Assessment of the Concentration of Inorganic Chemical Elements in the Pollution Status of Water Boreholes in Awka- Anambra Sedimentary Basin, Se, Nigeria

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Abstract

Since Awka town was made the capital of Anambra State, population growth, innumerable industries and other new land uses have been on the increase. There is the fear that inorganic geochemical elements may have contaminated the groundwater making it unfit for consumption. This research is thus intended to estimate the magnitude to which borehole waters and by extension the groundwater system in the area have been contaminated. Six borehole water samples were collected and analysed for inorganic geochemical elements. The parameters analysed were colour, acidity, pH, conductivity, total dissolved and suspended solids (TDS and TSS). Others are nitrate (NO_3), chloride (Cl^-), sulphate (SO_4^{2-}), phosphate (PO_4^3) copper (Cu^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), iron (Fe^{2+}), total hardness (calcium hardness and magnesium hardness) (total hardness) and alkalinity. The analyses were conducted with appropriate geochemical equipment. It was discovered that other anions

apart from phosphate are within the concentrations recommended for safe drinking water. The concentration of the cations is in the following order: Cl> HCO_3> SO_4> NO_3, and that for anions is Mg> Ca> K> Na, thus making the water in the area potentially magnesium chloride water. Iron and lead are the only heavy metals whose concentrations are high. Lead is toxic but iron only stains and causes intestinal disturbance.

Keywords: Inorganic, Geochemical, Elements, Land use, Anions, Cations, Pollution, Groundwater

1. Introduction

The creation of Anambra State with Awka as its capital has engendered high population growth rate, innumerable industries and other new land users have continued to generate wastes that are inappropriately disposed. The fear that groundwater in the area may have been contaminated and unfit for consumption is therefore certain and a cause for concern. The aim of the study is therefore to determine the extent to which inorganic chemical constituents in the study area has polluted the groundwater system as an appropriate measure for pollution control and sustainable development.

Awka area is located between Latitudes $6^o\,00^1$ and $6^o\,15^1$N and Longitudes $7^o\,01^1$ and $7^o\,11^1$E, Figure 1.
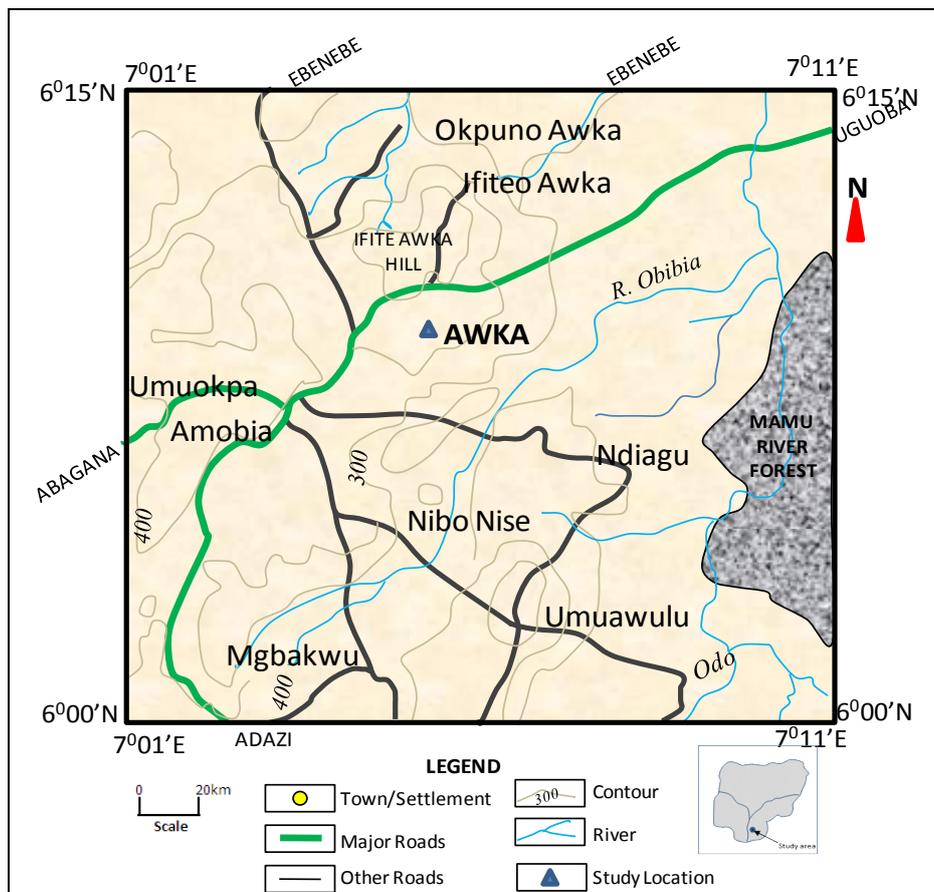
Figure 1. Topographical map of the study area

Geologically, Awka area is underlain by the Ameki (Eocene) Formation and Imo Shale Group (Paleocene) Figure (2). The Ameki Group consists of Nanka Sandstone, Nsugbe Formation and Ameki Formation (Nwajide, 1979). The Ameki Formation outcrops in the study area and consists predominantly of alternating shale, sandy shale, clay, sandstone and fine grained fossiliferous sandstone with thin bands of limestone (Reyment, 1965; Arua 1986). The age of the formation has been considered to be either early Eocene (Reyment, 1965) or early-mid Eocene (Bergeren, 1960; Adegoke 1969). The depositional environment has been interpreted as estuary and open marine based on faunal content. Nwajide (1979) and Arua (1986) suggested environments that ranged from nearshore to intertidal and subtidal zones of the shelf, whereas Fayose and Ola (1990) suggested that the sediments were deposited in shallow marine waters of 10 and 100 m paleobathymetry.
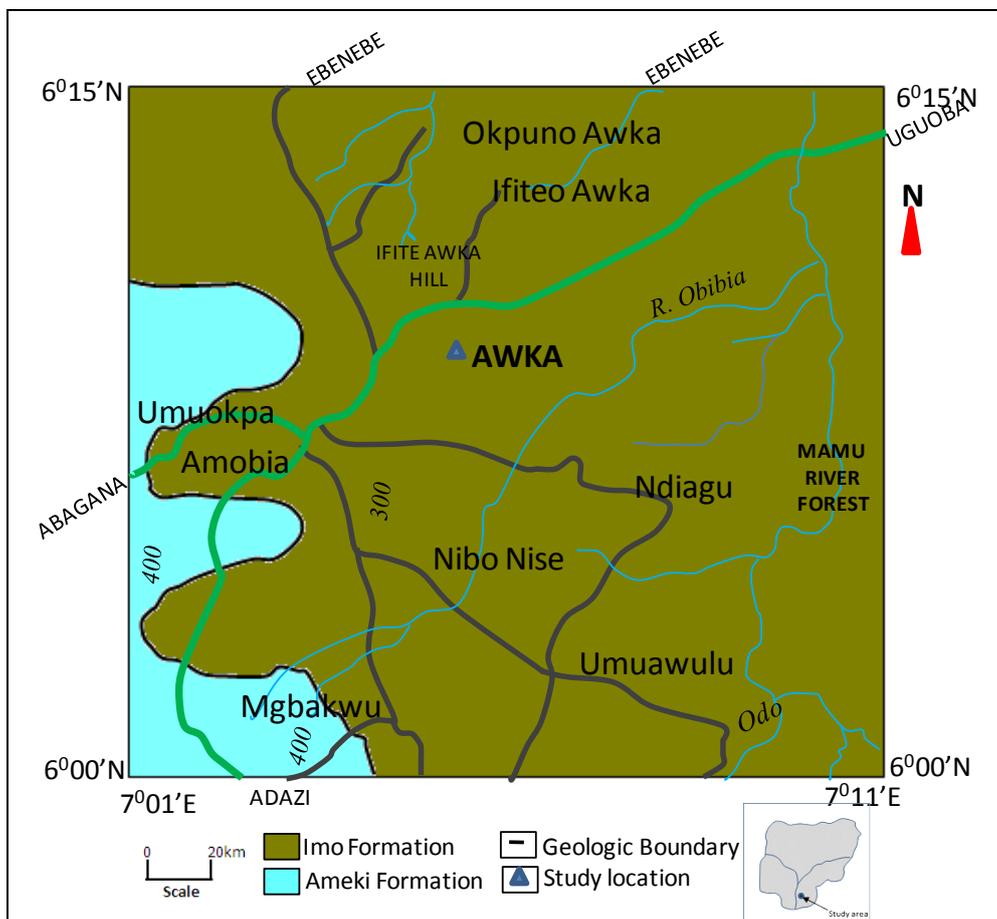
Figure 2. Geological map of the study area

The Imo Formation consists of blue-grey clays and shales with bands of calcareous sandstone, marl and limestone (Reyment, 1965). Imo Formation is the outcropping lithofacies equivalent of Akata Formation in the subsurface Niger Delta (Short and Stauble 1967, Avbovbo, 1978). The stratigraphic sequence of the study area is shown in Table 1.

Table 1. Stratigraphic sequence of the study area (Reyment, 1965)

AGE	Period	FORMATION	CHARACTERISTICS
33.9 - 55.8 ma	Eocene	Ameki /Nanka, Formation/ Nsugbe Sst (Ameki Group)	Sandstone- grey to green argillaceous sandstone, shales and thin limestone bands. Coarse-grained sandstone with abundant intercalations of calcareous shale and thin shaly limestone
65.5 ma	Paleocene	Imo Formation	Bluish to greyish clay, well laminated clayey shales

2. Climate and Physiography

The study area lies within the humid tropical rainforest belt of Nigeria. It is bounded by fresh water swamp to the south and the guinea savannah grassland to the north. The major climate variables are Rainy and Dry seasons brought about by the two predominant winds in the area. These winds are the south western monsoon wind from the Atlantic Ocean and the north eastern dry winds from across the Sahara desert, respectively. The rains last between April and October, followed by five months of dryness (November to March), (Illoeje, 1980). A short spell, the Harmattan period, is particularly dry and dusty, and commences in the study area by December. It is characterized by a grey haze that limits visibility and blocks sun rays.

Forest vegetation in the study area have been lost due to farming and other anthropogenic activities. Fringing forest however exit around rivers, streams and other wetlands that dot the area.

3. Materials and Method

Six water samples were collected from boreholes located at different points in the study area. The water samples were stored in pre-treated 50 cl plastic containers and taken to the laboratory for analyses. The water quality analyses followed recommended standard methods. The parameters analysed were colour, pH, conductivity, total dissolved solids (TDS) and Total suspended solids (TSS). Others are Nitrate (NO_3^-), Chloride (Cl^-), Sulphate (SO_4^{2-}), Phosphate (PO_4^3), Copper (Cu^{2+}), Lead (Pb^{2+}), Cadmium (Cd^{2+}), Zinc (Zn^{2+}), Iron (Fe^{2+}), total hardness (calcium hardness and magnesium hardness) and alkalinity.

The analyses in the laboratory were carried out using atomic absorption spectroscopy for Ca^{2+}, Na^+, Mg^{2+} and Cl^-, while Pb^{2+}, Cd, and Cu were analysed with the aid of spectrometer. K^+ was determined using the flame photometer. pH was measured with standard pH meter, while the concentration of the total iron (Fe^{2+}) was determined calorimetrically using Spekker absorption meter. Total dissolved solids (TDS) were determined using glass fibre. Turbimeter was used to assess turbidity. Physical parameters like pH and dissolved oxygen were measured in situ in the field with the appropriate standard meters. Anions like HCO_3 were estimated by titrimetric method. All details of analytical procedures used, have been reported in Freeze and Cherry (1979).

The concentrations of cations like Ca^{2+}, Mg^{2+} and Na^+ in milliequivalent per litre were later used to obtain sodium absorption ratio (SAR).

4. Results and Discussion

The results of the analyses Table 2, show the concentrations of the physicochemical constituents of the underground water borehole samples in Awka area with the corresponding WHO, 2006 standard for safe drinking water.

Table 2. Physiochemical Data of measured parameters of Awka Water boreholes

PARAMETERS	BH1	BH2	BH3	BH4	BH5	BH6	AVER	WHO, 2006
pH (31°C)	6.91	6.84	7.01	6.89	6.90	6.93	6.97	6-8.5
Sodium (Na+)	0.86	0.45	1.23	2.82	0.89	1.54	1.30	50
Potassium (K+)	1.46	3.11	4.44	4.01	4.84	2.53	3.40	10
Calcium (Ca^{2+})	4.86	3.37	3.46	8.03	9.86	4.04	5.60	200
Magnesium (Mg^{2+})	2.53	2.86	2.43	3.99	6.47	3.00	3.55	150
Total Hardness	7.39	6.23	5.89	12.02	16.33	7.04	9.15	500
TDS	5.16	7.04	12.45	8.01	19.61	9.02	10.22	500
Chloride (CL$^-$)	4.01	4.15	6.71	8.23	4.14	3.48	5.12	250
Sulphate (SO$_4^{2-}$)	3.16	1.41	2.39	5.64	2.45	2.13	2.86	400
Nitrates (NO$_3^-$)	2.43	2.33	1.93	2.66	3.33	2.18	2.48	50
Phosphates	6.01	4.30	6.70	5.43	5.05	3.40	5.15	1.0
Iron (Fe^{2+})	0.82	0.019	0.220	.060	0.473	.090	0.157	0.3
Lead (Pb^{2+})	ND	ND	ND	ND	0.0013	ND	ND	0.05
Copper (Cu^{2+})	0.0010	ND	ND	.0030	0.0110	ND	0.003	1.00
Cadmium (Cd^{2+})	ND	ND	ND	ND	0.0012	ND	ND	0.05
Zinc (Zn^{2+})	1.0030	0.0940	0.0031	0.0213	1.0460	0.0011	0.36	5.00
Manganese (Mn^{2+})	ND	ND	ND	ND	ND	ND	ND	0.02
Bicarbonate (HCO$_3^-$)	6.03	4.92	5.11	5.28	9.67	4.34	5.90	380
Conductivity	5.14	5.73	6.62	6.98	7.30	5.11	6.15	500
TSS	2.79	1.99	3.01	2.82	3.31	2.55	2.75	1000
Turbidity	6.14	8.38	6.66	8.01	12.37	6.06	7.94	000

From Table 2, all the parameters are in Mg/l except for conductivity (Ms/cm), turbidity and pH.

ND = Not detected

Using the world Health Organization standard for safe drinking water (WHO, 2006), it was observed that a few of the inorganic chemical elements are in excess of the recommended concentrations for some of the borehole waters in the study area. For example phosphate with concentrations ranging between 3.40 to 6.70 mg/l, are well above the standard of 1.00 mg/l recommended by WHO, 2006 Figure (3); Table 3. The concentrations of the other anions and cations like bicarbonate, sulphate, nitrate, chloride, calcium, sodium, etc. are within acceptable limits prescribed by WHO, 2006, Figure (3) and Table 3. It should be pointed out that phosphate that is high in groundwater in the area is probably introduced from agricultural activities, leachates and seepages from dump sites and animal farms. Even though sulphate and nitrate concentrations are below their respective limits, their future status should be monitored because they together with phosphate are associated with fertiliser applications.

Excess sulphate in water causes diarrhoea and purgatives in humans while high nitrate is dangerous to pregnant women and poses serious problems to infant less than three to six months of age, because of its ability to cause methemoglobinaemia or blue baby syndrome, in which blood losses its ability to carry sufficient oxygen.

The concentrations of total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS), are well below the limits recommended for safe drinking water Figure (4) and Table 4. This result is indicative of excellent borehole construction and development.

Table 3. Values of Phosphates (PO4-3), Sulphate (SO42-), Nitrate (NO32-) and Chloride (Cl-) as well as bicarbonate (HCO3-) in the six boreholes

Parameters	BH1	BH2	BH3	BH4	BH5	BH6	WHO 2006	REMARKS
Phosphates	6.01	4.30	6.70	5.43	5.05	3.40	1.00	Very high
Sulphates	3.16	1.41	2.39	5.64	2.45	2.13	400	Low
Nitrates	2.43	2.33	1.93	2.66	3.33	2.18	45.50	Low
Chloride	4.01	4.15	6.71	8.23	4.14	3.48	250	Low
Bicarbonate	6.03	4.94	5.11	5.28	9.67	4.34	380	Low
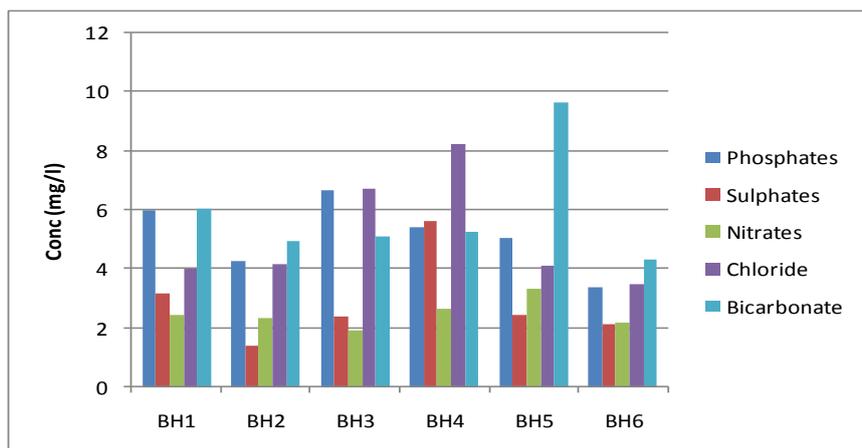
Figure (3) Major Anions in the analysed samples expressed as a bar chart

Table 4. TS, TSS and TDS of the area

Parameters	BH1	BH2	BH3	BH4	BH5	BH6	WHO
TS	7.9	8.03	15.45	10.83	22.92	11.57	1000
TDS	5.16	7.04	12.45	8.01	19.61	9.02	1000
TSS	2.79	1.97	3.01	2.28	3.31	2.55	1000
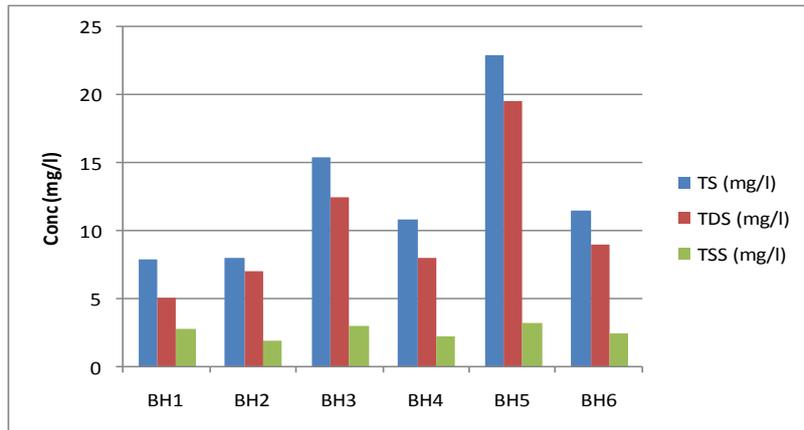
Figure 4. Representative Histogram Plots of TS, TSS, and TDS for BH6 in the study area

The pH of the groundwater is neutral to alkaline Figure 5; Table 5. This result shows that mean pH value of 6.90 for the groundwater in Awka area is potable and indicates also that the groundwater will not corrode pipes and other metal fittings (Corrodible materials).

Table 5. Values of pH, turbidity, TSS, TDS, conductivity and total hardness

S/n	Parameters	BH1	BH2	BH3	BH4	BH5	BH6	WHO 2006
1	pH	6.91	6.84	7.01	6.89	6.90	6.93	6-8.8
2	Turbidity	6.14	8.38	6.66	8.01	12.37	6.06	100
3	TSS	2.79	1.97	3.01	2.28	3.31	2.55	1000
4	TDS	5.16	7.04	12.45	8.01	19.61	9.02	1000
5	Conductivity	5.41	5.73	6.62	6.98	7.30	5.11	50
6	Total hardness	7.39	6.23	5.84	12.02	16.33	7.04	500
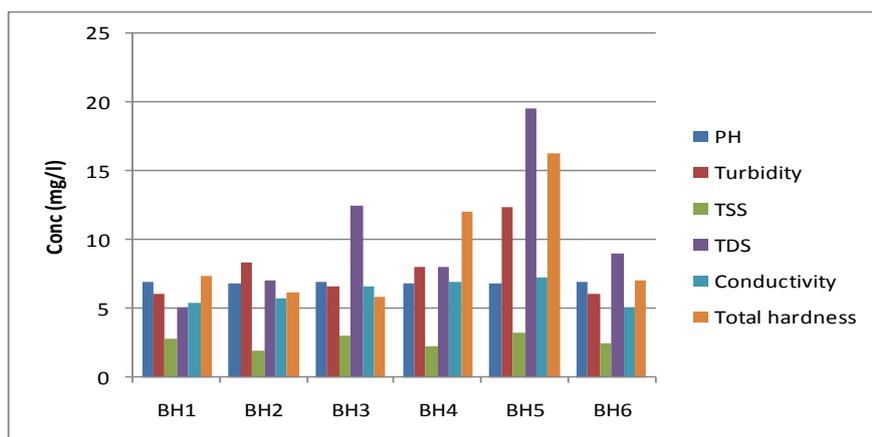
Figure 5. The histogram plots of pH, turbidity, TSS, TDS, conductivity and total hardness

The measured heavy metal contents of iron, copper, cadmium, zinc and lead are displayed in

Table 6. The results showed that while zinc and copper were not detected in most of the groundwater in the area, iron and lead are in excess in some of the boreholes according to the scale of WHO, 2006. It also showed that the high iron content for example is localised (in BH1, BH3 and BH4), which may be indicative of point sources, like an auto village or the direct result of the geology of the affected areas. High concentration of iron in water is not generally poisonous but causes brownish precipitates due to oxidation of iron in form of $Fe_2(OH)_3$ which does not present an aesthetic appeal to toilets and other household items. Lead is toxic (Short and Stauble 1967) as it forms lead oxide (PbO_2) when mixed with blood.

Table 6. Results of heavy metals analysis

No.	Parameters	BH1	BH2	BH3	BH4	BH5	BH6	WHO 2006	REMARK
1	Iron	0.82	0.019	0.220	0.060	0.473	0.090	0.3	High
2	Copper	ND	ND	ND	ND	0.0013	ND	1.00	-
3	Cadmium	0.0010	0.002	ND	0.003	0.0110	ND	0.05	Low
4	Zinc	ND	ND	ND	ND	0.0012	ND	5.00	-
5	Lead	1.0030	0.0940	0.0031	0.0213	1.0460	0.0011	0.05	High

SAR VERIFICATION: Sodium absorption ratio (SAR) according to Richard, 1985 is an important parameter for determining the suitability of water for irrigation. It is a measure of alkali/sodium hazards to crops. Sodium absorbed clay minerals displace Mg^{2+} and Ca^{2+} ions. This process reduces the permeability of soils resulting to poor internal drainage (Collins and Jenkins, 1960). Richard (1985) classified water standard for irrigation based on sodium absorption ratio Table 7.

SAR of water in the area was obtained using equation 1 to generate SAR values, Table 8 which were compared with the Richard (1985) classified standard for irrigation. On comparism it was shown that the inorganic elements of the groundwater in the study area are excellent for irrigation purposes Table 8.

$$SAR = \frac{Na+}{\sqrt{(Ca2+ + Mg2+)1/2}} \quad \dots\dots\dots\dots (1)$$

Where Na^+, Mg and Ca^{2+} are the respective concentrations of sodium, magnesium and calcium in Mg/l contained in the groundwater.

Table 7. Water classification scheme using SAR (Richard, 1985)

SAR	Water Class
0-10	Excellent
10-18	Good
18-28	Fair
➢ 26	Poor

Table 8. SAR status of boreholes 1-6

Sample	Na^{2+}	Ca^{2+}	Mg^{2+}	SAR	Remark
BH1	0.86	4.86	2.53	0.32	Excellent
BH2	0.45	3.37	2.86	0.18	Excellent
BH3	1.23	3.46	2.43	0.51	Excellent
BH4	2.82	8.03	3.99	0.81	Excellent
BH5	0.89	9.86	6.47	0.22	Excellent
BH6	1.54	4.04	3.00	0.58	Excellent

The average concentrations of major cations and anions were used in equation 2 to derive values, which are converted values from mg/l to meq/l Table 9. The converted values were plotted into the piper trilinear diagrams (Piper, 1944) in order to decipher the potability, water types and classes of the borehole waters in Awka area Figure (6).

$$Conc. = \ Conc.\, Mg/L\ / Equivalent\ weight$$

(2)

Table 9. Conversion of anions and cations from mg/l to meq/l

Measured Parameters CATION	Conc. Mg/l	Atomic weight	Charge	Equiv. Wt	Conc. Mg/L	% of component
Ca^{2+}	5.60	40.0	+2	20.04	0.28	38.89
Mg^{2+}	3.55	24.31	+2	12.16	0.29	40.28
Na^+	1.30	22.98	+1	22.98	0.06	8.33
K^+	3.40	39.10	+1	39.10	0.009	12.5
Total					**0.72**	**100**
ANION						
HCO_{3-}	5.90	61.02	-1	61.02	0.10	33.33
SO_4^{2-}	2.86	96.06	-2	48.03	0.06	20.0
Cl^-	5.12	35.45	-1	35.45	0.14	46.7
Total					**0.3**	**100**
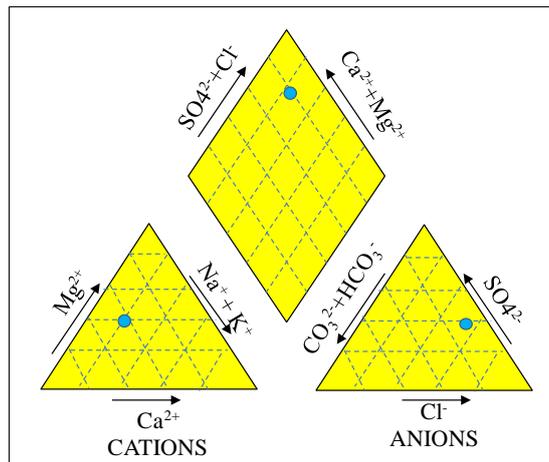
Figure 6. Piper Trilinear diagram using average compositions of major cations and anions in the study area

The piper trilinear diagram of Figure (6) indicates that the water is potable based on its position at the diamond end of the plot.

The spatial distribution of anions and cations in the study area were also used to compute the water types of the groundwater system at various locations in the study area Table 10 and Figure 7. The spatial distribution shows that the dominant water type is tending toward magnesium chloride.

Table 10. The spatial distributions of the anions and cations of the groundwater in Awka area

Parameters	Conc. Mg/l	Atomic Weight Mg/l	charge	Equivalent Weight Mg/l	Conc Mg/l	% of component Mg/l
BH1 CATION						
Ca^{2+}	4.86	40.0	+2	20.04	0.24	45.28
Mg^{2+}	2.53	24.31	+2	12.16	0.21	39.62
Na^+	0.86	22.98	+1	22.98	0.04	7.55
K^+	1.46	39.10	+1	31.10	0.04	7.55
Total					0.53	100
BH1 ANION						
HCO_{3-}	6.03	61.02	-1	61.02	0.10	35.71
SO_4^{2-}	3.16	96.06	-2	48.03	0.07	25
Cl^-	4.01	35.45	-1	35.45	0.11	39.29
Total					0.28	100
BH2 CATION						
Ca^{2+}	3.37	40.0	+2	20.0	0.24	33.33
Mg^{2+}	2.86	24.31	+2	12.16	0.02	47.061
Na^+	0.45	22.98	+1	22.98	0.08	3.921
K^+	3.11	39.10	+1	39.10	.51	15.69
Total						99.96

BH2 ANION						
HCO_3^-	4.92	61.02	-1	61.02	.08	34.78
SO_4^{2-}	1.41	96.06	-2	48.03	.03	13.04
Cl^-	4.15	35.45	-1	35.45	.12	52.17
Total					.23	99.99
BH3 CATION						
Ca^{2+}	3.46	40.0	+2	20.04	.17	32.08
Mg^{2+}	2.43	24.31	+2	12.16	.20	37.73
Na^+	1.23	22.98	+1	22.98	.05	9.43
K^+	4.44	39.10	+1	39.10	.11	20.75
Total					.53	99.99
BH3 ANION						
HCO_3^-	5.11	61.02	-1	61.02	.08	25
SO_4^{2-}	2.39	96.06	-2	48.03	.05	15.63
Cl^-	6.71	35.45	-1	35.45	.19	59.38
Total					.32	100
BH4 CATION						
Ca^{2+}	8.03	40.01	+2	20.04	.40	56.33
Mg^{2+}	3.99	24.31	+2	12.16	.09	12.68
Na^+	2.82	22.98	+1	22.98	0.12	16.90
K^+	4.01	39.10	+1	39.10	0.10	14.08
Total					0.71	99.9
BH4 ANION						
HCO_3^-	5.28	61.02	-1	61.02	.09	22.45
SO_4^{2-}	5.64	96.06	-2	48.03	.12	27.27
Cl^-	8.23	35.45	-1	35.45	.23	52.27
Total					0.44	99.99
BH5 CATION						
Ca^{2+}	9.86	40.0	+2	20.04	.45	39.47
Mg^{2+}	6.47	24.31	+2	12.96	.53	46.49
Na^+	0.89	22.98	+1	22.98	.04	3.51
K^+	4.84	39.10	+1	39.10	.12	10.53
Total					1.14	100
BH5 ANION						
HCO_3^-	9.67	61.02	-1	61.02	0.16	48.48
SO_4^{2-}	2.45	96.06	-2	48.03	0.05	15.15
Cl^-	4.14	35.45	-1	35.45	0.12	36.36
Total					0.33	99.99
BH6 CATION						
Ca^{2+}	4.04	40	+2	20.04	0.20	34.48
Mg^{2+}	3.00	24.31	+2	12.16	0.25	43.10
Na^+	1.54	22.98	+1	22.98	0.07	12.07

K^+	2.53	39.10	+1	39.10	0.06	10.34
Total					0.58	99.99
BH6 ANION						
HCO_{3-}	4.34	61.02	-1	61.02	.07	22.58
SO_4^{2-}	2.13	96.06	-2	48.03	.04	12.90
Cl^-	3.48	35.45	-1	35.45	.20	64.52
Total						
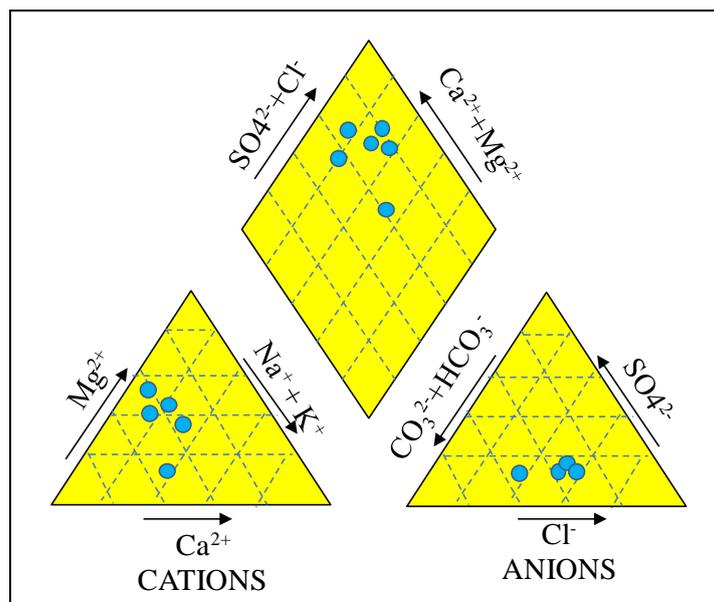
Figure 7. Spatial Distribution of cation and anions in Piper Trilinear

It is also possible to examine the extent of pollution of the groundwater based on the application of Hortons scales (1995). Hortons scale stipulates the scale of rating of pollution extent Figure 8. If the value of pollution falls at zero, it is of critical value. If it plots to the right of zero value (positive side), the water is polluted in that order. If it plots to the negative side, the water is not polluted in that order.
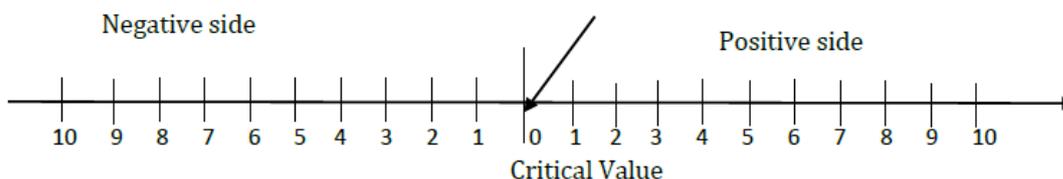
Figure 8. Horton index scale (Horton, 1995)

The computation of Horton Index number is shown in Table 11.

Table 11. Computation of reference number of Horton (1995)

S/N	PARAMETERS	AVERAGE VALUE IN SAMPLE	WHO STANDARD 2006	MEAN AI/WIJ
1	pH (at 31°C)	6.91	6.85	1.15
2	Potassium	3.40	10	0.34
3	Sodium	1.30	50	0.026
4	Calcium	5.60	200	0.28
5	Magnesium	3.55	150	0.024
6	Total Hardness	9.15	500	0.018
7	Total Dissolved Solid (TDS)	10.22	500	0.020
8	Chloride	5.12	250	0.020
9	Sulphate	2.86	400	.007
10	Nitrate	2.48	50	0.05
11	Iron	0.16	0.3	0.53
11	Lead	ND	-	-
12	Copper	ND	-	-
13	Cadmium	ND	-	-
14	Zinc	0.36	5	0.072
15	Manganese	ND	-	.02
16	Bicarbonate (HCO_3^-)	5.90	380	.01
17	Conductivity	6.15	500	.003
18	TSS	2.75	1000	
19	Turbidity	9.94		

Pollution index was calculated from the relation in equation 3:

$$P_{iji} = \frac{\sqrt{\left(\frac{MAXA_i}{W_{ij}}\right)2 + \left(\frac{Mean\ A_i}{W_{ij}}\right)2}}{2} \tag{3}$$

Where Piji is pollution index,

Ai = Average value of sample analysed,

Wij is WHO Standard.

From equation 3:

$$P_{iji} = \frac{\sqrt{(1.15^2) + (0.0135^2)}}{2} = 1.13$$

Therefore, pollution index Piji = 1.13

From the Hortons scale of Figure (8), the water is slightly polluted. The pollution is probably

due to the fact that the groundwater is heavily polluted by phosphate and in some cases, iron. Phosphate is high probably due to the fact that the surrounding villages use excess phosphate fertilizer in agriculture. Animal defecation may also be a factor.

5. Conclusion

Iron content in the area is high (WHO, 2016). High iron may be due to the effect of industrial activities relating to the release of iron compounds. The composition of some heavy metals like lead is on the increase due probably to effluent from battery industries. High concentrations of Chloride in groundwater in the study area, though not in excess, may be due to wastes from nearby markets and septic tank leakages. High concentration of Phosphate can also be traced to leachates from waste disposals. Again sources of phosphates may be runoff from agricultural sites using phosphate fertilizers, poor management of sewage and /or due to decayed plant tissues, since phosphates are tied up in plant tissues. The area might have been used as cemetery in the past as phosphates are present in fossilized bones or animal droppings, especially, cattle reared by Fulani nomads. It may also be that apatite is somewhere in the subsurface rock. As potassium is found in aluminates $KAL_3(SO_4)^2(OH)_6$, the phosphate may have originated also from the laterite of Ameki Formation. Lead could also be due to sawmills, woodworks, auto repair workshops and can affect red blood cell chemistry in humans (Franson, 1995). Finally, the water tilted to magnesium chloride water which is good for irrigation and other household activities. Periodic monitoring of the groundwater system in the area is recommended as a management strategy.

Acknowledgement

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