

Evaluation of Groundwater Quality of Coastal Aquifer Systems in Buguma City, Rivers State South-Southern Nigerian

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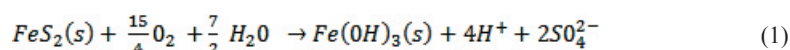
Abstract-

Saline intrusion has been a major source of groundwater contaminant in coastal regions. The situation has adversely affected groundwater quality . Being an essential source of freshwater for the teeming population over the world and indeed Nigeria and its suitability for various uses is largely dependent on physico-chemical quality, this study therefore selected for its quality assessment, the coastal aquifer of Buguma in rivers state Nigeria. Water samples collected from various locations using systematic random sampling were subjected to physico-chemical analysis . sodium (Na^{2+}) (288mg/l) chloride(Cl^-) (414.7mg/l) and nitrate (NO_3^-) (64.45 mg/l) ions dominated the major ions of sample results and also exceeded the Nigerian Standard for Drinking Water Quality NSDWQ 2007 and WHO drinking water standard 2006. Among the trace elements, Fe^{2+} and As ions were above the drinking water regulatory limits of NSDWQ and WHO. Classification techniques were employed to provide an assessable information on the chemical composition of the water samples like the major ions in the analysis. The high proportion of Na^{2+} , K^+ and Cl^- as typified by the graphs classified the water as Na-K, Cl^- type which confirmed saltwater intrusion. The water therefore needs adequate treatment to raise it to portable standard.

Keywords; Groundwater, Water Quality, Buguma, Major ions, Trace Elements, Geochemistry.

1.0 Introduction

Groundwater quality is usually determined from the interpretive analysis of major ions that dominate the chemical composition of the water. Adepelumi, et al 2009 revealed that hard water is dominated by the following ions; calcium magnesium, carbonate and bicarbonate whereas sodium, potassium, carbonate and bicarbonate ions are prominent in salt water regime. Also, chloride, sodium and potassium ions mainly dominate the salty water (Annappoorania et al 2012). The aforementioned substances which determine the chemical composition of ground water naturally occur due to chemical weathering of subsurface sediments and ion-exchange by clay and glauconite (Leslie and Taniguchi, 2002). Values of these substances are specific in deep wells but varies in shallow wells due to short flow paths between recharge and discharge areas and perhaps due to substances originating from anthropogenic sources (Longe et al 2007). Apart from the major substances mentioned above, other substances which constitute groundwater components get into it through different pathways. Fluoride in groundwater, originates through desorption process from phosphatic sedimentary materials (oxyhydroxides) onto which fluoride belt is formed. In shallow wells iron, manganese, nitrate and ammonium are mainly produced in groundwater through reaction of organic matter with oxyhydroxides and ion-exchange process (McFarland 2010). Temperature and pH factors wield overwhelming influence on groundwater quality. At temperature above 10°C groundwater dissolves dolomite and calcite with concomitant abundance of calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions (Rao 2006). Also, pH determines the values of most groundwater elements. From the geochemical point of view, pH of groundwater is altered when carbon(iv) oxide (CO_2) reacts with oxygen (O_2) generated by the decomposition of organic matter and plant root respirations to cause pyrite (FeS_2) oxidation . The geochemical process of this oxidation showed that decrease in pH level was observed as the oxidation reaction of pyrite and oxygen supplied from the earth's atmosphere occurred in the soil-moisture zone (Freeze and cherry 1979). The reaction equation is shown as follows



At low pH range, dissolution of calcite and precipitation of gypsum at sandstone zones results to rise in value of total dissolved solids(TDS) occasioned by calcium ion Ca^{2+} discharge. Ordinarily, concentration of trace elements in the groundwater is very low in ground water, but due to variations in acidity level, complexes are formed with the traced elements resulting to increase in their values. For instance, zinc (Zn) ion forms complexes with other ions such as chlorine ion (Cl^-), sulphate ion(SO_4^{2-}) carbonate ion (CO_3^{2-}) etc to form zinc chloride ($ZnCl_2$), zinc sulphate ($ZnSO_4$) and Zinc carbonate ($ZnCO_3$) at low pH range(Valiela et al1993). At pH level typical of the coastal groundwater, arsenic oxidizes to As_2O_5 and As_2O_3 . the dissolution of the complexes results to high arsenic concentration (Al-Mikhlaifi et al 2003).

Groundwater in coastal regions is characterized by high salinity, due to seawater intrusion. Several criteria have been suggested by researchers as indicators for seawater intrusion into coastal aquifer. EL-Moujabber et al 2006 pointed out that increase in total dissolved salt (EC) is not sufficient proof for seawater intrusion. The most obvious indicator of seawater intrusion is an increase in chlorine ion concentration. Jin-yong and Sung-Ho 2007, EL-Moujabber et al 2006 observed that a large proportion of groundwater in wells located in coastal regions is classified as Na-Cl and Ca-Cl types and also lower ratios of Na/Cl and SO_4/Cl than seawater values indicate seawater intrusion. In addition to sea and saline water intrusion from seas and canals, high salinity of groundwater in coastal regions could be attributed to excessive abstraction, prawn culturing and pollution (Annapoorania et al 2012, Bear et al., 1999). Aside salinization process, rainfall, landform, soil, lithology and anthropogenic sources could be determinant factors in groundwater quality of wells in coastal regions(Ganeshkumar and Jaideep 2011). Wells located at the coastal regions are liable to contamination with pathogenic bacteria. Bacteria contamination of groundwater is a function of the geological structure of the area (CPCB 2001). In saturated zones, the bacteria are removed through straining, die-off and adsorption but in a homogenous porous media of sand, gravel etc, bacteria penetrate more than tens and hundreds of meters along the groundwater flow path. Given its vulnerability to pollution, groundwater in coastal regions requires adequate monitoring to assess the level of pollution. This article therefore assessed and evaluated the groundwater characteristics of a typical coastal region of Buguma city in south-south region of Nigeria.

2.0 Materials and methods

The study area is Buguma city, headquarter of Asari-Toru local Government Area of Rivers State, Nigeria. The city is located on longitude $4^\circ 44' 8''$ N and latitude $6^\circ 51' 48''$ E. people of Buguma city are predominantly farmers. They are mainly crop and fish farmers. The water samples were collected from twenty-one locations within the study area. Physico-Chemical parameters and trace elements were analyzed in the sample. All the analysis were carried out using standard methods. To check the correctness of the analysis, quality control of the water analysis data was carried out using two major methods; (a) Ratio of measured TDS and calculated TDS with the ratio range of >1.0 and <1.2 expressed as $1.0 < \frac{TDS_{measured}}{TDS_{calculated}} < 1.2$. (b) calculation of charged (ion)

balance. In this case, the solution must be electrically (anion-cation) balanced where the percentage difference expressed as the ratio of the difference of summation cation and anion must be five(5%);

$$\% \text{ difference} = \left(\frac{\sum_i^n \text{cations} - \sum_i^n \text{anions}}{\sum_i^n \text{cations} + \sum_i^n \text{anions}} \right) \times \frac{100}{1}$$

3.0 Results and Discussions

Results of water analysis from respective sampling locations, comprising of physico-chemical and trace elements are shown in table1. Regional mean values of the water samples, Nigerian Standard for Drinking Water Quality NSDWQ 2007 and WHO drinking water standard 2006 values are shown on table 2. Figs 1,2,3 and 4 describe geochemistry evaluations of the groundwater using Stiff diagram, Schoeller diagram, ion-balance and radial plots respectively.

3.1 Physico-Chemical Parameters;

Table 1 shows that pH status of the water samples in all the locations except Cottrall, Edi, Ikpo,jeckreech, Lawson and Okorosa was slightly acidic with Abbi having the lowest pH of 5.11 while the highest pH value of 7.7 was recorded in Tariah . Comparing the pH values with WHO standards 2006(6.5-9.0) and (NSDWQ) 2007 (6.5-8.5), pH water sample values in Cottrall, Edi, Ikpo,jeckreech, Lawson and Okorosa locations fell within acceptable (NSDWQ) 2007 pH limit for portable water . pH values in other locations tend towards acidity . According to (Longe et al2007) certain factors such as presence of carbonic acid(H_2CO_3) produced in the soil zone due to reactions of carbon(iv)oxide with water increases the acidity level of water and could be responsible to the glaring increase in acidity. Carbon(iv)oxide in the soil zone is generated by the decay of organic matter and the respiration of plant roots(Suk and Lee 1999). pyrite (FeS_2) is another source of acidity. Hydrogen ion(H^+) produced in the course of its oxidation with free oxygen(O_2) at the soil-moisture zone also enhances soil acidity level(Manikanden et al 2012). Similarly, the in situ temperature of the water samples varied between $20^{\circ}C$ at Abbi to 31.3 at Bakobo with a mean value of $27.27^{\circ}C$. The average salinity value in the study area was $4140mg/l$. However, the lowest and the highest salinity value of $1100mg/l$ and $9400mg/l$ respectively were observed at Wokoma and johnwest respectively. Although WHO 1993 and Nigerian Standard for Drinking Water Quality(NSDWQ) 2007standard for portable water is silent on the salinity value, water at that salinity level cannot be described as fresh but slightly saline with objectionable taste (Jin-Yong and Sung-Ho 2007). The slight increase in salinity could be attributed to sea water intrusion (Mulas et al 2005). Hardness values of the water samples were observed to range from the lowest value of 75.9 at Horsefall to $993mg/l$ Johnwest. In Most locations of the study area hardness values were beyond WHO 1993 and (NSDWQ) 2007 drinking water standard of $<150mg/l$ and $150mg/l$ respectively except Horsefall,Cottrell, Pepple and Young-aney locations. High salinity value observed at Johnwest might account for seemingly high hardness value recorded in the same study location.(Al-Mikhlafl 2003). in line with this observation, (Edet et al 2011) revealed that high total hardness is one of the indicators of seawater intrusion. Glaring variations in Bicarbonate (HCO_3^-) values with locations were observed in the water samples. The Highest HCO_3^- value of $98.3mg/l$ was observed at Tariah location while the lowest value of $12.5 mg/l$ was observed at Igba with Mean HCO_3^- value calculated at $69.65mg/l$. Values of HCO_3^- at some locations seemed to vary linearly with the values of total dissolved solids(TDS). For instance, the highest value of HCO_3^- observed at $102mg/l$ has a corresponding highest TDS value of $39322mg/l$ at Johnwest study location. Also the high HCO_3^- value of $98.3mg/l$ in Tariah which was next to that recorded in Johnwest has a corresponding high TDS of $13114mg/l$. Some other few locations assumed the same trend. This relationship could be possible in view of the fact that high HCO_3^- which results to low pH, leads to dissolution of limestone(calcite) and corresponding precipitations of gypsum, and dissolution of calcite at sandstone(quartz and plagioclase) zone((Longe et al 2007,). The axiom that bicarbonate is available in large quantity in groundwater due to other geochemical processes (Chachadi and Terasa 2002), further buttressed the prevailing high HCO_3^- value. It is Therefore obvious that dissolution of these earth deposits increased TDS value of the water in the study locations. Comparing the mean TDS value of the water sample with that of a typical saline water, it was discovered that TDS of the water sample under study cannot pass for a fresh water($TDS<1000mg/l$) standard, rather the value tended towards saline water which further confirm seawater intrusion (Micheal et al 2004). Although there is no consistent trend in temperature variation with the measured parameters, but highest temperature values observed at Lawson and johnbull axis of the study area have corresponding highest TDS values. The trend observed could be attributed to activation of geochemical properties, such as increase in weathering and biological processes, resulting to high concentration of solid concentrations and consequent contamination (Kropp 2007). Values of NO_3^- at various locations are also presented on table 1 . The highest($89.8mg/l$) and lowest ($34mg/l$)values of NO_3^- were recorded at Okorosa and Horsefall study locations respectively with its mean value at $64.5mg/l$. From this result, NO_3^- exceeded WHO 1993 and (NSDWQ) 2007standards of $40-70mg/l$ and $50mg/l$ respectively for domestic use. High value of NO_3^- observed at Okorosa and Horsefall could be attributed to leaching of fertilizer from agricultural lands (Simeonov et al 2003) . As people from these areas are predominantly farmers, leaching of fertilizer applied to increase crop yield might increase the NO_3^- value of the areas under study. . Also, oxidation of naturally occurring nitrogen in the soil could also contribute to high NO_3^- value(EL-Mouyabber 2006). It was adduced that high nitrate concentration observed in shallow wells was because freshwater floats on top of seawater due to density differences between salt and freshwater(Bobba 2002). Being shallow wells, this observation could as well be a contributing factor to high nitrate value observed in the study area,

Table 1; Results of water analysis from respective sampling locations

Location	Cd	Mg	Fe	Na	Mn	K	Zn	Ca	Cl	As	ph	temp	TDS	Alk	HC0 ₃ ⁻	N0 ₃ ⁻	S0 ₄ ²⁻	P0 ₄ ³⁻	Hardne	Sal
	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l		Mg/l	Mg/l	Mg/l	Mg/l				
Abbi	0.009	70	4.64	311	0.007	49.9	0.01	10.3	790	0.01	5.11	20	24960	25	84.1	45	42	0.91	851	2400
pepple	BDL	79	4	413	0.009	40.1	6.3	11.3	618	0.003	5.23	29	18403	19.5	75.8	57	93	1.98	76.71	8700
Okorosa	BDL	64	2.6	201	BDL	29.7	7.3	11	635	0.006	6.51	25	22255	12	56.4	34	80.9	0.35	811.1	7100
Bakubo	0.003	61	1.07	340	0.03	37.11	11.3	34.4	501	0.04	5.81	31.3	11301	18.9	70.1	49.1	73.3	0.78	650	2900
Ombu	0.001	67	2.52	110	0.04	22.6	0.1	36.1	309	0.001	6.23	27	26334	17.9		79.1	12.9	1.99	814	8674
Lawson	0.009	69	4.11	377	0.008	20.01	5.1	18.1	411	4.6	6.7	32.3	38453	14.1	40.1	78.1	95.1	1.77	795	1420
tyger	BDL	51	3.11	319	0.001	19.78	4.3	11.7	201	0.007	6.4	26.5	20195	15.7	45.3	79.1	101.3	1.11	658	4329
Tariah	0.001	54	2.98	196	0.079	21.24	0.12	9.7	280	0.02	7.7	27.5	38114	30.3	98.3	46.2	11.3	0.55	593	2100
Young-aney	BDL	31	3.19	89	0.005	35.11	0.3	37.7	119	BDL	5.9	29.5	15531	21.3	41	40.3	23.4	1.71	103.1	7254
Igba	BDL	66	3.99	289	0.002	40.23	0.9	29.1	104	0.2	6.3	30.1	13012	40.1	12.9	33.8	29.7	1.29	973	2176
Johnwest	0.003	89	3.04	219	0.03	39.1	1.4	13.9	209	0.029	5.9	32.9	39322	20.9	102	50.1	75.9	1.9	993.4	9431
Johnbull	0.002	75	1.9	374	0.02	45.23	3.9	14.9	745	0.013	5.71	27.3	24284	32.7	69	47.2	84.5	1.5	854.5	4800
Jackreash	0.001	84	4.01	245	0.12	27	17.2	14.3	451	0.015	6.8	28.9	21371	50.8	98	54	130	2.4	959	1423
Wokoma	0.006	93	3.5	275	0.043	35.3	13.4	36.9	432	0.091	6.24	30.1	25639	31.3	75	78.5	98.4	1.7	947	1198
Warmate	0.007	73	2.7	412	0.005	45.7	11.5	24.11	533	0.23	6.1	27	24372	42.1	83	98	85.7	0.4	563	1860
Ombo	0.004	78	2.6	235	0.03	39.1	12.4	32.4	362	0.46	5.74	23.4	21532	45.3	93	86.8	84.3	1.4	841	4014
Ikpo	0.008	69	3.1	285	0.02	49.2	0.12	32.1	353	0.54	6.9	26	7594	26.1	47	89.8	75.3	2.7	864	8640
Edi	BDL	48	3.8	361	0.05	32	3.22	28.4	473	0.64	6.52	25.8	4131	1432.1	58	75.4	58.1	1.9	590	1220
Horsefall	0.009	68	2.1	386	0.004	35.9	1.45	3.4	385	0.56	5.98	28.4	21290	38.9	86	83.0	45.6	1.7	75.9	2400
cottrell	0.003	92	1.8	314	0.03	48.4	1.1	23.94	275	0.45	6.9	26.5	23841	65	97	73.2	63.1	1.8	109	1339

Table2 ; Mean Concentrations of the field samples, Nigerian Standard for Drinking Water Quality and WHO Limits

parameters	Field sample Concentrations(Mg/l)	Nigerian Standard for Drinking Water Quality(mg/l) 2007	WHO Limits (mg/l)(2006)
Cd	0.0033	0.003	0.05
Mg	69.1	0.20	150
Fe	3.40	0.3	0.5
Na	288	200	500
Mn	0.027	0.20	0.01-0.2
K	35.63	-	50
Zn	5.07	3.0	5.0
Ca	21.7	-	200
Cl	414.3	250	500
As	0.096	0.01	0.01
Ph	6.234	6.5-8.5	6.5-9.0
Temp	27.147	ambient	ambient
TDS	21389.8	500	1500
Alk	29.071	-	-
HC0 ₃ -	69.65	-	500
N0 ₃ -	64.45	50	40-70
S0 ₄ 2-	64.02	100	400
P0 ₄ -	1.5	-	10
Hardness	656.189	150	<150
Salinity	4140	-	-

Mean values of other anions were observed and shown in table 2 were 414, 65 and 1.5 for Cl^- , SO_4^{2-} and PO_4^{2-} respectively. Chloride ion exceeded (NSDWQ) 2007 drinking water standard of 200mg/l. The ratio of chloride/bicarbonate + carbonate can be used as criteria to evaluate seawater intrusion. Chloride is the dominant ion in seawater and under normal circumstances, it is available in small quantity in groundwater while bicarbonate which is available in large quantity in groundwater occurs only in very small quantity in seawater (Chachadi and Terasa 2002). Therefore High value of chlorine ion observed virtually in all sample locations is obvious indication of seawater intrusion. Sulphate concentration was well below (NSDWQ) 2007 and WHO standard of 100mg/l. and 400mg/l respectively. The depressed sulphate concentration could be attributed to activities of microbial sulphate reduction (Finch 2007) which is common with shallow wells like those of the study area. The value of sodium exceeded the acceptable (NSDWQ) 2007 drinking water standard of 200mg/l in all the sampling locations except Ombo, Tariah and Young-aney. The reason was not far from the earlier observed limestone and calcites dissolution. Although, Mcfarland 2010 further observed that at shale (Na-montmorillonite) calcium (Ca) exchanges for sodium (Na) making Na abundant. Also, average values of Mg^{2+} , Ca^{2+} , K^+ , Mn^{2+} , Fe^{2+} were recorded at 69.1, 21.7, 35.6, 5.07, 0.03, 3.04 mg/l respectively. Apart from Fe^{2+} ion which has a mean value of 3.04mg/l as against the WHO 1993 drinking water standard of 0.3mg/l, mean values of other anions did not exceed the standard for drinking and other domestic water usage and therefore pose no health hazard. High Fe^{2+} mean value could be attributed to infiltration of substances down the sub-surface from the following sources; industrial effluent, sewages and landfill leachate (Joseph et al 2002). The fact that the entire study location is an urban area surrounded with industries, both medium and large scale, and these companies discharge their effluents on land buttressed this observation. In the light of this, the effluent with high proportion of metallic substances could migrate through the soil matrix to pollute the aquifer, especially the unsaturated type of soil typical of the study area (Chatterjee et al 2010).

3.2 Trace Elements

The ground water sample contained varying concentrations of Zn, Mn, Cd and As at various locations of the study area. table 2, Zn has the highest mean value of 5.07, followed by As with the value of 0.63. Cd has the least value of 0.003. Mn was observed to have a mean value of 0.03mg/l. However, presence of trace elements in the study were arranged in this order; $\text{Zn} > \text{As} > \text{Mn} > \text{Cd}$. Values of Zn, As, and Zn exceeded the drinking water standard. At the natural state of ground water, concentrations of trace elements are low, but high concentrations of most trace elements observed in groundwater researches are as a result of complexes these elements form with other anions especially at pH value below neutral which is typical of this study (Ganeshkumar and Jaideep 2011). in the light of this, values of the traced elements are assessed with respect to total elements in each complex thereby increasing thereby increasing the trace element values. For instance, high value of zinc observed beyond the drinking water standard in this study could be attributed to complexes it formed with Cl^- , SO_4^{2-} , and CO_3^{2-} , to produce ZnCl , ZnSO_4 and ZnCO_3 respectively. In this case, it is possible that Zn values were assessed as the total Zn value in all the complexes. Also, high As value could be attributed to the aforementioned reason. At slightly low pH value typical of groundwater and a case with the study area, the stable Arsenic forms soluble oxides such as $\text{As}_2\text{O}_5(\text{s})$, $\text{As}_2\text{O}_3(\text{s})$ (Roa 2006, Valiela,) which are readily soluble to release arsenic species. The released Arsenic leads to arsenic existing at concentration well above the permissible limit stipulated by the regulatory agencies. Again the land use of the study area is mainly agricultural practice therefore, high Arsenic values could stem from pesticides and herbicides applied on crops to check pest invasion and frequent weed growth as Arsenic is a major component of these two substances ((Chachadi and Terasa 2002)).

3.3 Water type;

Geochemistry of the Water samples was evaluated to characterize the groundwater using the groundwater information system (GWIS) software. In figures 3, 4, 5 and 6 the major chemical compositions of the water samples were represented in, Stiff, Schoeller and radial plot diagrams and ion-balance respectively for on-the-spot ionic comparisons.

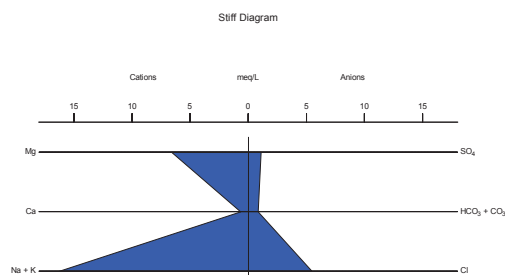


Fig 1 ; the stiff diagram showing the dominant major ions

As shown by stiff diagram the major ions of both Cations and Anions were plotted on left and right hand sides respectively .. The cations (Na+K, Ca, and Mg) were plotted at the left hand side while anions(SO_4^{2+} , HCO_3^- , Cl^-) were plotted on the right hands of the diagram, . From the diagram , Na+ -K+ and Cl- ions dominated the water sample and therefore could be regarded as Na +K --Cl water type, typical of saline water.

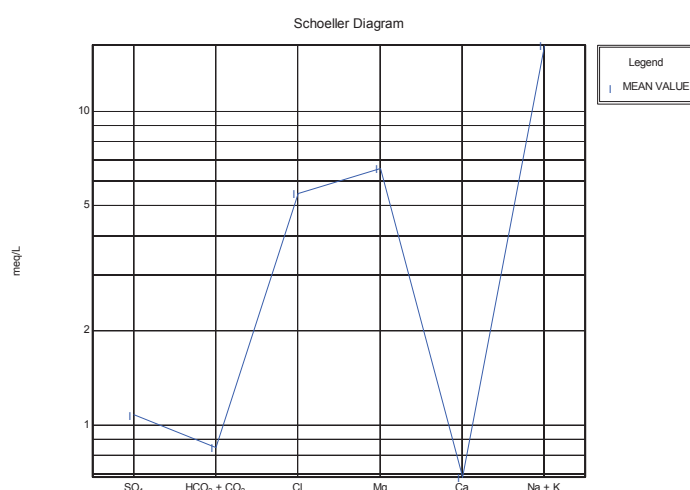


Fig 2 ; the Shoeller diagram showing the dominant major ions

To Further evaluate the geochemistry of groundwater in Buguma city, the major constituents were plotted in shoeller diagram. In this case, the major cations(Na+, K+, Mg^{2+}) were plotted on the right side of the diagram with the anions(Cl^- , SO_4^{2-} , HCO_3^-) plotted on the left side. the plot shows that the value of Na-K exceeded other Cations while the value of Cl- ion exceeded that of other Anions, clearly indicating salt content dominance in the wells .

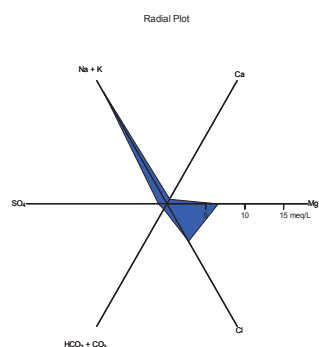


Fig 3 ; the Radial plot showing the dominant major ions

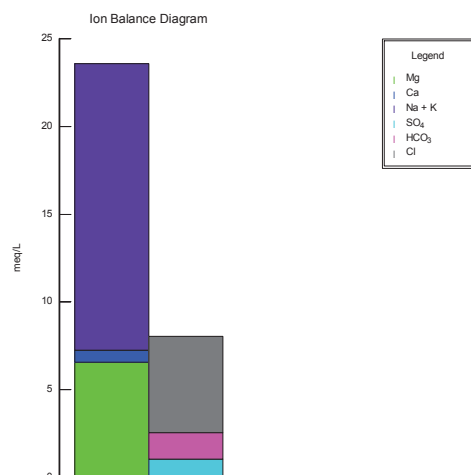


Fig 4 ; the ion balance diagram showing the dominant major ions

ion-balance and radial plot further confirmed high Cl⁻ and Na-K values which also show that the water sample is of Na-K and Cl⁻ water type.

3.4 Conclusion.

Groundwater quality of the study area has been studied. Analysis from the sample locations indicates that large proportions of the water is not portable. The water has an appreciable saline water intrusion due to the coastal nature of the area. There was high presence of Fe²⁺ and As ions in the water samples. The water needs adequate treatment for sustainable usage.

3.5 Reference

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