Geochemical evaluation of groundwater quality in Abakaliki area, Southeast Nigeria

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Abstract

The study area comprises Abakaliki town and the mineralized villages in the south, 14km away from the town. It lies between latitudes 6008'N and 6024'N, and longitudes 8000'E and 8016'E, and is underlain by the Abakaliki Shale which belongs to the Asu River group of Albian age. The study aimed at determining the groundwater quality of the area as evaluated from both physical and chemical conditions. Eighteen (18) parameters, (11 chemical and 07 physical) were analyzed for each of twenty (20) samples collected from three different sources; sixteen (16) from boreholes, three (03) from hand-dug wells and one (01) from pipe borne town water supply. Spectrophotometer of HACH DR/ 2010 series was used to analyze the ions. The laboratory results were compared with water quality criteria according to the World Health Organisation (WHO, 2004), European Union (EU, 1998) and United States Environmental Protection Agency (USEPA, 2004) for drinking water. Results showed that about 50% of the samples are polluted with nitrate (N03) with values above the maximum permissible limit of 50mg/l in many places. Concentrations of Fe are also above the permissible limits of 0.30mg/l, in some places, especially in the southern part of the study area. The sources of nitrates are suspected to be from agricultural fertilizers as well as sewage effluents. The iron is suspected to be from dissolution of iron-rich ore minerals (siderites and pyrites) which occur in the southern part of the area. The groundwater of the area is moderately hard (due to bicarbonate (HCO3)) and fresh (due to TDS < 1000 mg/l at temperature range of 270C to 310C), and is dominantly alkaline.

1. Introduction

The importance of groundwater as an alternative water supply is increasingly recognized in response to escalating costs of portable surface water (Emmanuel et al., 2008), especially in the developing countries. By estimation, approximately one third of the world population use groundwater for drinking and other purposes (Zottan, 2004). This enormous use of groundwater has resulted to over- abstraction and consequently, the drastic reduction in groundwater level, which is sometimes accompanied by degradation of its quality. Among the various reasons for over-abstraction, the most serious are the poor availability of portable surface water and the general belief that groundwater is purer due to the protective quality of the soil cover. But then, the soil which is supposed to be protective, is most often not free from adverse effect of chemicals from indiscriminate discharge of sewage and solid wastes, agricultural/industrial effluents especially in developing countries, and natural mineralization, all of which contaminate the groundwater via the soil partition, and cause health hazards. Contamination of groundwater in Abakaliki area, southeastern Nigeria is believed to be high because of the availability of sulfide ore deposits, and because anthropogenic and geogenic effects increase the rate at which these mineral deposits weather and release

elements into the soil. Subsequent rainfalls leach the elements from the soil zone into the groundwater regime through the structural pathways in the sediments. The plume disperses within the groundwater environment and introduces some hydro geochemical reactions between the groundwater and the hosting rock. According to Prasanna et al. (2011), geochemical processes occurring within the groundwater and reaction with aquifer minerals have profound effect on water quality. That is why Atwia et al. (1997) stated that the hydro geochemical character of groundwater in different aquifers over a space of time has proven to be important in solving groundwater management problems. It is therefore important that the quality of the groundwater of Abakaliki area where iron, sulfate, bicarbonate, nitrates, chloride, calcium, magnesium, sodium, and potassium, which are associated with Pb-Zn mineralization are commonly present. Although the mining of the lead-zinc has been abandoned, the devastative effects on the groundwater may have continued to linger. Thus, the poor handling of mine drains constitute a potential threat to the quality of the usually shallow groundwater in the mining axis of Abakaliki (Uma, 2004). This study aimed at evaluating the groundwater quality in the area as such evaluation will assist in groundwater resource management as stated by Atwia et al. (1997).

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2. Local Geology and Hydrogeology

Abakaliki, the study area lies between latitudes 6^o08^1N and 6^o24^1N and longitudes 8^o00^1E and 8^o16^1E. It includes Abakaliki town and the highly mineralized rural communities (Amagu, Ameri, Enyigba and Ameka) which are about 14km, south of the metropolis (fig 1). The area is underlain by poorly bedded shales of the Abakaliki Shale Formation, which is part of the Asu River Group of Albian age. The shales are dark, occasionally sandy with intercalations of fine-grained sandstone, mudstones and limestone lenses. They are often calcareous and pyritic, because, the Formation is locally rich in ammonites, such as the mortoniceras and elobiceras, which paleo-ecologically indicate that the Asu River sediments were deposited under stagnant shallow marine environment (Reyment, 1965). According to Offodile (2002), Abakaliki Shale is about 200 meters thick. Dip varies from 50 at Abakaliki town to the highest value of about 800 around Ameka hill. Pyroclastics, tuffs and agglomerates occur along the axis of the Abakaliki Anticlinorium (a major structural feature of the Benue Trough which houses the Abakaliki Basin and the anticlinorium) and within the series of hills at the central part of Abakaliki town. The Abakaliki Shale sandwiches many mineral veins, anomalous bodies and mineral lodes, all of which are associated with lead-zinc mineralization in the area. Hydrogeologically, the Abakaliki Shale forms an aquiclude, which is a problem to groundwater occurrences, but it is aquiferous where the shale is extensively weathered and fractured.
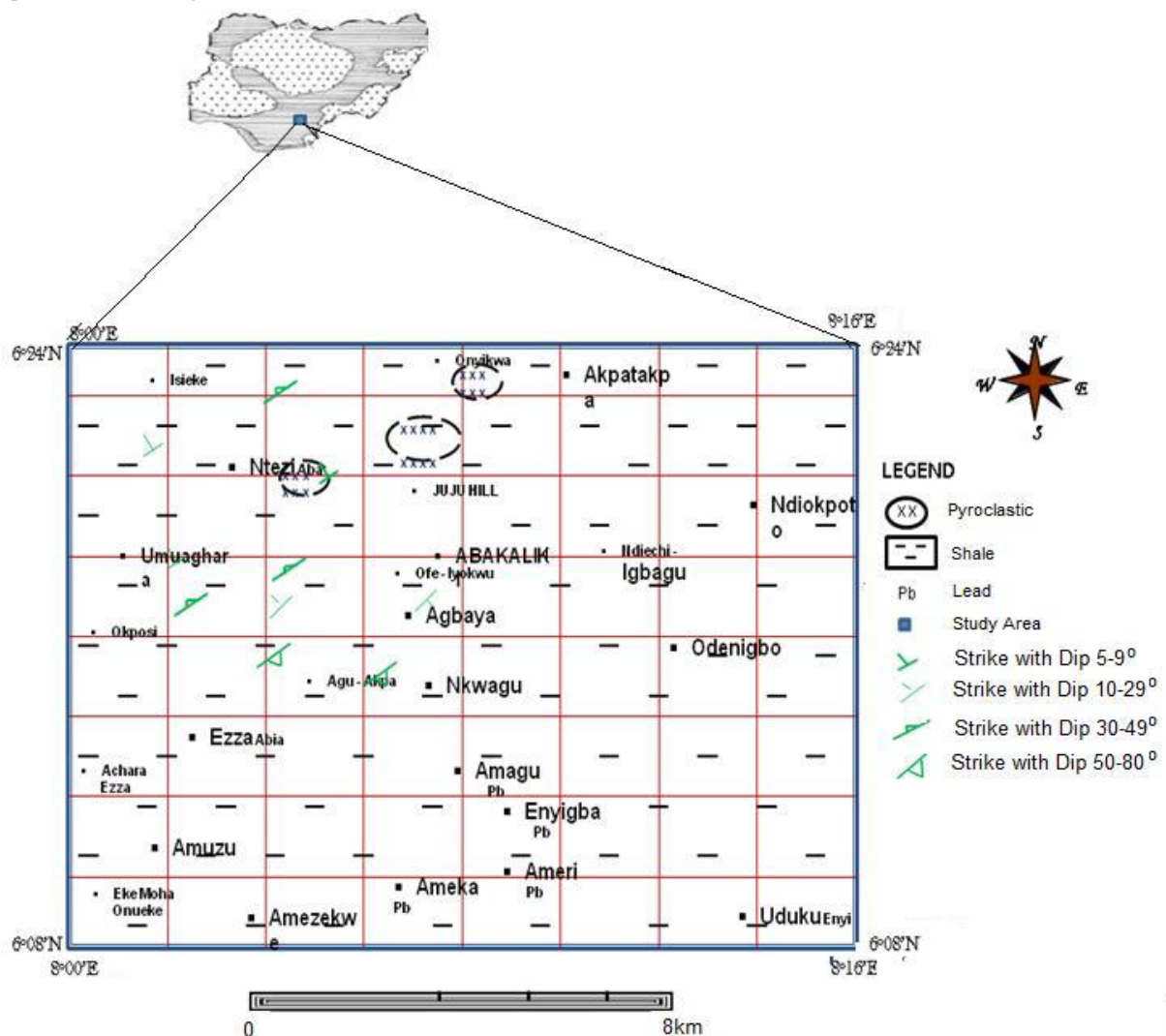

Figure 1. Geological map of the study area

3. Methodology

3.1. Sample collection

Sample locations were determined using a Global Positioning System (GPS) of eTrex model and were plotted in Fig 2. Twenty (20) groundwater samples were collected from different locations spread across the study area, sixteen (16) from boreholes, three (03) from hand-dug wells and one (01) from the city water supply reservoir. The reservoir sample was collected in order to compare the quality of the pipe-borne water with that of the groundwater. Each sample (groundwater and pipe-borne water) was collected and filtered with 0.45 micro meter filter membrane into a clean 1 litre plastic water bottle and labelled according to the location name. Each plastic bottle was rinsed with the same water to be sampled before the collection to avoid any contamination from the bottle. Physical parameters such as the electrical

conductivity (EC) and temperature relevant to the study were measured in situ using a portable WTW LF 90 conductivity meter. pH was also measured in-situ using

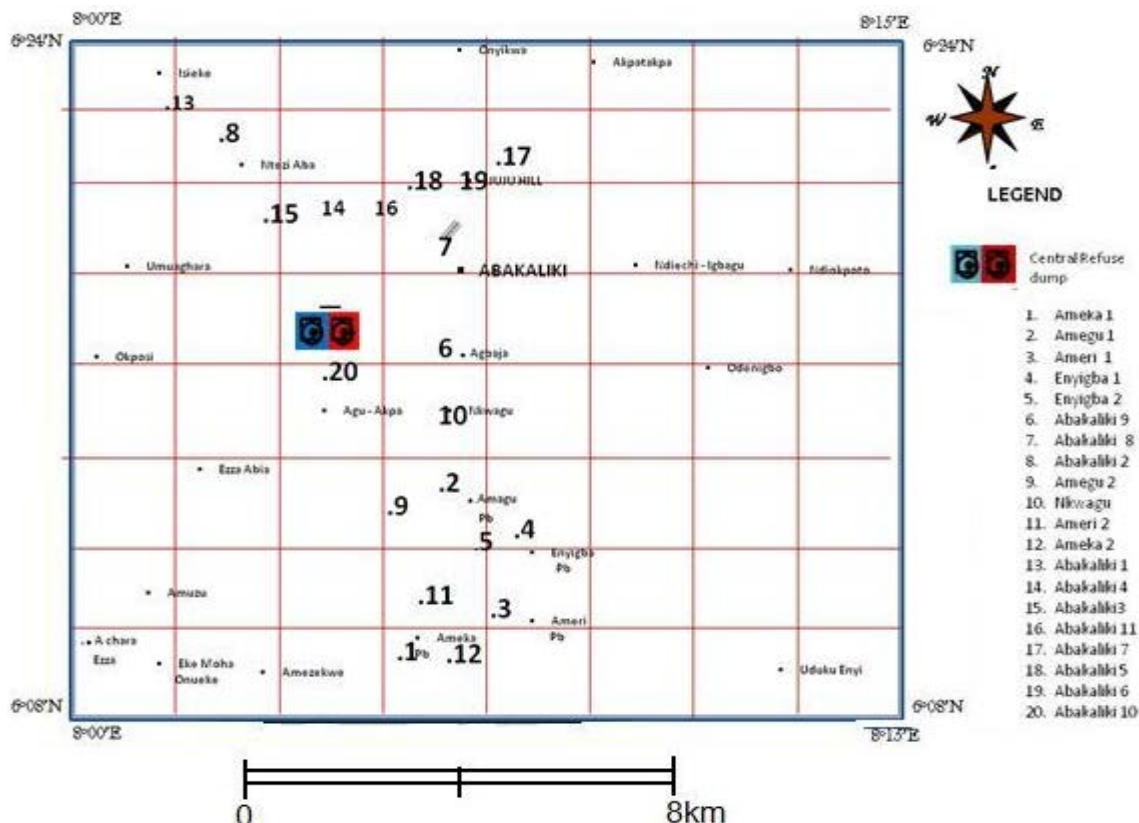HACH pH sension meter. All samples were transported for analysis within 24 hours after collection.

Figure 2. Map showing the distribution of sampled locations

3.2. Laboratory Analysis

Fifteen (15) parameters were analyzed for, in each of the 20 samples, giving rise to 300 results. The analytical procedure was according to the World Health Organization (WHO, 2004) as follows:

Total Dissolved Solids (TDS) was measured with TDS meter while Total Suspended Solids (TSS) was determined photometrically with the HACH DR/2010 spectrophotometer at the wavelength of 810nm. The instrument was zeroed with de-ionised water while the sample was mixed thoroughly before being placed in the sample holder and measured. Total Solids (TS) was calculated arithmetically from the other parameters using the equation

TS (mg/l) = TSS (mg/l) + TDS (mg/l).

Alkalinity was determined titrimetrically with standard solution of sulphuric acid (H_2SO_4). The sample was titrated with the 0.1N H_2SO_4 using phenolphtalein and methyl orange indicators. 100ml water was measured into a conical flask and 3 drops of phenolphthalein indicator added. When the sample remained colourless, it indicated in all cases that phenolphthalein alkalinity was zero. A few drops of methyl indicator was then introduced, and the titre value noted when the first perceptible colour change from yellow to orange took place. Alkalinity was calculated as

Alkalinity (HCO_3^-) [mg/l $CaCO_3$] = Volume of 0.1N H_2SO_4 acid used (ml) x 50

Turbidity was determined spectrophotometrically at wavelength of 450nm on the HACH DR/2010 spectrophotometer. The instrument was zeroed with

filtered deionised water (the blank) while the turbidity was measured. Total Hardness was determined titrimetrically using 0.01N tetra sodium salt of Ethylene Diamine Tetra Acetic acid (EDTA). 50ml of each water sample was put in the conical flask; 1 ml of buffer hardness solution was added, followed by 2 drops of a solution of eriochrome black indicator. The water sample was immediately titrated with continuous stirring using the standard EDTA till the end point when some blue colouration was observed. Total hardness was calculated as

$$CaCO_3 (mg/l\,CaCO_3) = \frac{Volume\,of\,0.01M\,EDTA(m)\,x\,1000}{Volume\,of\,water\,sample\,taken\,(ml)}$$

For the determination of Calcium Hardness and Bicarbonate, the water sample was titrated using 0.01N EDTA solution. 50ml of each water sample was placed in the conical flask followed by 2 ml 10N sodium hydroxide and 3 drops of calcon indicator. The end point was taken when the colour changed. Calcium hardness was calculated as

$$Chloride\,(Cl)\,(mg/l) = \frac{Volume\,of\,silver\,nitrate\,solution\,used\,(ml)}{Volume\,of\,water\,sample\,taken\,(ml)}$$

For the determination of Chloride, 25ml water sample was placed in a conical flask followed by 1ml of solution of potassium chromate indicator. The sample was titrated with a standard solution of silver nitrate. The end point was when the colour changed from yellow to dirty brown. Chloride was calculated as

$$CaCO_3\ (mg/lCaCO_3) = \frac{Volume\ of\ 0.01M\ EDTA(m)\ x\ 1000}{Volume\ of\ water\ sample\ taken\ (ml)}$$

Nitrate was determined using the HACH DR/2010 spectrophotometer by the principle of the cadmium reduction method. The instrument was zeroed with a fresh sample and the nitrate measured at a wavelength of 500nm while placing the treated sample in the sample holder. Sulphate was determined using the HACH DR/2010 spectrophotometer by the principle of turbidimetry. The instrument was zeroed with a fresh sample and the sulphate measured at a wavelength of 450nm while placing the treated sample in the sample holder. Iron, Calcium and Magnesium were determined from the water samples using the Bulk Scientific Atomic Absorption Spectrophotometer (AAS), 200A Series model while Potassium and Sodium were determined with the aid of flame photometer.

4. Results and Discussion

Table 1 presents the summary results of the physical parameters while table 2 presents the major ions concentration of the analysed groundwater samples. The pH ranges from 5.28 to 8.10 with an average of 7.26. All samples except five show pH values above 7.0 thus, indicating minor variability in pH. The groundwater in the area will therefore be described as being dominantly neutral to weakly alkaline and falling within 6.5 to 8.5 pH range of the World Health Organization (WHO 2004) for water quality standards. It is observed from the table that two out of the three samples with pH values in the acidic range are from hand dug wells (samples 10 and 16) while the most acidic sample (lowest pH, sample 18) is pipe borne water. The acidity may be due to the influence of carbonic acid at the near surface because of high CO_2 dissolution in the area, while the treatment of the pipe borne water with chlorine could be responsible for the increased acidity of the pipe-borne sample. The major ions are indiscriminate of the pH range (compare Tables 1 and 2). High dissolution of CO_2 is attributed to the temperature of the groundwater, which ranges from 270C to 310C with average of 29.40C. At such temperature range, gases such as CO_2 are held in solution and increase the solubility of minerals (Freeze and Cherry, 1979). The electrical conductivity (EC) values are moderate with mean value of 583.5µS/cm except sample 7 with 1130µS/cm, a value which could be attributed to high concentration of TDS, although still within the WHO (2004) tolerable limit of 1400µS/cm specified for drinking water. The TDS concentration of the groundwater is generally less than 1000mg/l; hence, the groundwater can be classified as fresh groundwater (Carroll, 1962).

Turbidity values range up to 45 NTU, although most of the waters are less than 3.4 NTU, which is the average value. This parameter, which is a measure of cloudiness of water or suspended (such as clay, silt, colloidal inorganic and/or organic particles) matters in water and used to indicate water quality and filtration effectiveness is noticed mostly in hand dug wells, particularly sample 16 (Table 1). It may be due to flow alterations in the unsaturated zone. American Public Health Association (APHA, 1998) reported that although 2.5 NTU is the aesthetic guideline value, highly turbid water does not necessarily constitute a health hazard. While turbidity above 1 NTU can protect harmful micro-organisms from the effects of chlorine disinfection, the particles can also adsorb toxic organic or inorganic compounds. In the later case, turbid water can be said to adsorb toxic elements that would have polluted the water, making it safer for use after a simple means of treatment, perhaps filtration. The order of cation chemistry for most of the groundwater samples is $Ca^{2+}>K^+>Na^+>Mg^{2+}$ with few in the order $Ca^{2+}>K^+>Mg^{2+}>Na^+$. The concentrations of major cations are all below WHO (2004) water quality criterion (see Table 2).The sources may be from geologic materials of clay residue (illite, and montmorillonite in some places) that intercalate the shale of Asu River Group in the area. Freeze and Cherry (1979) had opined that when CO_2 charged groundwater with low TDS encounters clay residue such as kaolinite, illite, or montmorillonite, Na^+, K^+, Mg^{2+} and Ca^{2+} are released to the groundwater system.

The dominant order of anion concentration is $HCO_3^->NO_3^->Cl^->SO_4^{2-}$. The concentration of bicarbonate can be attributed to natural processes such as dissolution of carbonate minerals in the presence of soil CO_2 by the action of percolating water from precipitation. Bicarbonate with average concentration of 62 mg/l could mean that the area is generally recharged by water from precipitation.

Iron concentrations are low and within the WHO (2004) limit of 0.30mg/l (average of 0.26mg/l) except for samples 4, 5, 9, 11, 17 and 18 with values of 0.64mg/l, 0.81mg/l, 0.67mg/l, 0.98mg/l, 0.78mg/l and 0.40mg/l respectively, which are above the specified limit of 0.30mg/l. Thus, about 30% of the samples (six out of 20) are contaminated of iron. According to Freeze and Cherry, (1979) ferric ion is absent above a pH of 3.0 and ferrous ion diminishes rapidly as pH increases above 6.0. Thus, the observed concentration of iron agrees to a very reasonable extent with the pH conditions of the area as presented in Table 1. The high iron concentrations in samples 4, 5, 9 and 11 are attributed to the presence of iron-rich ore deposits (siderite and pyrite) in those locations (Enyigba, Amagu and Ameri) from where the groundwater samples were taken. Dissolution of these minerals may have allowed for the release of irons to the groundwater even to the extent of pollution. The value of 0.40m/l of iron in the pipe-borne water (sample 18) may have resulted from rusting of the distribution pipe which rusting may have raised the concentration of iron, as iron oxide, in the water.

Sulfate and chloride ions are high only in sample 14 with 150mg/l for sulfate, and samples 7, 10 and 14 with respective value of 98mg/l, 100mg/l and 80mg/l for chloride. Each value is nevertheless below the 250mg/l standard limit of WHO (2004). The chloride and sulfate concentrations may be attributed to the leaching of sewage effluents down to the groundwater system in the highly populated areas (mechanic site, site 7; Nkwagu Central School, site 10 and Ebonyi State University Teaching Hospital, site 14) where indiscriminate disposal of sewage is suspected to be responsible for the pollution of groundwater by sewage effluent. Meanwhile the total hardness as equivalent $CaCO_3$ (carbonate hardness due to calcium ion) ranges from 57mg/l to 228 mg/l except in samples 4 and 18 with 21 mg/l each.

Table 1: Results of Physical Parameters of Ground water samples in the study area

Sample Number	Sample Location	Water Sources	pH	EC (µS/cm)	TDS (mg/l)	TSS (mg/l)	TS (mg/l)	Turbidity (NTU)	Temperature (°C)
1	Ameka 1	BH	7.49	760	494	1	495	2	29
2	Amegu 1	BH	7.27	300	195	1	196	0	30
3	Ameri 1	HW	7.37	560	364	0	364	1	29
4	Enyigba 1	BH	6.00	80	52	0	52	1	30
5	Enyuigba 2	BH	7.91	650	422.5	0	422.5	0	30
6	Abakaliki 9	BH	7.37	520	338	1	339	0	30
7	Abakaliki 8	BH	7.91	1130	734.5	0	734.5	0	30
8	Abakaliki 2	BH	8.10	420	273	3	276	0	31
9	Amegu 2	BH	7.35	690	448.5	0	448.5	0	29
10	Nkwagu	HW	6.92	280	186	3	189	8	27
11	Ameri 2	BH	6.54	620	403	0	403	0	30
12	Ameka 2	BH	7.74	650	422.5	5	427.5	0	29
13	Abakaliki 1	BH	7.27	300	195	0	195	0	30
14	Abakaliki 4	BH	7.21	920	598	2	600	3	30
15	Abakaliki 3	BH	8.10	420	273	7	280	0	30
16	Abakaliki 11	HW	6.68	880	572	4	576	45	28
17	Abakaliki 7	BH	7.09	290	188.5	25	213.5	5	29
18	Abakaliki 5	PW	5.28	100	65	2	67	1	30
19	Abakaliki 6	BH	7.16	500	325	1	326	0	28
20	Abakaliki 10	BH	7.48	950	617.5	0	617.5	2	29
Mean			7.26	583.5	373.35	2.75	376.1	3.4	
Minimum			5.28	80	52.00	1.00	52.00	1.00	29.40
Maximum			8.10	1130	734.00	25.00	734.00	45.00	27.00
WHO (2004)			6.5-8.5	1400	500	5**	500**	5***	31.00

BH =Bore hole; PW= pipe borne water; HW= Hand dug Well; ***= USEPA (1975); **= WHO (1993)

Table 2: Results of chemical parameters

Sample Number	Sample Location	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^+ (ppm)	K (ppm)	Fe (ppm)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)	NO_3^- (mg/l)	Total hardess (mg/l)	Ca hardess (mg/l)
1	Ameka 1	37.8	13.67	12.151	26.198	0.12	12	4	110	55.00	150	94
2	Amagu 1	24	2.19	12.136	20.986	0.05	12	15	40	55.88	69	60
3	Ameri 1	20	1.70	13.775	24.198	0.01	14	21	42	62.04	57	50
4	Enyigba 1	8	0.24	8.25	10.216	0.64	2	10	20	44.22	21	20
5	Enyigba 2	32	4.64	9.741	18.741	0.81	24	13	70	85.67	99	80
6	Abakaliki 9	43.2	10.99	12.138	20.841	0.09	46	9	124	68.84	153	108
7	Abakaliki 8	24	1.47	9.981	19.216	0.02	98	21	28	35.20	66	60
8	Abakaliki 2	36	11.72	7.251	16.721	0.04	12	7	122	43.56	138	90
9	Amagu 2	40	8.55	9.081	31.081	0.67	24	58	92	35.64	135	100
10	Nkwagu	24	6.35	9.751	16.581	0.01	100	12	34	75.68	86	60
11	Ameri 2	32	9.77	11.241	27.341	0.98	16	15	82	66.08	120	80
12	Ameka 2	49.6	10.26	8.975	19.095	0.03	34	0	102	35.20	228	124
13	Abakaliki 1	27.2	0.24	12.136	27.986	0.18	12	7	38	31.68	69	68
14	Abakaliki 4	74.4	10.26	10.025	21.061	0.03	80	150	82	41.36	228	186
15	Abakaliki 3	40	2.44	10.841	24.181	0.12	8	3	100	28.60	110	100
16	Abakaliki 11	40	7.81	9.225	17.316	0.06	24	41	80	64.24	132	100
17	Abakaliki 7	32	9.77	10.986	25.097	0.78	20	21	68	38.28	120	80
18	Abakaliki 5	8	0.24	10.092	22.081	0.40	12	29	8	33.44	21	20
19	Abakaliki 6	60	12.21	9.981	27.198	0.02	8	20	20	51.48	200	150
20	Abakaliki 10	48.8	14.16	10.986	21.981	0.01	56	4	98	38.72	180	122
Mean		35.05	6.93	10.45	23.11	0.264	30.70	23	62.0	47.84	119.10	83.60
Minimum		8	0.24	7.25	10.22	0.01	2.00	4.00	8.00	28.60	21.00	50.00
Maximum		74.4	14.16	13.78	31.08	0.98	80.00	150.00	124.0	85.00	228.00	24.00
WHO (2004) limit		75	50	200.00**	12*	0.30	250.00	250.00		50	100 **	

*=Pratt, 1972**=WHO, 1993

The mean concentration of the total hardness is 119.1 mg/l (Table 2) which falls between 75mg/l and150 mg/l acceptable range of water hardness prescription according to Sawyer and McCarty (1967). The result shows that the hardness of the groundwater of the area is generally moderate, but up to the hard water range in samples 12, 14 and 19.

All the groundwater samples are contaminated with nitrate (NO_3) (concentrations less than 50mg/l) but only samples 1,2, 3, 5, 6, 10, 11, 16 and 19 are polluted with their concentrations above 50mg/l maximum limit for drinking water standard specified by WHO (2004). A close look at Table 2 reveals that although boreholes samples are among those polluted (samples 1, 2, 5, 6, 11 and 19), most borehole samples are only contaminated (10 of them) but

not polluted. All the three hand-dug wells sampled (samples 3, 10 and 16) are polluted. The variability and wide spread concentration of nitrate in the study area (fig 3) indicates its origin from nonpoint sources, probably sewage and agricultural land use such as the general fertilizer application to rice plantations in the area. This implies therefore, that the sources of the nitrate to the groundwater environment could be as a result of leachates from urban and farm wastes. Excessive concentrations of nitrates in groundwater have the potential to harm infant human beings and livestock if consumed on a regular basis (Freeze and Cherry, 1979). It follows therefore that the groundwater of the study area poses threat to the health of users especially the infants, because of the nitrate pollution.
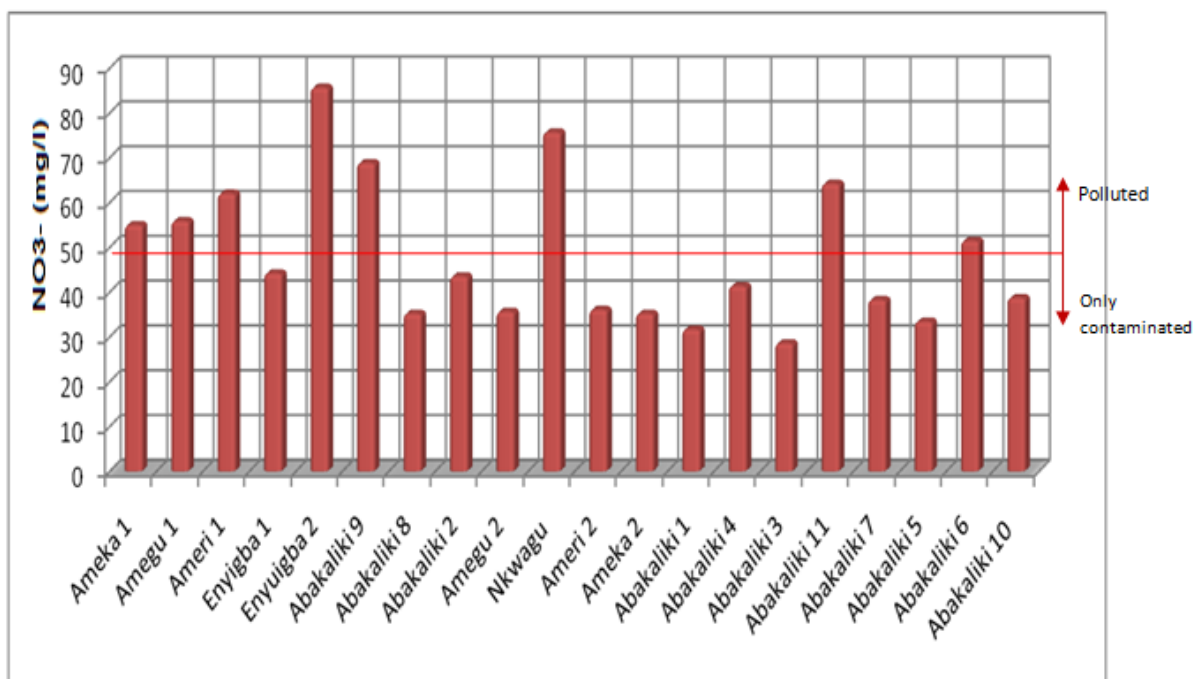

Figure 3. Spread of nitrate ion (NO_3^-) concentration in the study area.

In order to facilitate rapid comparison of ionic strengths, Stiff diagram was constructed for each sample. Stiff's diagram gives information on the ionic strength of a water sample which information can be used to deduce the type of water the sample represents, whether soft or hard. Figure 4 shows Stiff diagrams that represent each of the 20 water samples in this study. In almost all the diagrams, the graphs point towards calcium ions (Ca^{2+}) indicating that Ca^{2+} is the dominant cation, followed by Mg2+ with Ca^{2+} and Na+ being proportional in fig.4[4]. 75% of the Stiff diagrams point towards the dominance of bicarbonate ion (HCO_3) showing that water hardness due to the HCO_3, otherwise called carbonate hardness or temporary hardness characterizes almost all the waters of the study area. Carbonate hardness is that part of total hardness equivalent to HCO_3^- and CO_3^{2-} of calcium and magnesium (or alkalinity) (Kelvin, 2005), and can be removed by boiling. In fig. 4[18], sulfate ion (SO_4^{2-}) is dominant, making the

total hardness to exceed the hardness due to HCO_3^- and CO_3^{2-} of calcium and magnesium. The excess, termed non carbonate hardness is traditionally called permanent hardness which cannot be removed by boiling. SO_4^{2-} and Cl^- are in equal proportion in fig. 4[14] representing sample from EBSU Teaching Hospital while Chloride (Cl^-) is prevalent in figs 4[7] and 4[10] representing samples from Mechanic site and Central School Nkwagu respectively. Cl^- and HCO_3^- are in equal proportion in fig 4[20] representing sample from Nkaliki while HCO_3^- and SO_4^{2-} are in the same proportion in fig 4[9] representing water sample from Amagu. Waters from the above-mentioned sites are likely to exhibit permanent hardness and can only be softened by addition of sodium carbonate and lime and filtration through natural or artificial zeolites, which absorb the hardness producing metallic ions and release sodium ions to the water.
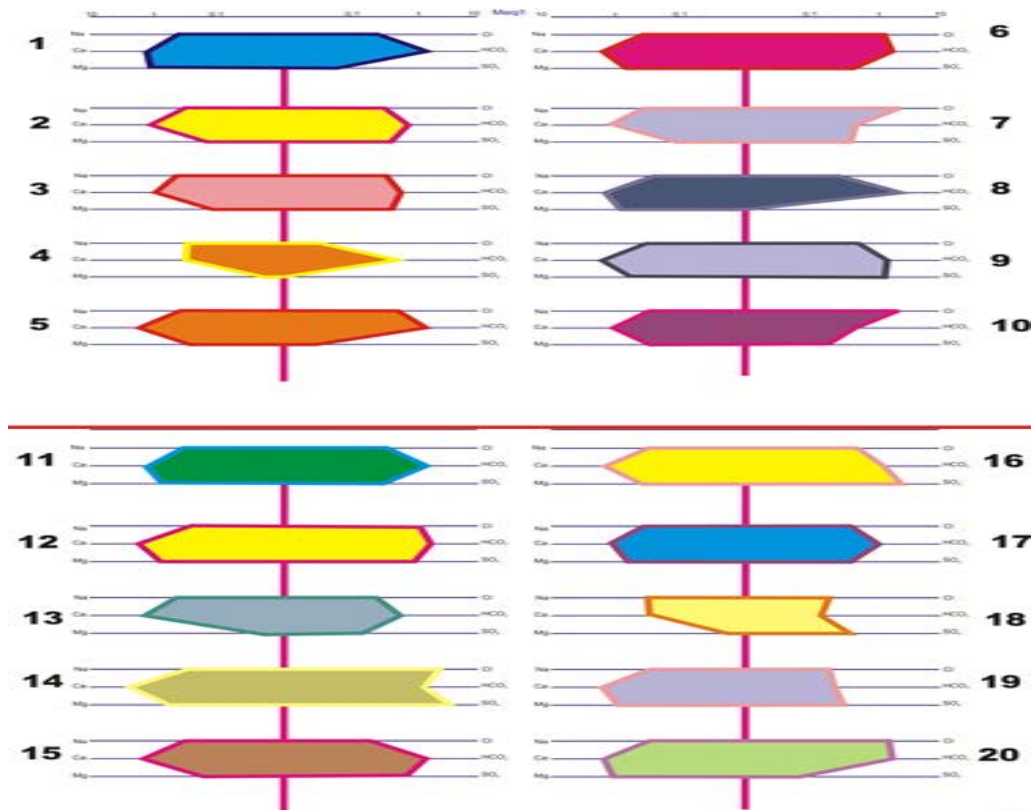
Figure 4. Stiff diagram showing ionic strength of the major cations and anions concentration in meq/l of the groundwater samples.

5. Conclusions

Abakaliki area is underlain by poor groundwater yielding aquiclude (the Abakaliki Shale of the Asu River Group), but produces prolific aquifers where the shale is weathered and fractured. Prior to this work the quality of the water and the contributing factors to that quality have not been studied nor documented. This study has shown that the groundwater is moderately hard due to bicarbonate (HCO_3), calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions as delineated in the Stiff diagrams where the ionic strength of all the samples are shown to be controlled by HCO_3, Ca^{2+} and Mg^{2+} The groundwater is also fresh as total dissolved solids (TDS) is less than 1000mg/l at the temperature range of 270C to 310C. Samples from hand dug wells and boreholes have comparable acidity; while those from hand-dug wells have pH range of 6.68 to 7.37, those from boreholes have pH range of 6.00 to 8.10. Generally, however, acidity seems to decrease with depth indicating that its source may be from near surface processes. Analyses of the groundwater samples showed that much of the groundwater is of poor quality as a result of contamination of inorganic matters and particularly polluted with iron (Fe) and nitrate (NO_3).

Acknowledgement

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