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Hydrogeochemical characterization of groundwater in Afe Babalola University, Ado-Ekiti Southwestern Nigeria

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Groundwater composition can be altered significantly due to geogenic and anthropogenic inputs from bedrocks and human activities respectively. Such impacted water may be injurious to health if consumed. Water quality depends on the physical, chemical and bacteriological composition of water. Hydrochemical assessment of groundwater within Afe Babalola University (ABUAD) and its adjoining environments was undertaken with the aim of determining its chemical composition and suitability. A total of 26 boreholes were sampled randomly within ABUAD during the dry stable weather condition. Two set of samples were collected from each sampled borehole one for anions and the other one for cations and heavy metals. The water samples were analyzed for heavy metals, cations and anions using Atomic Absorption Spectrometry, Flame Photometry Emission and titration method at the Department of Geology, and Multi-Disciplinary Research Center, University of Ibadan and National Geo-Hazard Research Center, Ibadan respectively. Results obtained were subjected to statistical analysis and qualitative evaluation to determine the quality of the groundwater. The results of the analyses showed cations (major and trace elements) variations in mg/l; Ca²⁺ (14.0 - 69.0), Mg²⁺ (20.0 - 62.3), K⁺ (0.1 - 42.5), Na⁺ (12.3 - 54.0), Pb²⁺ (<0.01 - 3.93), Cu²⁺ (<1.00-0.43 mg/l; Cd²⁺ (<1.00 - 5.80), Co²⁺ (< 0.01 - 3.86 mg/l) and Cr²⁺ (0.01 - 3.79 mg/l) while anions variations in mg/l HCO₃⁻ (4.6 - 26.8 mg/l), Cl⁻ (60.0 - 180.0), NO₃⁻ (<0.01- 2.8 mg/l) and SO₄²⁻ (0.6 - 4.7 mg/l). The concentrations of anions and major cations in most of the investigated boreholes were found to be chemically conformable with WHO standard for safe water. However, most of the trace elements with exception of Cr and Co were found to be significantly higher than the WHO standards for safe water.

Key words: Groundwater, hydrochemical assessment, Afe Babalola University, Ado-Ekiti (ABUAD), geogenic, anthropogenic.

INTRODUCTION

The source of water for any specific purpose is not as important as the sustainability of water for the desired purpose. The demand of water has increased drastically in recent times. With increasing population,

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industrialization, urbanization and the consequent increase in demand for water both domestic and industrial uses, the attendant increase in the implication of polluted water on man and the environment have been severally studied (Asiwaju-Bello and Akande, 2004; Onipede and Bolaji, 2004).

Groundwater has immensely become an important water supply in urban and rural areas in both developed and developing nations for domestic, industrial and agricultural purposes (Ramkumar et al., 2010; Olayinka et al., 1999). Groundwater is replenished with precipitation and surface run-off. The dominant role of groundwater is clear and their uses and protections are, therefore, of paramount importance to human life and economic activity.

In any hydrogeological setting, surface water and groundwater are the main sources of water supply. These sources of water are prone to contamination and pollution by anthropogenic activities. Until recently, surface water has been the major source of water supply for domestic and industrial uses but, due to high population growth, the government has shown interest in the exploitation of groundwater over the years. Hence the need for water quality assessment for enhanced socio-economic growth and development (Ishaku, 2011).

Safe drinking water is a basic need for human development, and well-being and therefore an internationally accepted human right (Garg et al., 2009). According to Oloke (1997), drinking water can act as a passive means of transporting nutrients into the body system. So therefore, the provision for good quality water for drinking, domestic and agricultural uses is very crucial for sound and good human and environmental health, economic and sustainable development (Al-Bassam and Al-Rumikhani, 2003). Water quality depends on the physical, chemical and bacteriological composition of water. Variation in groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Magesh and Chandrasekar, 2011; Krishna et al., 2011). According to Davis and De Wiest (1966), drinking water standards are based on two main criteria namely; the presence of objectionable tastes, odour and colour and the presence of substances with adverse physiological effects. However, mineral enrichment from underlying rocks can change the chemistry of groundwater, making it unsuitable for consumption (Ako et al., 1990; 2011). In addition, water of poor physio-chemical quality may have adverse health effects causing avoidable economic and human losses. According to Hutchinson and Ridgeway, the water cycle is an obvious mode of transmission of enteric diseases.

Groundwater chemistry is altered as a result of the interaction between the subsurface formation and the percolating water. This brings about the need to understand the influence of the bedrocks on the groundwater system of the study area. Besides this geogenic influence, anthropogenic activity makes

groundwater system prone to higher possibility of contamination. Therefore, a proper understanding of the groundwater in the study area is of importance as to maintain good quality water for drinking, domestic, industrial and agricultural purposes.

The present study was carried out to evaluate groundwater quality in Afe Babalola University Ado-Ekiti and its suitability for drinking, domestic and agricultural purposes. Data from this study will not only contribute immensely to improve the understanding of the factors that control groundwater quality and also provide for the first time groundwater quality data in the study area, hence contributing to the sustainable management of groundwater resources in this university.

MATERIALS AND METHODS

The study area (ABUAD) is located within Ado Ekiti southwestern Nigeria (Figure 1). It extends from latitude 07°35'59" to 36°50'N and longitude E005°18'0" to 18°45". It has a relatively low relief with isolated hills and insurbergs that are dome-shaped. The climate is characterized by the tropical type influenced by monsoon winds during rainy season with maximum rainfall in October and dry season. Annual temperature ranges between 28 to 30°C with a mean annual rainfall of 1500 mm.

It is located within the Basement Complex of South Western Nigeria. Major lithological units are basically crystalline basement rocks. These rocks include coarse grained charnockite, granite, migmatite gneiss, banded gneiss, with superficial deposit of clay and quartzite (Figure 2). Association of the fine-grained charnockite and the porphyritic biotite-hornblende granite suggest a common age. According to Davis and De-Wiest (1966), crystalline rocks are poor water bearing aquifers because of their low porosity and low permeability. The hydrogeological characteristics of these rocks depend on the degree of weathering and fracturing of the underlying rock within the tropical rainfall belt. The intense deformational structures of these rocks permit adequate aquifer properties needed to generate the well water.

Twenty six (26) water samples were collected randomly from twenty six boreholes between December 2015 and January 2016. Boreholes were allowed to pumped for at least 10 min before sampling. The samples were collected in 1 liter capacity plastic bottles after rinsing with the sample and preserved airtight in order to avoid evaporation. Physical parameters such as TDS, EC and pH of the sampled water sources were determined in situ using pH/EC/TDS/temp perklin multi-meter. Samples were kept under air-condition prior to analysis. Major ions' concentrations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were determined by ion exchange chromatography at the University of Ibadan Multidisciplinary Research Laboratory, trace elements content were determined using AAS at the Department of Geology, University of Ibadan while the major anions (Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} and CO_3^{2-}) were determined by flame photometry emission at the National Geo-Hazard Research Centre, Ibadan. Standard procedures (APHA, 1998) were used. Alkalinity measurements were carried out by acid titration with 0.02N H_2SO_4 added to each sample to reach its titration end point marked by a pH of 4.5. For quality control of the chemical measurements, standards and blanks were used in between runs to provide a measured of background noise, accuracy and precision.

RESULTS AND DISCUSSION

The results of the chemical analyses are presented in

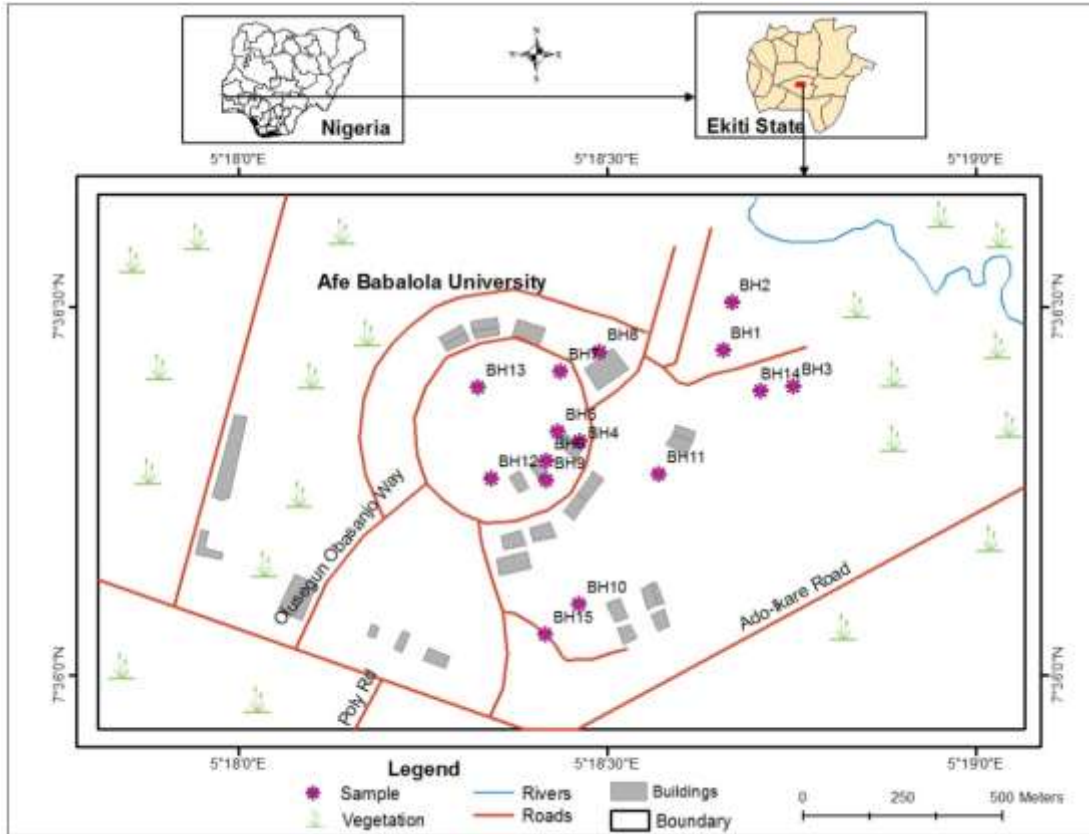


Figure 1. Location map of the study area showing sampling points.

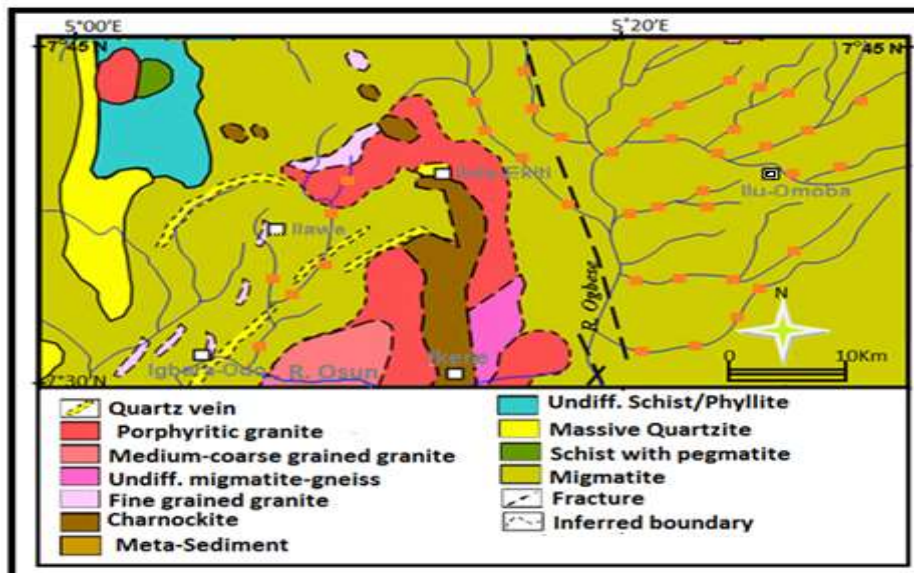


Figure 2. Geological Map of Ado Ekiti.

Table 1. The chemical composition of groundwater depends greatly on the general geology, degree of

chemical weathering of various rock types, quality of recharge water and inputs resulting from human

Table 1. Summary of the geochemical results of water samples in the study area.

| Chemical Parameters | Minimum | Maximum | Mean | W.H.O. Standard |
|-------------------------|---------|---------|-------|-----------------|
| pH | 6.95 | 8.20 | 7.56 | 6.5 - 8.5 |
| EC ($\mu\text{S/cm}$) | 23.7 | 1243.5 | 520.3 | 1400 |
| Pb | <0.01 | 3.93 | 3.92 | 0.01 mg/l |
| Cu | <0.01 | 0.43 | 0.40 | 1.0 ppm |
| Cd | <0.01 | 0.58 | 0.54 | 0.005 ppm |
| Co | <0.01 | 3.86 | 3.19 | - |
| Cr | <0.01 | 3.79 | 3.21 | - |
| Bicarbonate | 4.6 | 26.8 | 12.6 | 250 mg/l |
| Chloride | 60.0 | 180.0 | 93.1 | - |
| Nitrate | 0.00 | 2.8 | 1.2 | 50 mg/l |
| Sulphate | 0.6 | 4.7 | 1.7 | 250 mg/l |
| Mg | 20.0 | 62.3 | 36.5 | 30 mg/l |
| Ca | 14.0 | 69.0 | 21.9 | 75 mg/l |
| K | 0.00 | 42.5 | 17.5 | 12 mg/l |
| Na | 12.3 | 54.0 | 25.7 | 200 mg/l |

activities. It is therefore important to understand the groundwater chemistry as it is a main factor in determining its sustainability for drinking, domestic, agricultural and industrial purposes (Subramani et al., 2005).

In this study, the results of cations (that is, major and trace elements) and anions were subjected to statistical analysis. It was observed that there were significant and wider variability within the anions and the cations with the following order of magnitude among the trace and major elements $\text{Pb} > \text{Cr} > \text{Co} > \text{Cd} > \text{Cu}$, $\text{Mg} > \text{Na} > \text{Ca} > \text{K}$ while $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ among the anions (Tables 1). However, this order of absolute concentrations is not an indication of the relative degree of contamination but depends largely on the threshold values of the respective anions or cations.

Groundwater chemistry

The chemical composition varies over a wide range, and this indicates that the groundwater in the study area is not uniform but differs considerably, both in salinity and ionic composition. The pH values of the studied boreholes varied from 6.95 to 8.20 with an average of 7.56 suggesting that the groundwater within the study area are slightly alkaline in nature but still within the limit recommended by WHO (2004). The EC values ranged from 23.7 to 1243.5 $\mu\text{S/cm}$ with an average of 520.3 $\mu\text{S/cm}$, the lowest concentration of EC was found in samples collected within the Quarters while the highest concentration was observed in location 24 and 25. The measurement of EC is directly linked to the concentration of ionized substance in water and may be linked directly to the excessive hardness and other mineral

contamination.

Mg concentrations generally varied from 20.0 to 62.3 mg/l with an average concentration of 36.5 mg/l (Table 1). The highest concentration of Mg was found in location 9 collected within one of the colleges while the least concentration was observed in location 2 collected within one the Female Halls. The major source of Mg in natural water has been attributed to ions exchange of minerals in rocks and soils by water. Calcium concentration ranged from 14.0 to 69.0 mg/l and has an average concentration of 21.9 mg/l (Table 1). The highest concentration of calcium was found in location 3 while the lowest concentrations were observed in locations 6, 16, 18 and 24. Potassium ranges from 0.01 to 42.5 mg/l, high concentration of potassium water samples in the study area was observed in location 22 while location 3 has the least concentration. Sodium varies from 12.3 to 54.0 mg/l with an average of 25.7 mg/l. Location 17 recorded the highest concentration of sodium while locations 3, 19, 21 and 22 recorded the lowest concentrations.

In the analyzed trace elements, Pb varied from <0.01 mg/l in some of the samples to 3.93 mg/l with an average of 3.92 mg/l, Copper varied from <0.01 mg/l to 0.43 mg/l with a mean concentration of 0.08 mg/l (Table 1). Highest concentration of copper was recorded in locations 19 and 24 collected within one of the Colleges and the Female Halls while its lowest concentrations was observed in location 10 collected from one the Cafeterias. Cobalt ranged from <0.01 to 3.86 mg/l with a mean value of 3.19 mg/l (Table 1). Co recorded its maximum and minimum values in location 4 and 2 respectively. Cadmium concentrations varied from <0.01 to 0.58 mg/l with a mean concentration of 0.54 mg/l (Table 1). The highest concentrations of Cd were observed in locations 20 and 25 collected within the two of the Hostels while its lowest

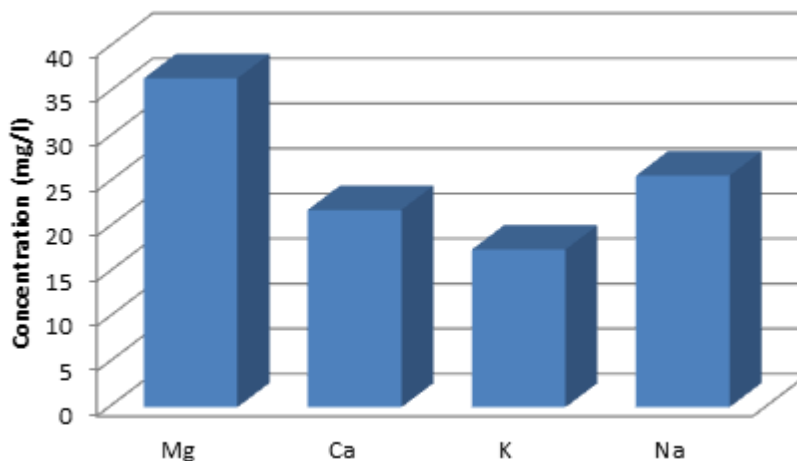


Figure 3. Comparison among the mean values of major elements.

was recorded in location 2. Chromium ranged from <0.01 to 3.86 mg/l, (Table 1), location 22 recorded the highest concentration of Chromium while location 2 has the least concentration. It has been confirmed that Pb and Cd have no beneficial effects in humans even at the lowest concentration and there is no known homeostasis mechanism for them. Any long-term exposure may therefore be expected to progressively cause more disruptions in the normal functioning of the organ systems where the metals are accumulating (Nriagu and Pacyna, 1988).

Similarly, among the anions, Bicarbonate varied from 0.46 to 2.68 mg/l in location 11 and 7 respectively with an average concentration of 1.26 mg/l (Table 1). All the samples were within the desirable permissible limit of WHO (2004) 500 mg/l. The primary source of bicarbonate in groundwater has been linked to dissolution of minerals such as calcite and dolomite. Chloride ranged from 60 to 180 mg/l with a mean concentration of 93.1 mg/l (Table 1). Cl has been described as the most common anion in natural water and it occurs naturally in all types of water. The highest concentration of Chloride (180 mg/l) in the study area is found in location 9 while locations 1, 14, 16, 17, 18, 21, 22 and 26 recorded low Cl⁻ concentrations. All sampled boreholes' water have their chloride concentrations below the desirable limit of 250 mg/l. Nitrate varied from <0.01 to 28.0 mg/l and a mean concentration of 12.0 mg/l (Table 1). The highest concentration of nitrate was observed in location 8 collected from one of the colleges, another sample collected from another borehole located some few meters away from this borehole within this same premise also recorded the highest chloride concentration among the samples collected for this study. Hot spot of these anions is suspected around this area which may probably be an infiltration from the septic tanks or percolation from the surface run-off. Sulphate varies from 0.6 to 4.7 mg/l with an average of 1.7 mg/l (Table 1). The highest

concentration of this anion was recorded in location 12. The sulphate concentrations in all the samples were below the permissible limit of 250 mg/l which shows that the groundwater is free from possible sulphate toxicity. The carbonate values were below detection limits in all the samples analyzed, this could be as a result of the observed pH which was below 8.0.

Comparative study of groundwater quality with WHO standards

From Table 1, the mean values of selected major elements were compared with one another and with the WHO standards. Magnesium showed the highest value (36.5 mg/l), this is followed by sodium (25.7 mg/l) then calcium (21.9 mg/l) while potassium (17.5 mg/l) has the least value (Figure 3). The dominance of Mg and Na as well as Ca was as a result of enrichment of ferromagnesian minerals in the underlying rocks of the study area which is mainly dominated by charnockite. This clearly demonstrates an interaction between the groundwater and underlying bedrocks weathering. It could be concluded that the origin of these cations are geogenic in nature. Mg and K have their mean values greater than the WHO desirable limit of 30 and 12 mg/l respectively while Na and Ca ions have their means less than WHO recommended limits of 2200 and 75 mg/l respectively.

Similarly, considering and comparing the mean of all the analyzed trace elements that are far greater than the WHO standard (0.01 mg/l) recommended for safe drinking water.

Pb has the highest mean value then Chromium and this is closely followed by Cobalt then Cu while Cadmium has the least mean value (Table 1 and Figure 4). The mean values of Pb, Cd and Cu were compared with the WHO standards for safe drinking water and it was discovered

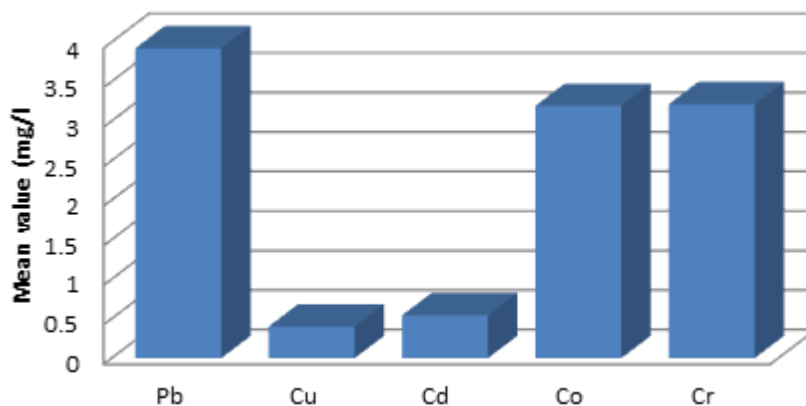


Figure 4. Comparison among the mean values of trace elements.

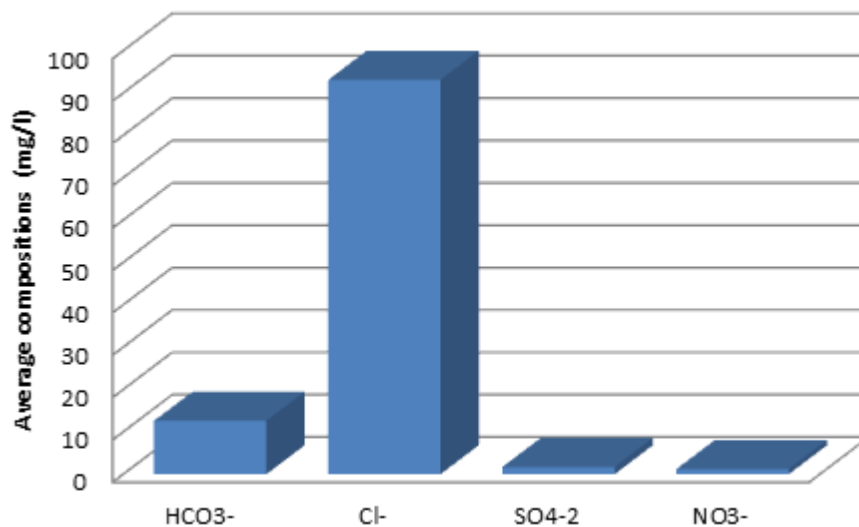


Figure 5. Comparison among the mean values of Anions.

that virtually all the water samples have Cd concentrations significantly higher than the maximum permissible level of Cd (0.005 ppm) in drinking water. Also most of the samples have their Cu concentrations with a mean of 8.0 ppm far above (eight folds) the maximum permissible level of Cu (1.0 ppm) while the average concentration of Pb in some locations is far above the WHO standard for safe water (Table 1, Figure 4). Cr and Co are more of lithogenic than anthropogenic origin while Cd, Pb and Cu can be considered as sourced from anthropogenic origin.

The dominance of chloride over the other anions is of significant importance as it almost marred the concentration effects of other anions. Chloride has an average composition of 93.1 mg/l followed by bicarbonate with a mean concentration of 12.6 mg/l and then sulphate and nitrate with a mean concentration of 1.7 and 1.2 mg/l respectively (Table 1, Figure 5). The mean concentration

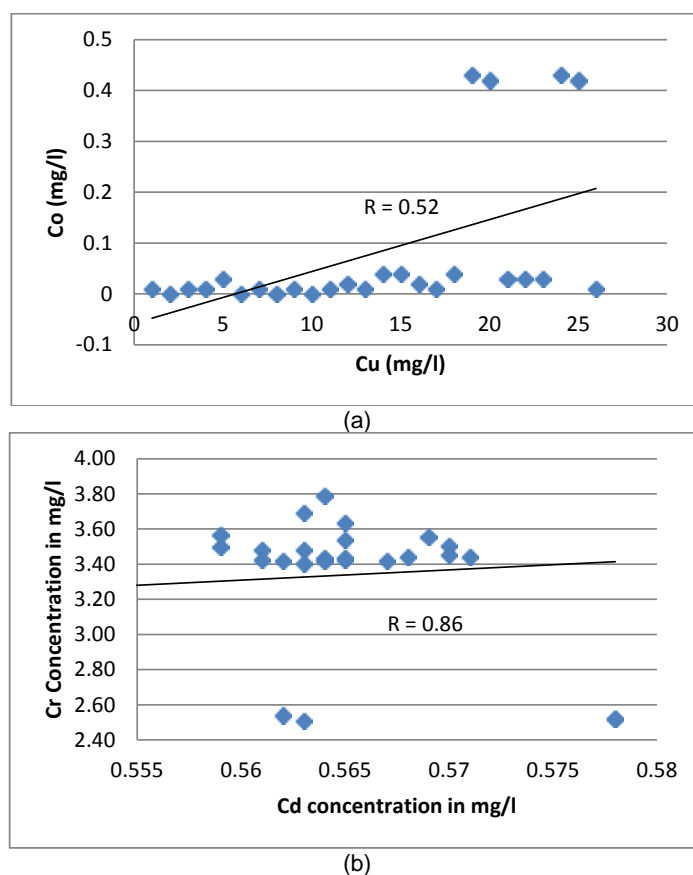
of these anions were compared with the WHO standards recommended for safe water and it was observed that all the anions were below their recommended values.

Correlation analysis

Pearson correlation analysis of the results was undertaken using the Statistical Programme for Social Science (SPSS, window 22.0). Correlation was done to state the relationship among metals and similarities in their geochemical behaviors. The analysis revealed a wide range of variation in the correlation values as both positive and negative correlations were established between some of the elements. The variability in the correlation amongst the elements is an indication that different geochemical factors have influenced their concentration in the samples.

Table 2. Correlation coefficient matrix of chemical parameters of groundwater samples of the study area.

| Sample | Cu | Cd | Co | Cr | HCO ₃ ⁻ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | Mg | Ca | K | Na |
|-------------------------------|-----------------|-----------------|----------------|----------------|-------------------------------|-----------------|------------------------------|-------------------------------|--------|--------|-------|----|
| Cu | 1 | | | | | | | | | | | |
| Cd | 0.126 | 1 | | | | | | | | | | |
| Co | -0.809** | 0.478* | 1 | | | | | | | | | |
| Cr | -0.375 | 0.861** | 0.843** | 1 | | | | | | | | |
| HCO ₃ ⁻ | 0.226 | 0.229 | -0.065 | 0.157 | 1 | | | | | | | |
| Cl ⁻ | -0.147 | -0.483* | -0.187 | -0.436* | -0.212 | 1 | | | | | | |
| NO ₃ ⁻ | -0.297 | -0.181 | 0.125 | -0.101 | -0.723** | 0.539** | 1 | | | | | |
| SO ₄ ²⁻ | -0.244 | -0.097 | 0.136 | 0.004 | -0.237 | 0.287 | 0.169 | 1 | | | | |
| Mg | -0.079 | 0.042 | 0.086 | 0.028 | -0.242 | 0.479* | 0.306 | 0.126 | 1 | | | |
| Ca | -0.065 | -0.572** | -0.283 | -0.475* | -0.102 | 0.305 | -0.051 | 0.205 | 0.119 | 1 | | |
| K | -0.166 | -0.085 | 0.073 | -0.050 | 0.062 | -0.003 | 0.041 | 0.142 | -0.216 | -0.227 | 1 | |
| Na | -0.219 | -0.647** | -0.185 | -0.495* | 0.013 | 0.313 | 0.026 | 0.139 | -0.103 | 0.093 | 0.230 | 1 |

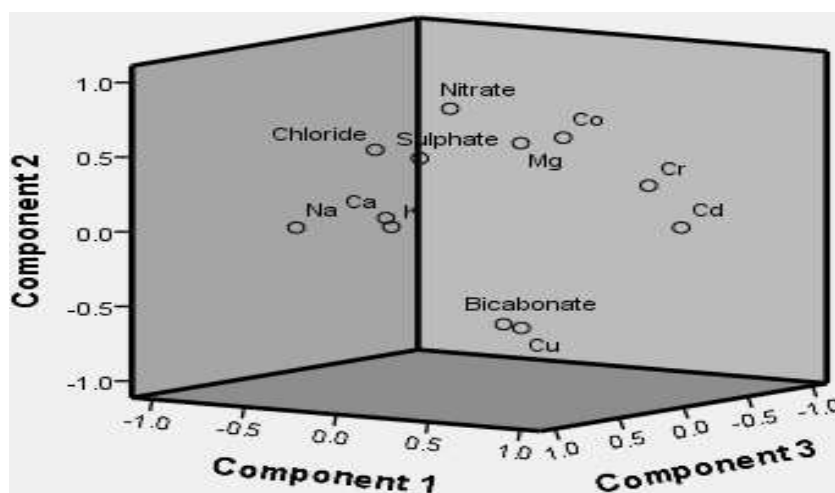
**Figure 6.** Scatter plots showing variations among a) Co vs Cu b) Cr vs Cd.

From Table 2, Cr and Cd (0.86) as well as Cr and Co (0.84) showed strong and positive correlation (Figure 6). This is a direct relationship which implies that similar geochemical processes have been responsible for their co-precipitation. K, Na, Ca, Mg, Co, Cd and Cu exhibit

low to negative correlations ranging from 0.48 to -0.81 with one another. This may be attributed to the fact that dissolution of metals in the aqueous phase is controlled by the chemical character and solubility of the respective metal as well as other chemothermodynamic conditions.

Table 3. Results of the R-Mode factors analysis.

| Sample | 1 | 2 | 3 | 4 | 5 | Com. |
|-------------------------------|--------------|--------------|--------------|--------------|-------------|------|
| Cr | 0.92 | 0.35 | -0.00 | 0.12 | 0.05 | 0.99 |
| Cd | 0.91 | 0.03 | -0.27 | -0.09 | 0.20 | 0.95 |
| Co | 0.63 | 0.68 | 0.25 | 0.21 | -0.08 | 0.98 |
| NO ₃ ⁻ | -0.33 | 0.71 | -0.24 | -0.47 | -0.13 | 0.90 |
| HCO ₃ ⁻ | 0.33 | -0.60 | 0.28 | 0.35 | 0.45 | 0.86 |
| Mg | -0.17 | 0.45 | -0.56 | 0.16 | 0.46 | 0.78 |
| SO ₄ ²⁻ | -0.21 | 0.45 | 0.16 | 0.23 | 0.30 | 0.42 |
| K | -0.02 | 0.08 | 0.66 | -0.44 | 0.31 | 0.73 |
| Na | -0.57 | 0.01 | 0.61 | -0.08 | 0.09 | 0.70 |
| Cu | -0.10 | -0.77 | -0.47 | -0.29 | 0.20 | 0.94 |
| Ca | -0.59 | -0.03 | -0.11 | 0.64 | -0.23 | 0.82 |
| Cl ⁻ | -0.68 | 0.41 | -0.16 | 0.03 | 0.41 | 0.82 |
| Initial Eigen values | 3.49 | 2.61 | 1.66 | 1.18 | 0.93 | |
| % of Variance | 29.11 | 21.77 | 13.84 | 9.85 | 7.78 | |
| Cumulative % | 29.11 | 50.88 | 64.72 | 74.57 | 82.35 | |

**Figure 7.** Screen plot of R-mode analysis showing elemental fractionations.

However, when compared to the WHO standards, the observed concentrations of these metals were generally below the permissible levels of drinking water. Although, this does not mean an absence of contaminations as the observed low concentrations could be attributed to partitioning and accumulation within the immediate environment of the aquifer. Therefore, possible change in the chemothermodynamic conditions can lead to remobilization into liquid phase.

R-Mode analysis

Principal component (PC) analysis was performed on the groundwater data for better understanding of their interrelationships and probable source of major ions. Table 3 presents the results of the R-mode components

analysis, eigen values and associated variance explained in the chemical data.

Factor 1 accounts for 29.11% of the total variance with eigen value of 3.49. This component is strongly and positively loaded with Cd, Co and Cr, strong but negatively loaded with Cl⁻ and moderately loaded with Cu (Table 3). This implies that all these parameters have similar source of input. Factor 2 is strongly and positively loaded with Co and HNO₃⁻ but negatively loaded with Cu and NO₃⁻. This factor accounts for 21.8% of the total variance with eigen value 2.6. Factor 3 has the highest positive loadings of Na and K and accounts for 13.8% of the total variance. Factor 4 has the highest positive loading for Ca which accounts for almost 10% of the total variance while Factor 5 is weakly and positively loaded with Mg, HNO₃⁻ and Cl⁻ (Table 3 and Figure 7).

Conclusions

This study has thrown light on the hydrogeochemistry and quality of groundwater in Afe Babalola University. The dominance of Mg and Na was as a result of enrichment of ferromagnesian minerals in the underlying rocks of the study area which is mainly dominated by charnockite and quartzite. This clearly demonstrated interaction between the groundwater and the underlying bedrocks. All the water samples are found to have their major cations and anions to be fairly conformable with the WHO Standards for safe drinking water with the exception of K. However, trace elements such as Pb, Cd and Cu their concentrations far above the WHO recommended standard for safe drinking water which implies that these borehole waters are not suitable for drinking. If the present concentrations of Cd and Pb continue to increase with time without been attended to, there is possibility of Pb and Cd health hazards outbreak in the nearest future in some of the locations.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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