

Hydrogeochemistry of Water Samples from some Boreholes in Umuahia North Local Government of Abia State

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ABSTRACT

Groundwater chemistry is affected by many factors such as original composition of recharge water, rock type, residence time in the host rock, and other characteristics of the groundwater flow path. This study was done using the analytical techniques to evaluate the physico-chemical quality of groundwater in Umuahia metropolis, Nigeria.

Eight water samples were collected using 75 ml bottle that had been thoroughly prewashed with the target water. The samples were sent to the Research Laboratory Services at Orji Kalu Housing Estate, Umuahia, Abia State for analysis within 24 hours. The quality of the groundwater as revealed by the hydrogeochemical analysis of these samples are suitable for various usages.

The result compared with WHO 2017 standard for drinking water shows that majority of the analyzed parameters such as Na^{2+} , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , PO_3^{3-} , are within the range stipulated by WHO 2017 except iron concentration which ranges from 0.62 to 0.84mg/L. The average value of chlorine is as low as 6.1mg/L in the samples suggests that the saltwater contamination in the adjacent coastal aquifers of the Niger Delta has not reached Umuahia, which is more hinterland. Low calcium and magnesium concentrations of the samples signify soft to slightly hard water. The ground water quality of the study area is suitable for domestic purposes, since most of the parameters measured were within the WHO recommended values for drinking.

(Keywords: groundwater chemistry, host rock, hydrogeochemical analysis, drinking water, Piper trilinear diagram, Umuahia, Nigeria)

INTRODUCTION

One of the most important aspects of groundwater studies is the water quality analysis. What controls this groundwater chemistry are hydrogeochemical processes such as chemical weathering, cation exchange, evaporation, and anthropogenic activities (Sako, et al., 2018). Moreso, the filtering effect of aquifer made the groundwater the cleanest form of groundwater (Kumar, 2013).

The pattern and level of life development depends, to a great extent, on the quality, quantity, and rate of water supply species (Olasehinde, 2010). There is need for frequent checks of the groundwater quality in an urban area because according to Forster, et al. (1998) urbanization affects the quality and quantity of ground water by changing the pattern and rate of recharge initiating new abstraction regimes and adversely affecting the quality.

Measurement of some chemical constituents of groundwater from Umuahia metropolis was carried out to ascertain the quality of the groundwater in that area. The objective of this work is to evaluate the hydrogeochemical quality of the groundwater of the area and to determine the suitability of this water for domestic use. The hydrogeochemical analysis can reveal quality of groundwater suitable for drinking as well as change in water quality due to rock water interaction or any type of anthropogenic and environmental influence (Sadashivaiah, et al., 2008, Houria, et al., 2020).

Environmental and anthropogenic factors include geological context, climate, precipitation, and interaction between groundwater, aquifers, and human activities. Presentation of chemical analysis in graphical form makes for better understanding of a complex groundwater

system of an area. A Piper trilinear (Piper, 1944) diagram was used to determine the hydrogeochemical facies.

METHODOLOGY

A total of 8 water samples were collected from boreholes at different compounds with 75ml plastic bottles. The samples were stored in the refrigerator in order to keep them fresh. The next day, within 24 hours after the collection, it was taken to the Research Laboratory Services at Orji Kalu Housing Estate, Umuahia, Abia State for analysis.

The following methods were used for the different parameters that was determined. Electrical Conductivity (EC) was estimated by direct reading using Hanna EC test meter. The calcium and magnesium content of the water samples were determined using the titration method on the standard versenate (EDTA) described by James (1995). Nitrate determination method described by Apha (1985) was used. Chlorides were estimated using standard solution of silver nitrate (AgNO_3). Sodium and potassium were determined using Flame photometry method described by James (1995). The TDS was determined by evaporating the sample solution after filtering to remove suspended water particles. The TDS meter is based on the electrical conductivity (EC) of water. Pure H_2O has virtually zero conductivity.

The method for the determination of sulphate is adapted from ALPHA (1985). 10 ml of water sample was pipette into 100ml volumetric flask, 1ml of gelatin-bacl2 reagent was added and shaken thoroughly and allowed to stand for 30 minutes. The percentage optical density was determined at 420 nm with 30 minutes. All water samples were stored in a cool box until being analyzed using the well-known standard measures as documented by American Public Health Association. Quality assessment for drinking. The standard guideline values by World Health Organization (WHO). The results of chemical parameters of the groundwater samples are compared with the standard guideline values as documented by the World Health Organization (2017) to determine the groundwater suitability for both drinking and domestic purposes. The Piper trilinear diagram was plotted using rockworks software. The concentrations of Ca^{2+} , Mg^{2+} and Na^{2+} in milliequivalent per liter were used to obtain sodium absorption ratio (SAR).

HYDROGEOLOGY OF THE AREA (NIGER DELTA AREA)

The underlying lithosphere in the delta area undergoes thermal cooling and as a result of this, the delta subsides. The basin flexes seaward direction due to increased sediment loading (Reijers, 2011). Three lithostratigraphic units in order of decreasing age were deposited: Akata Formation, Agbada Formation, and the Benin Formation (Short and Stauble, 1967) make up the Niger Delta basin.

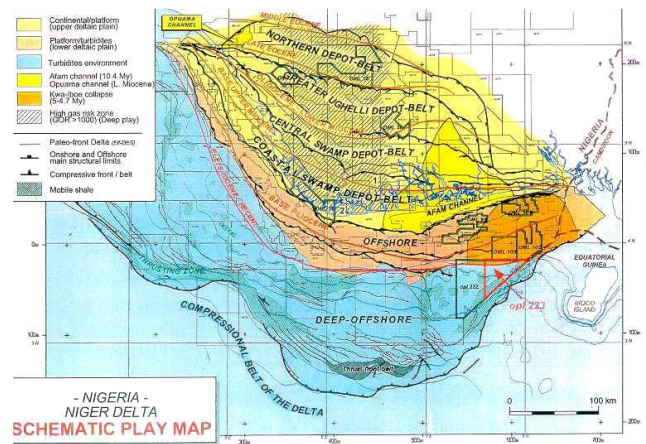


Figure 1: Geology of Niger Delta (Turtlr, et al., 1999).

The Benin Formation is composed of the present-day Quaternary land and swamp outcrops, the Agbada Formation reflects the beach ridges and the Akata Formation offshore sands, silts, and clays. The source of groundwater in the area is from deep aquifers of Benin Formation (Nwankwoala and Ngah, 2014) and is situated in the Eastern Niger Delta sedimentary basin. This basin was formed in the Tertiary period from the interplay between subsidence and deposition arising from a succession of transgressions and regressions of the sea (Hosper, 1965).

The Benin Formation from Miocene to recent is the prolific auriferous zone. This Formation is characterized by a multi-aquifer system in most places where it outcrops. The sand-clay intercalations in the area are indicative of a multi aquifer system (Etu-Efeotor, 1981; Udom, et al., 1999; 2002). The Benin Formation consists of continental deposit of sand and gravel (Murat, 1972) and of greater significance to the groundwater (Abam and Nwankwoala, 2020). Two aquifers of the upper unconfined to confined

aquifer between 30-60 meters depth, and an underlying confined aquifer between 80-160 meters depth characterized the study area.

among groundwater samples because water of similar qualities will tend to plot together (Kumar, et al., 2014).

Piper Diagram

The Piper diagram, used to understand problems concerning the geochemical evolution of groundwater, is made up of three distinct fields which include two triangular fields and a diamond-shaped field (Figure 2). Cations are expressed as a single point and as percentage of total cations in meq/l on the left triangle (Piper, 1944). It is used to understand similarities and differences

Water types and hydrochemical facies can be unraveled by the use of a piper diagram. From the water samples, all plotted towards the top on the right corner of the diamond are primarily composed of Ca^{2+} , Mg^{2+} , and Cl^- - SO_4^{2-} which depicts areas of permanent hardness and can be classified as calcium/magnesium – chloride/sulfide water type, demonstrating the dominance of alkaline earth over alkali ($\text{Ca}^+ > \text{Mg} > \text{Na}^+ \text{K}$) and strong acidic anions over weak acidic anions ($\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$).

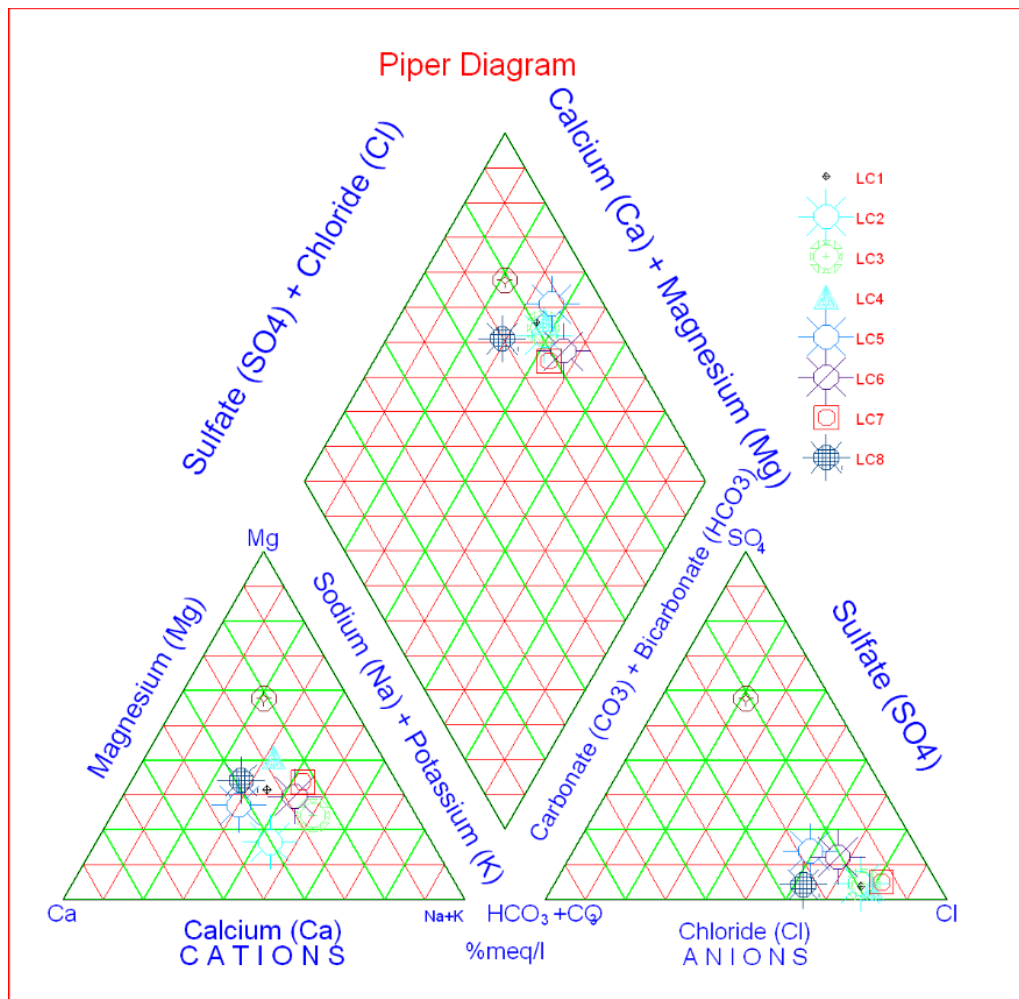


Figure 2: Piper Trilinear Diagram.

RESULTS AND DISCUSSION

Description of the Physical Parameters in the Study Area

Conductivity/pH: This was detected using direct reading with Hanna EC Test meter. It also included measurement of pH, EC, and TDS which can require representation values of ambient aquifer (Mahmoud, 2019). A pH meter was used to estimate the pH value. The pH of all the water samples taken, ranged between 6.94 and 7.19. In natural water, the pH scale runs from 0 to 14. A pH value of 7 is neutral; a pH of less than 7 is acidic and greater than 7 represent base saturation or alkalinity (Keith, 2013). This shows that some of the samples collected are in the neutral range.

The mean pH of the sample collected is 7.05 which is neutral and safe though there is no direct effect of pH value on human health but when the value of pH is high, it accelerates scale formations in water heating apparatus (Ravikumar, et al., 2009). The minimum pH value of 6.94 was obtained from groundwater sample in location BH2. The water samples were alkaline in nature, with a pH range of 6.94- 7.19.

The value of the electrical conductivity indicates that the water is not saline (Ukandu, et al., 2011). It ranges from 14.47 $\mu\text{s/cm}$ to 19.6 $\mu\text{s/cm}$. Conductivity values is directly related with total dissolved solids (TDS). Enrichment of salts in groundwater indicates higher electrical conductivity (Kailash, 2017). From the Table below, the conductivity ranges between 15.77 $\mu\text{s/cm}$ and 14.47 $\mu\text{s/cm}$.

The highest Dissolved Oxygen (DO) was observed at Amuzunta old Umuahia BH6 {5.51(mg/L)}. Biochemical Oxygen Demand (BOD) varies between 9.63(mg/L) that is Avonipupe Ubakala (BH6) and 10.46(mg/L) that is Trinity College Road Afaraukwu (BH6). This means that hardness values lie between 0(mg/L) and 75 (mg/L) and 150 (mg/L) (WHO, 1984). Sample from NO. 46 Afara Street (BH8) and Trinity College Road (BH7) indicated the least TDS.

Total Dissolved Solids (TDS): This was determined by converting the Electrical Conductivity (EC) by a factor of 0.5 to 1.0 times the EC. The practical quantitation limit for TDS in water by this method is 10 mg/liter (M. Forbes,

personal communication, 1988). These are the inorganic salts and small amounts of organic matter occur in solution in water. Water with very low concentrations of TDS may not be acceptable to consumers because of its flat, insipid taste; it is also often corrosive to water-supply systems. TDS is used as an indication of aesthetic characteristics of drinking water and array of chemical contaminants. Elevated TDS adversely affects the palatability of water.

The TDS values of the samples are generally low, and this suggests there is no salt in the recharge water (Sako, 2018). Groundwater at all sites is fresh water according to the classification based on TDS (fresh: <1000 mg/L, slightly saline: 1000–3000 mg/L, moderately saline: 3000–10,000 mg/L, highly saline: 10,000–35,000 mg/L) suggested by the US Geological Survey.

Dissolved Oxygen: When the dissolved oxygen is depleted in water, it encourages microbial reduction of nitrates to nitrites and sulfates to sulfides while very high levels of dissolved oxygen could exacerbate corrosion of metal pipes. Concentration of ferrous iron in solution is also high with subsequent discoloration at the tap when the water is aerated.

Sodium Adsorption Ratio: According to the U.S. Department of Agriculture, Natural Resources Conservation Service, Sodium Adsorption Ratio (SAR) is a measure of the amount of sodium (Na^+) relative to calcium (Ca^{2+}) and magnesium (Mg^{2+}) in the water extracted from a saturated soil paste. It is the ratio of the Na concentration divided by the square root of one-half of the Ca + Mg concentration. SAR is calculated from the equation:

$$\text{SAR} = \text{Na}^+ / [(\text{Ca}^{2+} + \text{Mg}^{2+})/2]^{0.5}$$

The value of sodium absorption ratio when the units of calcium, magnesium, and sodium are in milli-equivalent/liter (mEq/l) is in Table 1.

Predicting the effect of SAR in water is important for water quality, agricultural and irrigation purposes (Basim, et al., 2020). It also has significant effect on infiltration rate of soil. The high concentration of Sodium in irrigation water increases the salinity of the water that affects conversion from natural to saline water, thereby reducing hydraulic conductivity and infiltration rate of soil (Saha, et al., 2017).

Table 1: Results of the 11 Parameters determined in the Laboratory.

S/N	BOD (mg/L)	pH	Ca (mg/L)	Mg (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	Fe (mg/L)	PO ₃ (mg/L)	Cl (mg/L)	Na (mg/L)	K (mg/L)	SAR
BH1	9.82	7.03	1.19	0.68	1.17	0.37	0.62	0.14	5.48	1.06	2.96	0.240
BH2	9.73	6.94	1.35	0.78	1.35	0.52	0.84	0.19	6.36	1.43	3.56	0.19
BH3	10.18	7.04	1.25	0.74	1.25	0.46	0.73	0.14	6.18	1.27	3.56	0.16
BH4	10.46	7.02	1.20	0.68	1.17	0.35	0.68	0.16	6.46	1.19	2.78	0.09
BH5	9.63	7.05	1.29	0.66	1.23	0.31	0.65	0.15	5.45	1.25	3.61	0.22
BH6	10.46	7.08	1.35	0.75	1.50	0.44	0.71	0.81	7.16	1.31	2.92	0.22
BH7	9.64	7.05	1.19	0.65	1.40	0.41	0.72	0.17	5.64	1.59	3.67	0.29
BH8	9.85	7.19	1.45	0.93	1.29	0.54	0.79	0.24	6.42	1.65	3.14	0.26

Table 2: Physical Parameters in the Study Area.

S/N	Turbidity (NTU)	TDS (Mg/L)	Conductivity (µs/cm)	DO (Mg/L)
BH1	2.65	0.06	14.47	2.65
BH2	2.73	0.06	19.6	2.61
BH3	2.66	0.04	19.36	2.35
BH4	1.94	0.03	15.77	1.17
BH5	3.06	0.02	14.31	2.79
BH6	2.94	0.03	15.93	5.51
BH7	2.87	0.02	15.93	2.41
BH8	2.88	0.08	18.9	2.88

NTU- Nephelometer unit
TDS- Total dissolved solid
DO- Dissolve oxygen
Mg/L- milligram per liter

Table 3: Result of the determined 11 Parameters in MEq.

S/N	Ca (mEq)	Mg (mEq)	SO ₄ (mEq)	PO ₃ (mEq)	Cl (mEq)	Na (mEq)	K (mEq)
BH1	0.0595	0.0559	0.0077	0.0090	0.1548	0.0460	0.0758
BH2	0.0675	0.0642	0.0108	0.0123	0.7797	0.0622	0.0912
BH3	0.0625	0.0609	0.0096	0.0090	0.1746	0.055	0.0913
BH4	0.0600	0.5597	0.0071	0.0103	0.1825	0.0517	0.0713
BH5	0.0645	0.0543	0.0065	0.0097	0.1540	0.0543	0.0925
BH6	0.0675	0.0617	0.0092	0.0523	0.2023	0.0570	0.0749
BH7	0.0595	0.0535	0.0085	0.0109	0.1593	0.0691	0.0941
BH8	0.0725	0.0765	0.005	0.0155	0.1813	0.0717	0.0805

According to when the SAR is >3, the water is sodic, and can increase the exchangeable sodium percentage (ESP) of the soil. The average SAR value in the water sample is low (0.21) and suitable for irrigation (Abdulwahed, et al 2018).

Description of Anions in the Samples

Four anions were analyzed. The anions in the order of abundance are Cl⁻, SO₄²⁻, NO₃⁻ and PO₃⁻.

Nitrate: In amounts less than 5 ppm, nitrate has no effect on the value of water for ordinary uses (Criner, et al., 1961). Agricultural activity like excess application of inorganic nitrogenous fertilizers and manures add nitrate to groundwater. Drinking water makes significant contribution to nitrate intake but generally the most important supplier of nitrate to the body is through vegetables and meat in the diet (WHO, 2017). Nitrate concentrations in all the samples are more than 10 mg/L allowable limit for drinking

water. Sample from location BH2 has the highest nitrate content while sample in location BH1 has the least content. Most chemicals arising in drinking water are of health concern when exposed for many years, rather than months. The principal exception is nitrate (WHO, 2017). The high concentration of nitrate in this sample could be attributed to onsite sanitary sewage because of the closeness of the borehole to soak away on the location and/or leaching of agricultural waste. Nitrite is used as a preservative in many cured meats. In some circumstances, however, drinking-water can make a significant contribution to nitrate and, occasionally, nitrite intake. In the case of bottle-fed infants, drinking-water can be the major external source of exposure.

Sulphate (SO₄): Rocks with gypsum, iron sulphides, and other sulphur compounds, on dissolution give rise to sulphate (WHO, 2017). The highest levels of sulphate occur in groundwater and are from natural sources. Sulphate in water with combinations of other irons gives a bitter taste (Criner, 1961). Sulphate concentration has an average value of 0.42 mg/L and ranges from 0.37 mg/L in BH1 borehole to 0.54mg/L in BH8 borehole. The sulphate content is within the maximum permissible limit of WHO standard and USEPA (1994) which are 200mg/L and 250mg/L, respectively. All the groundwater samples under investigation area were suitable for drinking usage in respect to sulphate content. Through industrial wastes and atmospheric deposition, sulphate is discharged into water, however, the highest levels usually occur in groundwater and are from natural sources (WHO, 2017).

Phosphite (PO₃): Phosphorus, an essential nutrient for plants, animals and humans is one of the 20 most abundant elements in the solar system and 11th most abundant in the Earth's crust (MPCA, 2007). The principal source is apatite while the dietary sources include meat, milk, and soya beans. PO₃ has an average value of 0.25 mg/L and highest and lowest values of 0.81 mg/L at location BH6 and 0.14 mg/L at locations BH1 and BH3, respectively. Sediments rich in phosphorus are known as phosphites (Mackey and Paytan, 2009). Phosphorus is essential in humans for proper skeletal and nervous system formation and function. The form of phosphorus that is common in water is orthophosphate (PO₄³⁻) ion. Phosphorus is added to the soil through municipal waste, chemical fertilizers, and manure applications (Silveira, et

al., 2010). Phosphorus movement into groundwater from soil results in potential contamination of the ground water resources due to algae growth in water bodies, when there is too much of it in water, it can speed up eutrophication. This is a reduction in dissolved oxygen in water bodies caused by an increase of mineral and organic nutrients in groundwater (USGS, 2018).

Chlorine: Chlorine is used as an important disinfectant and bleach industrially and domestically (WHO, 2017). Chlorine has an average value of 6.14 mg/L and highest value of 7.16 mg/L was recorded in sample BH6. The lowest value is 5.48 mg/L in sample BH5. All the samples are within permissible limit of 250mg/L for drinking water as prescribed by WHO, 2017. With the high chlorine content of adjacent coastal aquifer of Niger Delta, one would expect a high concentration of chlorine in those samples but the low value of chlorine on them suggests that the saltwater contamination in the adjacent coastal aquifers of the Niger Delta has not reached Umuahia, which is more hinterland. Chlorine is the dominant anion in the samples of the study area, but it may be related to the weathering and dissolution processes to produce iron oxides alongside with clay minerals.

Iron is a heavy metal and abundant in the Earth's crust. The highest iron content is in sample BH2 and the value is 0.84 mg/L and lowest content of 0.62 mg/L in sample BH1 sample. In natural fresh water, it is found at levels ranging from 0.5 to 50 mg/L. According to WHO 2017, Iron at level above 0.3 mg/L stains laundry and plumbing fixtures. Iron contamination could be by iron fixing bacterial association with sedimentary environments of decaying vegetative matter but the high iron content in the area is likely to be due to lateritic nature of the outliers of Nsukka Formation (Uzoeji, 2014).

Weathering and dissolution processes may also produce iron oxides alongside with clay minerals (Duke et al 2007). However, concentration of iron of range from 0.62 to 0.84mg/L for ground water is above the maximum permissible level of water for domestic use (WHO, 1997). The source of the iron contamination could be by iron fixing bacteria associated with decaying vegetative matter in the sedimentary environment (Abam and Nwankwoala, 2020).

Description of Cations in the Samples

Four cations were analyzed in each sample. The cations in the order of abundance are $K^{2+} > Na^{2+} > Ca^{2+} > Mg^{2+}$. The average values of the cations are potassium 3.28mg/L, Sodium 1.34mg/L, Calcium 1.28mg/L and magnesium 0.35 mg/L, respectively.

Potassium: The source could be from sea water, ancient and industrial brines, and sewage (Crines, et al., 1961). It occurs widely in the water and also in the environment. According to Rail (2000), potassium concentrations in groundwater up to 10 mg/L are due to orthoclase or clay weathering, while concentrations above 10 mg/L may be due to external sources of K+ abundance. Potassium is generally higher in felsic/acidic rocks, and this was confirmed in the research done with hand-held RS-125/230 state-of-art portable radiation spectrometer instrument carried out by Eze, et al.(2019) in the nearby Southern basin. Potassium is the dominant cation in this study area. Potassium varied from 2.92 mg/L in BH1 to 3.67 mg/L in BH7 and averaged 3.28mg/L (Table 1).

All the samples have potassium concentrations within the permissible limit of 200 mg/L as stipulated by World health organization (WHO) in 2017. More than 300mg/L of potassium is required per day in human body. Potassium intake from drinking-water is well below the level at which adverse health effects may occur (WHO, 2017).

Sodium: Sodium ranges between 1.06 mg/L in location BH1 to 1.65mg/L in location BH8 with average value of 1.34 mg/L. The sources of sodium in the water samples could be attributed to host rock dissolution. World health organization (WHO 2017) permissible limit is 200mg/L, All the samples have sodium concentrations within the permissible limit of 200 mg/L as stipulated by World Health Organization in 2017.

Calcium: The range of calcium concentration is between 0.0595 mg/L in location BH1 and BH7 and 0.0725 mg/L in location BH8 and the average value is 1.28 mg/L. Low calcium and magnesium concentrations of the samples signify soft to slightly hard water. The various ionic concentrations are within the maximum acceptable limits of WHO standards. The calcium and magnesium in the water samples are thought to be from the dissolution of the limestone and shale in the study area.

Magnesium: Magnesium concentration ranges from 0.65mg/L at location BH7 to 0.93mg/L at location BH8. Higher concentration of magnesium is considered as a laxative agent while lower concentration could result to structural and functional changes in human body (Eyankware, et al, 2017).

CONCLUSION

Continuous monitoring of groundwater to determine its quality status is a necessity. Septic fields, toilets, run-off sources, and dumpsites must be sited away from hand-dug wells. Good hygiene practice is also suggested for the people of the area to avoid water borne disease in the future. The most appropriate means of controlling contaminant in groundwater, is the prevention of contamination. This is through appropriate management of agricultural practices (e.g., management of fertilizer and manure application and storage of animal manures) and sanitation practices. Pit latrines should not be sited near a well or where a well is to be dug and ensure that animal manure is kept at a sufficient distance to ensure that runoff cannot enter the well or the ground near the well.

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