Major contributors to factor 1 and 3 (Salinization and Sulphate factors respectively) are natural phenomena while factor 2 is partly geogenic. The Isogeogenic lines show places of equal geogenic concentration and also with 3D Elevation modelling showed a high peak of Arsenic and Fluoride in the Sango area. The correlation test showed that there is a positive relationship between As and SO_4^{2-} 0.889 ($P < 0.05$) and also a positive relationship between As and Mg 0.43 ($P < 0.05$). The significant relationship between As and SO_4^{2-} , shows a partly geogenic source resulting from the reduction of sulphate to sulphide for the mobilization of As. The positive relationship between Fluoride and pH 0.242 ($P > 0.05$) implies that the concentration of F within the rock formation depends on high pH value.

Keywords:
Geogenic,
Factor analysis,
Fluoride,
Arsenic,
isogeogenic lines,
hydrogeochemical

Introduction

There is growing concern about the deterioration of groundwater quality due to geogenic and anthropogenic activities. Currently the United Nations estimates that between 1.5 and 2 billion people, some 25% of the world population, have no access to safe water, and by 2025 about the same number of people are estimated to be living under conditions of

absolute water scarcity (Gleick 2009). Also, approximately 2.6 billion people lack safe water sanitation facilities (Ban Ki-moon, UN headquarters speech, September 22, 2010).

Many surface-water supplies have dried up, been polluted, or diverted, especially fresh water resources of rivers and lakes. Hence, there has been an unprecedented increase in the exploitation of groundwater resources, often without proper management, necessary controls, or characterization.

An estimated 2 billion people worldwide depend on groundwater for drinking water. Water tables have dropped dramatically causing subsidence and salinization. Disposal of contaminants into the subsurface continually interferes with groundwater that is needed for drinking and agricultural usage. Water quality is not determined adequately or routinely in many regions. Even when groundwater contains contaminants and facilities for treating groundwater do not exist, the water is drawn for drinking purposes anyway because there are no feasible alternatives.

The natural chemical composition of groundwater is influenced predominantly by the type and depth of soils and the subsurface geological formations through which groundwater passes (Amanambu, Egbinola 2015). Groundwater quality is also influenced by contributions from the atmosphere, human activities and surface water bodies. Groundwater contains a wide variety of dissolved inorganic chemical constituents in various concentrations, resulting from chemical and biochemical interactions between water and geological materials. Inorganic contaminants including chloride, fluoride, nitrate, iron and arsenic are important in determining the suitability of groundwater for drinking purposes.

The intake of excessive amounts of arsenic or fluoride poses a health risk for some hundreds of millions of people worldwide. These geogenic substances are mobilized from aquifer materials under certain conditions in the groundwater. In many developing countries, geogenic contaminated groundwater is used as a source of drinking water, for irrigation and in the preparation of food. In addition, groundwater is increasingly being tapped for drinking water supplies, partly because of the growing scarcity of water resources and also because groundwater is preferred as a source of "clean" drinking water. The adverse health effects of an excessive intake of arsenic or fluoride only become apparent after some years. This is important because it has been established that most residents in developing countries like Ibadan are not aware of these contaminants (Egbinola, Amanambu 2014). In this study, hydrogeochemical processes and geogenic contaminants in shallow aquifers of Ibadan can provide an explanation and better understanding of the occurrence of these contaminants within the groundwater in the area. The specific objectives include the following: (1) examination of the spa-

tial and seasonal variation in geogenic contaminants in different geologic formations, (2) categorization and characterization of the hydrogeochemical properties of the groundwater, (3) determination of the relationship between hydrogeochemical characteristics of the groundwater and (4) examination of the relationship between rock types and geogenic contaminants.

Study Area

Ibadan was founded in the 1820s (Mabogunje 1968) and lies between longitude 3° 54' East of the Greenwich meridian and 7° 32' North of the equator. Ibadan is the capital of Oyo state and has been an important administrative centre since colonial times. The study area is underlain by basement complex rocks of metamorphic origin of the Pre-Cambrian age (Fig. 1). These rocks can be grouped into major and minor rock types. The major types are quartzite of the meta-sedimentary series and the migmatite complex comprising banded gneiss, augen gneiss and magnetite, where the minor rock types include pegmatite, quartz, aplite, diorites, amphibolites and xenoliths (Akintola 1994). The area has a low gentle undulating top.

The type of rock in an area is an important factor governing the characteristics of its groundwater. Basement complex rocks, composed mainly of metamorphic and igneous rock types are relatively low in groundwater production in comparison with sedimentary rock areas to the south. The basement complex nature of the rocks in Ibadan does not however completely rule out the possibility of the presence of isolated good and productive aquifers, if proper searching is carried out. The factors which account for the presence of good aquifers in particular locations over the basement complex rocks are the thickness of the regolith (weathered layer), the size and density of fractures, fissures and other cracks, and the permeability and porosity of the rocks. Ibadan is located near the forest grassland boundary of South-western Nigeria (Amanambu, Ojo-Kolawole 2013). The latitudinal location (lat 07° 26'N) of Ibadan means it enjoys the characteristic West African monsoon climate, marked by a distinct seasonal shift in the wind pattern. It therefore

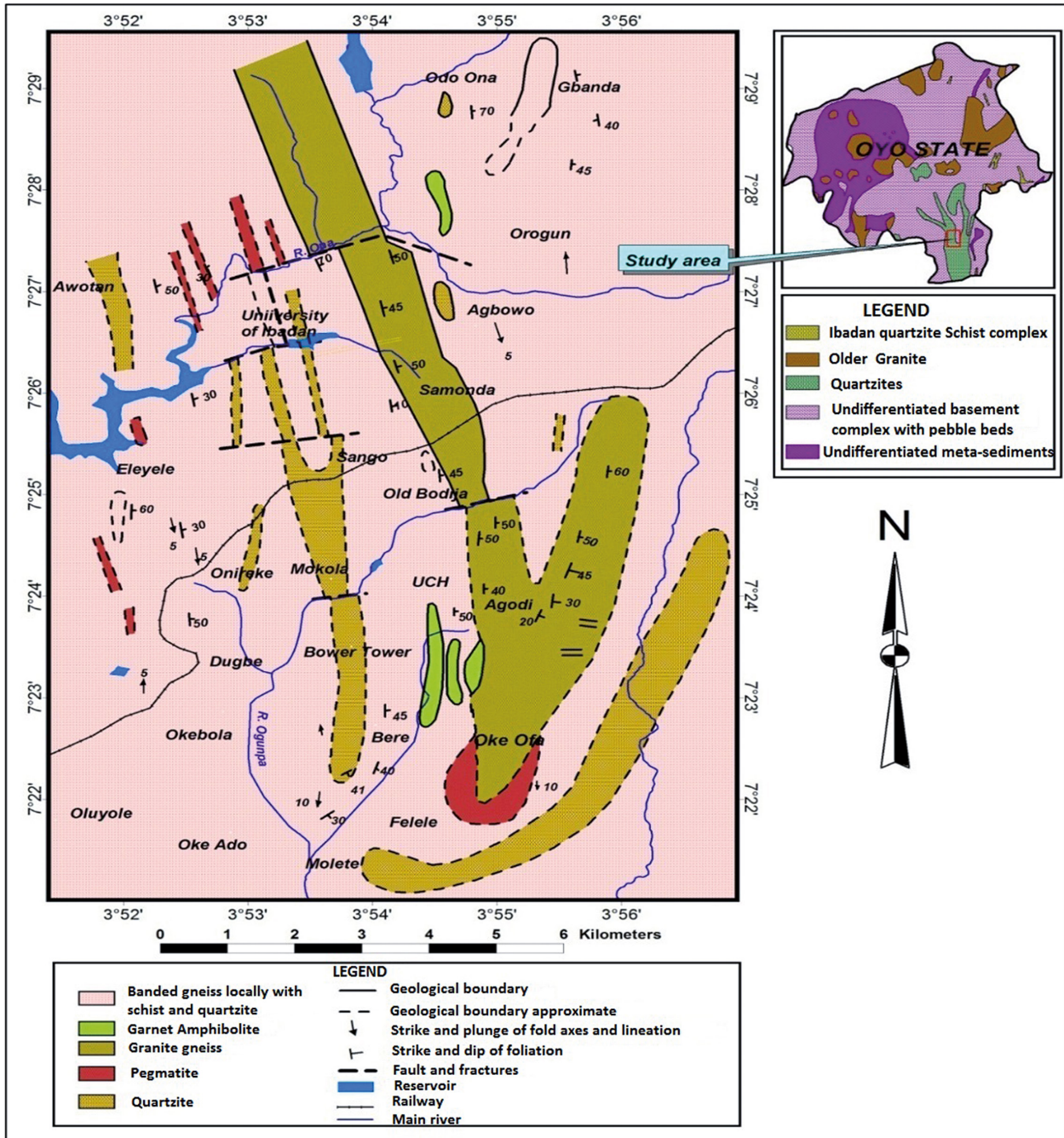


Fig. 1. Geology map of Oyo State showing the Geology of Ibadan

means that the climate of Ibadan is tropical with distinct wet and dry seasons and a mean annual temperature of 27.1°C (Egbinola, Amanambu 2013) but in consonance with seasonal variations in radiation, sunshine and cloud cover, the mean annual temperature could change. Between March and Oc-

tober, the city is under the influence of the moist maritime South-west monsoon winds, which blow inland from the Atlantic Ocean. This is the rainy season. The dry season occurs from November to February, when the dry dust-laden winds blow from the Sahara desert.

Research Methodology

Water quality parameters

Studies in geogenic contaminants entail the identification of the state of water by analysing some physico-chemical parameters. The physico-chemical parameters include pH, TDS, Arsenic (As), Fluoride (F), Sodium (Na), Sulphate (SO_4^{2-}), Calcium (Ca^+), Iron (Fe), Magnesium (Mg) and Zinc (Zn), which were utilized in this analysis. The selection of the parameters depended on the purpose of the research. The geogenic parameters considered in this research are Arsenic and Fluoride.

Sampling techniques

The rock of the study area is made up of the basement complex rocks of igneous and metamorphic type. The major rock formations of the study area are Banded gneiss, Quartzite, Augen Gneiss, Pegmatite, and Garnel Amphibolite (Akintola 1994; Tijani et al. 2006; Amanambu, Egbinola 2015). The geologic formation of the study area includes both major and minor types but only five major rock formations were used as the framework for the sampling procedure. The other minor rock formations are found in small outcrops; as a result it might be difficult to locate shallow aquifers in the rock formation (Amanambu, Egbinola 2015). Water sampling in groundwater from different shallow aquifers based on the major geology of the area was undertaken for the study. Samples were collected in polyethylene bottles (750 ml). A total of six water samples each were collected at random from five different major geologic formations making a total of 30 water samples (15 samples were collected in Dec./Jan. 2012–2013 and April/May 2013 for Dry and Rainy season samples respectively) from the study area. The GPS location of each sampling point was taken. Groundwater samples collected from the different rock formations in the study area were analysed in the Department of Agronomy Laboratory (University of Ibadan) using a Hatch 404 handheld instrument for pH and TDS. For Arsenic (As), Fluoride (F), Sulphate (SO_4^{2-}), Calcium (Ca), Iron (Fe), Magnesium (Mg) and Zinc (Zn), an AAS (Buck Scientific Atomic Absorption Spectrophotometer),

210/211 VGP, Spectrophotometer and the Beckman DU-7500 single beam spectrophotometer were used.

Statistical analysis

Summary statistics e.g. mean (\bar{m}), standard deviation (s) and minimum-maximum values of the hydrochemical data were used. The interrelationships between the constituents of the groundwater are important, from a hydrochemical point of view. For this purpose the data were subjected to simple correlation analysis using the Pearson Correlation Matrix. This was done using SPSS, 21.

Factor Analysis was also used. Factor analysis (FA) has been successfully used to sort out the hydrochemical processes and relationships of analysed groundwater data. Factor scores were plotted and used to categorize and characterize the hydrogeochemical characteristics of the various aquifers. The purpose of FA is to simplify the quantitative description of a system by determining the minimum number of new variables necessary to reproduce various attributes of the data. These procedures reduce the original data matrix from one having (n) variables necessary to describe the (N) samples to a matrix with (m) factors ($m < n$) for each of the (N) samples. It is also aimed at transforming the variables so that the axes become orthogonal, which then allows the definition of new independent variables. By so doing, the first factor is chosen to explain as much as possible of the total variance of the observations, the second factor to explain as much as possible of the residual variance, and so forth.

An isopleth map and 3D Elevation Modelling were used to show the spatial variation of the geogenic contaminants in the study area. The isopleth map was drawn using ArcGIS GIS 10.1. This method uses the GPS location of the sampling points and the concentration of each of the parameters to draw lines showing places of equal concentration of the geogenic contaminants. The isopleth map was able to interpolate for the whole study area showing places of equal concentration of Arsenic and Fluoride. The 3D Elevation Modelling was further used to show areas of peak concentration as they vary to the lowest peak in 3D. Suffer 8 software was used to generate this map.

Results and Discussion

Factor analysis

Factor analysis of the studied groundwater samples was performed in order to obtain an overall impression about assembling the samples in a multi-dimensional space defined by the analysed parameters. Factor analysis is a useful tool for better understanding of the relationship among variables and for revealing groups (or clusters) that are mutually correlated within a data body. Factor analysis was conducted for all samples which reveal a 0.734 value for the Kaiser-Maiyer-Olkin (KMO) and 162.890 ($p < 0.0001$) for Bartlett's sphericity, indicating that FA may be useful in providing significant reductions in dimensionality.

From the data, three factors (Table 1), explaining 71.884 % of the total variance, were estimated on the basis of the Kaiser criterion (Kaiser 1960) of the eigenvalues greater or equal to 1 and from a Cattel scree plot. A scree plot (Fig. 2) shows the eigenvalues sorted from large to small as a function of the factor number.

Table 1. Rotated Factor Loading Matrix, eigenvalues, % variance and cumulative variance values (TDS – Total Dissolved Solid, As – Arsenic, F – Fluoride, Na – Sodium, Ca – Calcium, Mg – Magnesium, Fe – Iron, Zn – Zinc, SO_4^{2-} – Sulphate)

PARAMETER	FACTOR		
	1	2	3
pH	0.012	-0.227	0.653
As [mg/l]	0.245	0.914	0.009
TDS [mg/l]	0.878	0.236	-0.081
F [m/l]	-0.098	0.181	0.694
Ca [mg/l]	0.939	0.051	-0.086
Mg [mg/l]	0.917	0.231	0.014
Na [mg/l]	0.913	0.099	-0.027
Fe [mg/l]	0.071	-0.14	0.624
Zn [mg/l]	-0.177	0.285	0.625
SO4 [mg/l]	0.24	0.924	-0.021
Eigenvalue	3.957	1.782	1.449
% Variance	34.902	19.946	17.036
Cumulative %	34.902	54.848	71.884

TDS, Ca, Mg and Na, marked factor 1, which explained 34.902% of the total variance. Factor 1 had a high positive loading in TDS, Ca, Mg and Na which were 0.878, 0.939, 0.917, and 0.913 respectively. High positive loadings indicated strong linear

correlation between the factor and parameters. Thus, factor 1 can be termed as the inorganic salt (salinization) factor. This is probably of natural origin. This is an indication that groundwater with high levels of dissolved inorganic salts must have originated from water that has flowed through a region where the rocks have a high salt content. Increased dissolution can increase salinity levels. Increased concentrations of dissolved solids can also have technical effects. Dissolved solids can produce hard water, which leaves deposits and films on fixtures, and on the insides of hot water pipes and boilers. Soaps and detergents do not produce as much lather with hard water as with soft water. As well as this, high amounts of dissolved solids can stain household fixtures, corrode pipes, and have a metallic taste. Hard water causes water filters to wear out sooner, because of the amount of minerals in the water.

Factor 2, with higher loading of As and SO_4^{2-} explained 19.946% of variance with loading of 0.914 and 0.924 respectively. This is a factor of sulphate precipitation. Here Arsenic tends to be formed because of the presence of sulphate ions. Arsenic contamination in groundwater can be accompanied by the reduction of sulphate to sulphide ions (Saumen et al. 2011). This shows that the presence of Arsenic in the area under study is partly geogenic (from sulphide minerals). Therefore, sulphate availability drives the evolution of the speciation of Arsenic, considering the fact that As can be derived from both natural and anthropogenic sources and can dissolve in rainwater, rivers or groundwater or the food chain through plants and animals (Mandal et al. 2002).

Factor 3 was responsible for 15.069 % of total variance and best represented by pH, fluoride, Zinc and Iron with loading of 0.653, 0.694, 0.625 and 0.624 respectively. Groundwater of high pH value encourages the mobilization of fluoride. This single fact confirms the relationship between pH and fluoride in this factor. Iron (Fe) could be conceived to mainly originate from the ionic dissolution in the course of groundwater migration. Leaching through the overlying lateritic sand can increase the iron content of the groundwater and the process is enhanced when the pH is low. The human body needs iron for strong teeth and bones. However, high concentration of iron in groundwater could impart taste, discoloration, deposits and turbidity (Adekunle et al. 2007; Amadi 2010).

Scree test

A Scree Plot is a simple line segment plot that shows the fraction of total variance in the data as explained or represented by each factor. The factors are ordered, and by definition are therefore assigned a number label, by decreasing order of contribution to total variance. The scree-plot is a graph of eigenvalues in order of magnitude. It shows a distinct break between the steepness of the high eigenvalues and the gradual trailing off of the rest of the factors (Fig. 2). In the present study, the three factors extracted (eigenvalues > 1) represent adequately the overall dimensionality of the data set and accounted for 71.884% of the total variance, while the remaining 7 factors (eigenvalues < 1) accounted for only 24.259% of the total variance.

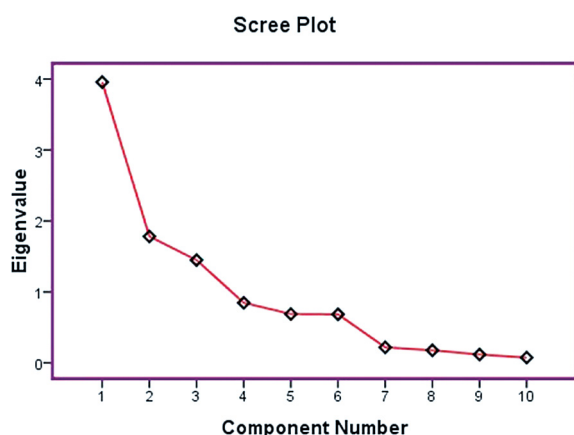


Fig. 2. Scree Plot test

The plot of loadings of the three factors (Fig. 3) indicates the contribution of different parameters to the chemical quality of the shallow aquifers.

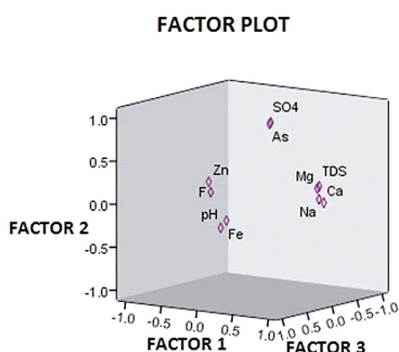


Fig. 3. Plot of loading of the three factors

Groundwater parameters were categorized (Fig. 3) based on the factor loading and the following groups were indicated:

- Factor 1: Ca, Mg, Na and TDS
- Factor 2: As and SO₄²⁻
- Factor 3: Fe, F, pH and Zn

Factor 1 can be referred to as the salinity index, factor 2 as the sulphate index and factor 3 as the fluoride index. The implication of this result is that the groundwater of the study area is composed mainly of inorganic salts (Ca, Mg and Na), sulphate, which experiences reduction to form arsenic, and finally fluoride, which is evident in places of high pH values.

Relationship between geogenic contaminant (arsenic & fluoride) and rock formation

Banded gneiss and geogenic contaminants

The result from Table 2 shows that the mean concentration of Arsenic (As) and Fluoride (F) in the geologic formation of Banded gneiss is 0.275 mg/l and 0.415 mg/l respectively being highest for F. As in the rock formation did not really show a marked variation in concentration (Fig. 4) compared to the concentration of F in the rock formation. The concentration of Arsenic and Fluoride in the geologic formation of banded gneiss is as a result of its basement complex origin.

Minerals of igneous rocks have been known to produce Arsenic (Sudipta 2007; Joseph et al. 2008). Banded gneiss contains mica and biotite minerals. This report supports the works of O’Shea et al. (2010), where they pointed out that Arsenic concentration in biotite varies with metamorphic grade. The presence of these minerals could be responsible for the concentration of Arsenic within the rock formation. Fluoride has also been found to occur in the minerals of Mica and Biotite (Joseph et al. 2008). The presence of this rock mineral in this rock formation could be responsible for the occurrence of fluoride within the groundwater of the rock formation.

Table 2. Hydrogeochemical concentration of geogenic contaminants

	BANDED GNEISS	QUARTZITE	AUGEN GNEISS	PEGMATITE	GARNEL AMPHIBOLITE
ARSENIC	0.35	0.38	0.03	0.17	0.07
	0.25	0.13	0.27	0.23	0.13
	0.21	0.06	0.36	0.26	0.05
	0.37	0.07	0.03	0.11	0.22
	0.13	0.06	0.19	0.03	0.18
	0.34	0.05	0.09	0.09	0.15
Mean	0.275 mg/l	0.125	0.162 mg/l	0.148 mg/l	0.1333 mg/l
FLUORIDE	1.2	3.6	0.2	0.53	1.3
	1.2	1.2	0.1	0.06	0.02
	0.01	0.2	0.04	0.02	0.01
	0.02	0.2	0.03	1.7	0.1
	0.02	0.1	0.02	0.01	2.2
	0.04	2.01	1.5	2.4	0.1
Mean	0.415 mg/l	1.218 mg/l	0.315 mg/l	0.787 mg/l	0.622 mg/l

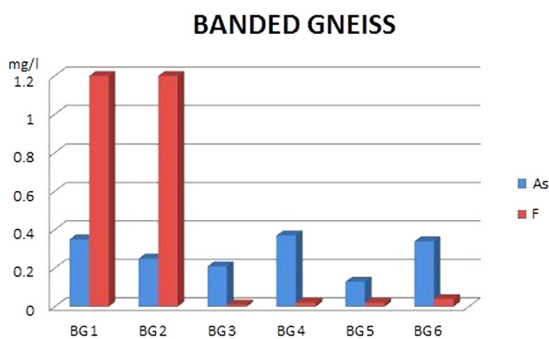


Fig. 4. Relationship between Banded gneiss and Geogenic contaminants (BG1-BG6 – samples of Banded gneiss)

Quartzite and geogenic contaminants

The mean concentration of Arsenic and Fluoride (Fig. 2) in the Quartzite formation of the shallow aquifer is 0.0125 and 1.218 mg/l respectively. Fluoride showed a marked variation in its concentration within the groundwater of the shallow aquifer (Fig. 5). Rock minerals found in quartzite include epidote, biotite, hornblende, iron oxides and Mica. It has been established that these minerals release Fluoride and Arsenic. For instance Mica and Biotite have been known to be a good source of As and F, hence the concentration of the contaminants within the groundwater of the rock formation. Iron oxide is also a viable source of Arsenic within the groundwater of the rock formation, hence the concentration of As. Fluoride occurs as fluormica (phlogopite) $[KMg_3(Si_3Al)O_{10}(F,OH)_2]$, biotite $[K(Mg,Fe)_3 Al-$

$Si_3O_{10}(F,OH)_2]$, epidote $[Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)]$, and hornblende $[Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2]$, mica (Haidouti 1991; Gaumat et al. 1992; Gaciri, Davies 1993; Kundu et al. 2009). The evidence of the occurrence of all these minerals that embody fluoride suggests the occurrence of fluoride in the groundwater within the shallow aquifer as evident in the result (Table 2, Fig. 5).

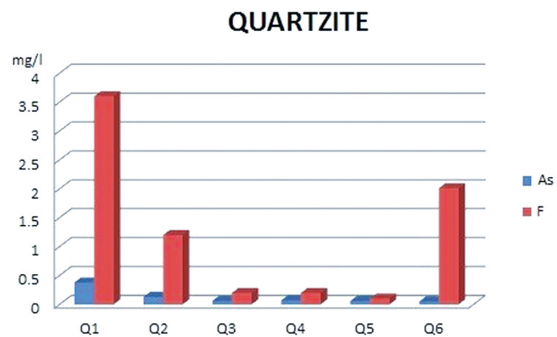


Fig. 5. Relationship between Quartzite and Geogenic contaminants (Q1-Q6 – samples of Quartzite)

Augen gneiss and geogenic contaminants

The result from table 2 shows that the mean concentration of Arsenic and Fluoride in the geologic formation of Banded gneiss is 0.162 mg/l and 0.315 mg/l respectively being highest for F. As in the rock formation showed a more marked variation in concentration (Fig. 6) compared to the concentration of F in the rock formation except for sample

six, where the concentration of Fluoride exceeds the value of any other. The concentration of Arsenic and Fluoride in the geologic formation of Augen gneiss is as a result of its basement complex origin. Augen gneiss as with Banded gneiss contains mica and biotite minerals. The presence of these minerals could be responsible for the concentration of Arsenic and Fluoride within the groundwater of the rock formation.

AUGEN GNEISS

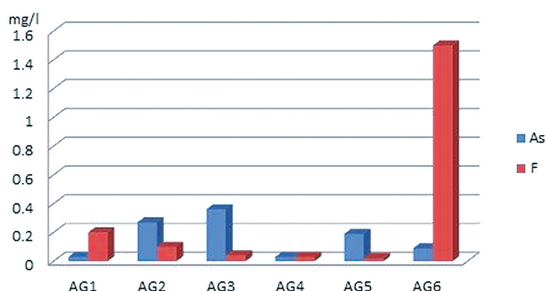


Fig. 6. Relationship between Augen gneiss and Geogenic contaminants (AG1-AG6 – samples of Augen gneiss)

Pegmatite and geogenic contaminants

The mean concentration of Arsenic and Fluoride (Table 2) in the Pegmatite formation of the shallow aquifer is 0.148 and 0.787 mg/l respectively. Fluoride showed a marked variation in its concentration within the groundwater of the shallow aquifer and no marked variation in the concentration of Arsenic within the groundwater of the geologic formation (Fig. 7). Rock minerals found in pegmatite include pyrite, apatite, fluorite (CaF₂), topaz and Mica. Pyrite is the most widespread and abundant naturally occurring sulphide in the world. The most important ore of As includes pyrites. It has been established that pyrite is a very good source of Arsenic (Thomas 2003; Mahimairaja 2005; Amini et al. 2008). The concentration of Arsenic within the groundwater of this rock formation implies the release of As through the presence of sulphide within the rock formation. Therefore, the arsenic-leaching mineral of pyrite is partly responsible for facilitating the release of Arsenic. Apatite, fluorite (CaF₂), topaz and mica are known to be minerals releasing Fluoride (Gaciri, Davies 1993; Kundu, Mandal 2009). These minerals of pegmatite facilitate the release of fluoride within the shallow aquifer of the Ibadan area.

PEGMATITE

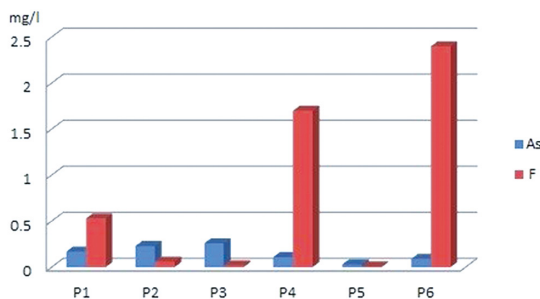


Fig.7. Relationship between Pegmatite and Geogenic contaminants (P1-P6 – samples of Pegmatite)

Garnel amphibolite and geogenic contaminants

The result from Table 2 shows that the mean concentration of Arsenic and Fluoride in the geologic formation of Garnel Amphibolite is 0.133 mg/l and 0.622 mg/l respectively being highest for F. As in the rock formation did not really show a marked variation in concentration but showed an even variation in concentration (Fig. 8) compared to the concentration of F in the rock formation. The concentration of Arsenic and Fluoride in the geologic formation of Garnel Amphibolite is as a result of its basement complex origin. Garnel Amphibolite contains minerals of amphibole such as tremolite [Ca₂Mg₅Si₈O₂₂(OH)₂] and hornblende [Ca₂(Mg,Fe,Al)₅(Al,Si)₈O₂₂(OH)₂]. These minerals embody Arsenic and fluoride (Haidouti 1991; Gaumat et al. 1992;) within the groundwater where they are formed. The presence of these minerals could be responsible for the concentration of Arsenic and Fluoride within the rock formation.

GARNEL AMPHIBOLITE

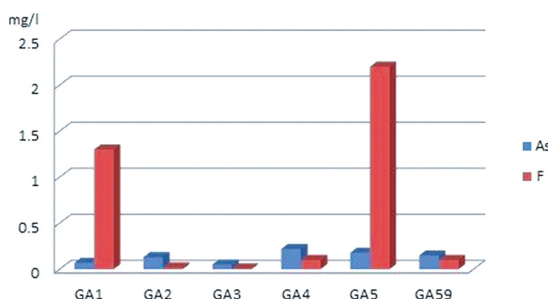


Fig. 8. Relationship between Garnel Amphibolite and Geogenic contaminants (GA1-GA6 – samples of Garnel Amphibolite)

Seasonal variation of geogenic contaminants

Table 3 shows the seasonal variation of geogenic contaminants of Arsenic and Fluoride. The mean concentration of Arsenic for different rock formations during the wet season is 0.27, 0.19, 0.22, 0.22 and 0.083 mg/l for Banded gneiss, quartzite, Augen gneiss, pegmatite and garnel amphibolite respectively. This can be compared to the dry season (Fig. 9) with the mean of 0.28, 0.06, 0.103, 0.07, and 0.18 mg/l for Banded gneiss, quartzite, Augen gneiss, pegmatite and garnel amphibolite respectively. It is obvious from the result that the concentration of As in the wet season is more than that of the dry season in quartzite, augen gneiss and pegmatite rock formations. During the wet season (April/May) the concentration of Arsenic varies between 0.03 to 0.38 mg/l. During the dry season (Jan/Feb) the concentration of Arsenic varies between 0.03 to 0.37 mg/l.

Table 3. Seasonal variation of Arsenic and Fluoride

ROCK FORMATION	Wet Season		Dry Season	
	As [mg/l]	F [mg/l]	As [mg/l]	F [mg/l]
BANDED GNEISS	0.35	1.2	0.37	0.02
BANDED GNEISS	0.25	1.2	0.13	0.02
BANDED GNEISS	0.21	0.01	0.34	0.04
MEAN	0.27	0.803	0.28	0.027
QUARTZITE	0.38	3.6	0.07	0.2
QUARTZITE	0.13	1.2	0.06	0.1
QUARTZITE	0.06	0.2	0.05	2.01
MEAN	0.19	1.667	0.06	0.77
AUGEN GNEISS	0.03	0.2	0.03	0.03
AUGEN GNEISS	0.27	0.1	0.19	0.02
AUGEN GNEISS	0.36	0.04	0.09	1.5
MEAN	0.22	0.113	0.103	0.517
PEGMATITE	0.17	0.53	0.11	1.7
PEGMATITE	0.23	0.06	0.03	0.01
PEGMATITE	0.26	0.02	0.09	2.4
MEAN	0.22	0.203	0.077	1.37
GARNEL AMPHIBOLITE	0.07	1.3	0.22	0.1
GARNEL AMPHIBOLITE	0.13	0.02	0.18	2.2
GARNEL AMPHIBOLITE	0.05	0.01	0.15	0.1
MEAN	0.083	0.443	0.183	0.8

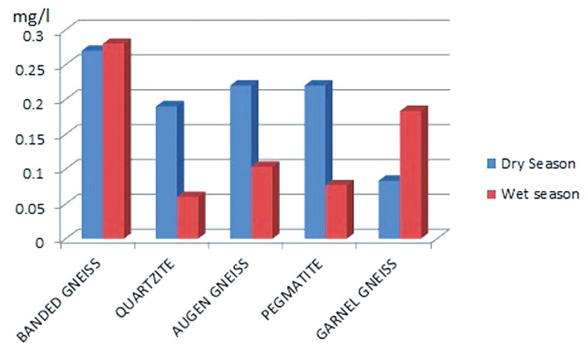


Fig. 9. Mean Seasonal variation of Arsenic

Arsenic is said to be found in arid regions where excessive evaporation leads to high pH and salinity (Amini et al. 2008). It is important to state that one can liken the aridity of this region of excessive evaporation to the dry season, where evaporation is more than precipitation. In this condition, it is expected that Arsenic concentration will be greater. But the result in this research does not support the increase in concentration of Arsenic during the period of excessive evaporation; rather it supports the increase in the concentration of Arsenic during the wet season, where rainfall will assist in the mobilization of Arsenic. The increase in As concentration in the study area during the wet season could also be due to reducing aquatic environments, where Arsenic is most probably released by reductive dissolution (Smedley, Kinniburgh 2002). Reducing aquatic environments are typically poorly drained and rich in organic matter content making them conducive to high microbial activity and, hence, low oxygen concentrations (Rowland et al. 2006). The increase in the concentration of As in this area could also be due to the period when the water samples were collected. The water samples were collected at the beginning of the rainy season; as such the resident time available for the total dilution of As is low. This short resident time concentrated the already mobilized Arsenic instead of diluting it. It is expected that in the mid rainy season with a longer resident time As in the shallow aquifer of the study area would be diluted resulting in lower concentration. In reducing regions with higher sulphate concentrations, dissolved arsenic could be low due to microbial sulphate reduction and subsequent precipitation of arsenic sulphides. According to Farooq et al. (2010), increase in rainfall intensity increas-

es the rate of dilution, which minimizes the arsenic concentration in the groundwater. This was only observed in the rock formation of Banded gneiss and Garnel amphibolite (Table 3, Fig. 9). The mean Arsenic concentration (0.027-0.443 mg/l) for all samples in the area under investigation (for both wet and dry seasons) has a concentration higher than that of the WHO (2008) standard (0.01 mg/l).

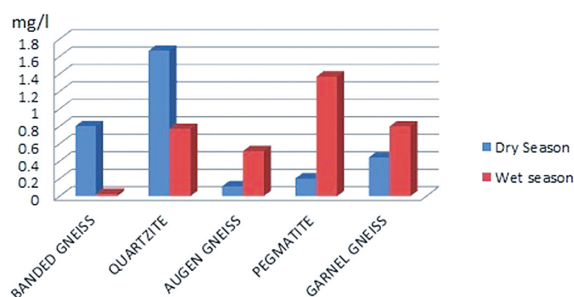


Fig. 10. Mean Seasonal variation of Fluoride

Figure 10 did not really show a particular trend in the concentration of Fluoride in the study area; rather it shows a fluctuation in its concentration. The concentration of Fluoride, table 3, during the wet season (April/May) varies between 0.01-3.6 mg/l. During the dry season (Dec/Jan) the concentration of fluoride varies between 0.01 to 2.01 mg/l being highest in the quartzite sample. The mean concentration of Fluoride for different rock formations during the wet season is 0.8, 1.67, 0.11, 0.20 and 0.44 mg/l for Banded gneiss, quartzite, Augen gneiss, pegmatite and garnel amphibolite respectively; being highest in quartzite rock formation compared to the dry season with the mean of 0.027, 0.77, 0.52, 1.37, and 0.8 mg/l for Banded gneiss, quartzite, Augen gneiss, pegmatite and garnel amphibolite respectively. Figure10 shows the average fluoride concentrations in dry and wet seasons. Average fluoride values in the wet season and dry season vary within the different rock types of the area under study. It is high for banded gneiss and quartzite. This implies that within this rock formation increase in precipitation encourages dissolution and subsequent mobilization of Fluoride. This result is supported by the works of Battaleb-Looie and Moore (2010), when they pointed out that the average fluoride values in the wet season are higher

than in the dry season. On the other hand evaporation or rather lack of rainfall increases the concentration of F in quartzite (0.77 mg/l), Augen gneiss (0.52 mg/l) and pegmatite (1.37 mg/l) geologic formation (Table 3). In the work of John and Rachel (2012), in South Africa on the study of Fluoride the authors established that fluoride concentrations in the groundwater decreased during the wet season and increased to a level slightly greater than 5 mg/l during part of the dry period Therefore climatic conditions (e.g., evapotranspiration, precipitation) have an influence on fluoride concentration (Amini et al. 2008). Fluoride concentration (Table 3) within some rock formations did not meet the standard of the WHO (2008) of 1.5 mg/l.

Spatial variation of geogenic (arsenic and fluoride) contaminants

The spatial distribution of geochemical parameters As and F of the region under study is presented in Figure 11 and 12 respectively. To obtain the spatial distribution of the above mentioned geochemical parameters the GPS location and the concentration of the parameters in different rock formations were plotted on the geology map of the study area in order to obtain an isopleth map combined with a digital elevation modelling. As observed on the isopleth map of the study area for Arsenic (Fig. 11), the highest concentration of arsenic was found in the Sango area (0.38 mg/l). The map also reveals a decrease in this concentration towards the western side of the map i.e. from Sango to Ijokodo (0.13 mg/l). It also shows a reduction in the concentration of Arsenic to the North of the map, showing a low concentration of 0.25 mg/l at Ojo compared to the Arsenic concentration at Sango. The concentration reduced from the North of the map to about 0.12 mg/l at Agbowo. The map showed a decrease in the concentration of Arsenic from the Western part of the map towards the Eastern (Iwo, 0.03 mg/l; Sabo, 0.06 mg/l) part of the map. Towards the Southern part of the isopleth map, there is an increase in the concentration of Arsenic from Bower Towers (0.06 mg/l) and Oke Offa (0.23 mg/l) to Agugu (0.36 mg/l) in the South Eastern part of the map.

A 3D Digital Elevation Modelling (Fig. 11) was further used to show clearly the variation in the

concentration of Arsenic in the shallow aquifers of the area under study; the map clearly shows that places like Sango (0.38 mg/l), Dugbe (0.36 mg/l) and Agugu (0.34 mg/l) show a high peak of Arsenic concentration against areas of very low concentration like Agowo (0.05 mg/l), Bower Towers (0.06 mg/l) and Agodi (0.03 mg/l).

As shown on the isopleth map (Fig. 12) of the study area, the highest concentration of fluoride was found in the Sango area (3.6 mg/l). The map also reveals a decrease in this concentration towards the western side of the map i.e. from Sango to Ijokodo and also a decreasing concentration towards Agbowo and Barika in the North area (Fig. 12). It also shows a reduction in concentration of Fluoride to the south of the map showing a low concentration of 1.2 mg/l at Mokola compared to the Fluoride concentration at Sango. It further shows a reduction towards the South-Eastern part of the isopleth map. The concentration decreased towards the East from Sango (3.6 mg/l) down to Iwo (0.03 mg/l) in the East of the map. Towards the Southern part of the isopleth map, there is a decrease in the concentration of Fluoride from Mokola (1.2 mg/l) down to Agodi (0.2 mg/l).

A 3D Digital Elevation Modelling (Fig. 12) was further used to show clearly the variation in the concentration of Fluoride in the shallow aquifers of the area under study. The map clearly shows that places like Sango (3.6 mg/l), Kudeeti (2.2 mg/l) and

Agodi (1.5 mg/l) show a high peak of Arsenic concentration against areas of very low concentration like Iwo road (0.03 mg/l), Agugu (0.04 mg/l) and Ijokodo (0.02 mg/l). One can also see areas of equal concentration of the contaminants within the isopleth maps; this is what the author has called Isogeogenic lines i.e. lines that represent areas of equal concentration of geogenic contaminants.

Relationship between geogenic contaminants and other hydrogeochemical variables

The correlation analysis result (Table 4) shows the relationship between Arsenic (As) and other hydrogeochemical properties of the shallow aquifer (pH, Zn, Fe, SO_4^{2-} , Na and Mg). The relationship between As and pH and between Iron shows a Pearson correlation coefficient -0.128 ($P > 0.05$) and -0.007 ($P > 0.05$) respectively. This implies that the relationship between the variables is negative. The increase in pH concentration does not result in an increase in the concentration of Arsenic. Put differently as pH decreases the concentration of Arsenic increases. This relationship between the two variables is not significant. Also the increase in Fe concentration does not result in an increase in the concentration of Arsenic and the relationship is not significant.

Table 4. Correlation between Arsenic and other Hydrogeochemical properties (As – Arsenic, Na – Sodium, Ca – Calcium, Mg – Magnesium, Fe – Iron, Zn – Zinc, SO_4^{2-} – Sulphate)

		pH	Ca [mg/l]	Zn [mg/l]	Fe [mg/l]	SO_4^{2-} [mg/l]	Na [mg/l]	Mg [mg/l]
As [mg/l]	Pearson Correlation	-0.128	0.264	0.123	-0.007	0.889**	0.315	0.423*
	Sig. (2-tailed)	0.499	0.158	0.518	0.971	0.000	0.09	0.02
	Valid N	30	30	30	30	30	30	30

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

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

The R coefficient of Calcium (0.264), Zinc (0.123) and Sodium (0.315) indicates that there is no significant relationship between these variables and Arsenic, with a significant level of $P > 0.05$. The Pearson correlation coefficient indicates a positive relationship between As and Ca between As and Na and between As and Zn. This means that the relationships are positive. As the concentration of calcium

increases, there is a corresponding increase in the concentration of Arsenic, although this relationship is not significant. Also as the concentration of Na increases, there is a corresponding increase in the concentration of Arsenic, though this relationship is not significant. Additionally, there is an increase in the concentration of Arsenic if the concentration of Zn increases but this relationship is not significant.

The Pearson correlation coefficient, R for SO_4^{2-} and Mg is 0.889 ($P < 0.01$) and 0.43 ($P < 0.05$) respectively (Table 4). This implies that the relationship between As and SO_4^{2-} is positive and that between As and Mg is also positive. The increase in SO_4^{2-} concentration results in an increase in the concentration of Arsenic. In other words, as SO_4^{2-} increases the concentration of Arsenic also increases. This can also be said of Mg because as it increases in concentration Arsenic also increases in concentration. This relationship for both SO_4^{2-} and Mg with As is significant. The reason for this significant relationship between Arsenic and Sulphate is because As is easily mobilized by the reduction of sulphate to sulphide. The increased concentration of Arsenic in highly reduced aquifers where arsenic is predominantly present in its reduced state As (III), and not as a result of high-pH aquifers where arsenic is relatively soluble in its oxidized state As (V) (Smedley, Kinniburgh 2002; Welch et al. 2006).

Table 5. Correlation between Fluoride and other Hydrogeochemical properties (Ca – Calcium, Fe – Iron, Na – Sodium, Mg – Magnesium)

		pH	Ca [mg/l]	Fe [mg/l]	Na [mg/l]	Mg [mg/l]
F [m/l]	Pearson Correlation	0.242	-0.152	0.245	-0.066	0.000
	Sig. (2-tailed)	0.197	0.424	0.192	0.729	0.996
	N	30	30	30	30	30

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

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

The Pearson correlation coefficient (Table 4) indicates a positive relationship between F and pH and between F and Fe. The R coefficients pH and Iron are 0.242 ($P > 0.05$) and 0.192 ($P > 0.05$) respectively. This means that the relationships are positive. As the concentration of pH increases, there is a corresponding increase in the concentration of fluoride although this relationship is not significant. The result reveals that the concentration of F within the rock formation depends on high pH value. Also as the concentration of Fe increases, there is a corresponding increase in the concentration of fluoride, though this relationship is not significant. The relationship between F and Ca and between F and Na shows a Pearson correlation coefficient -0.152 ($P > 0.05$) and -0.066 ($P > 0.05$) respectively (Table 5). This implies that the relationship between

the variables is negative or inverse. The increase in Ca concentration does not result in an increase in the concentration of Fluoride. This means that a decrease in the concentration of Ca will result in an increase in the concentration of fluoride. This relationship between the two variables is not significant. Also the increase in Na concentration does not result in an increase in the concentration of fluoride. This relationship is not significant.

The R coefficient value of 0.000 ($p < 0.996$) indicates that there is no significant relationship between the variable of interest i.e. there is no significant relationship between F and Mg. It should be noted that the R value shows that there is a positive or direct relationship between F and Mg. This implies that an increase in the concentration of Mg leads to an increase in the F concentration. This result confirms the works of Amini et al. (2008), (*Statistical Modeling of Global Geogenic Fluoride Contamination in Groundwaters*), where he pointed out that fluoride-rich groundwaters are often associated with low calcium concentrations. This is associated with rocks with low calcium content, or high pH conditions where sodium bicarbonate dominates the groundwater composition.

Conclusions

Groundwater is an important source of water supply and, in many parts of the world, the only source. However, we must recognize that it can be unfit for drinking, cooking, and sometimes even unusable for agricultural purposes unless properly treated for naturally occurring contaminants, especially arsenic and fluoride. To guard against afflicting large populations with unfit water, there must be a vigilant water-quality monitoring programme in Ibadan and Nigeria at large, where public groundwater supplies are a major source, and water treatment systems where needed. With the exponential increase in groundwater resources and limited water-quality facilities in many countries, such programmes (water quality monitoring programme) will be extremely difficult to deploy and maintain. Ultimately, the population growth may overwhelm the finite supply of water as seems to be the situation in many parts of the developing world today.

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