



## The hydrochemistry of Angwan Mallam and environs (PART OF KEFFI SHEET 208 NE)

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**ABSTRACT:** The rock types in the area are migmatite, granodiorite, pophyritic granodiorite, and biotite gneiss intruded by mineral bearing pegmatite dyke. The structural trend of the rocks conforms to the general pan-African Orogeny deformation trending NE - SW. Structures like fault, vein, joint and foliations were observed during the field mapping. Eleven water samples were collected from surface water and wells of the study area for physio-chemical analysis. The result of the water analysis shows the major cations, anions, and heavy element:  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^{+}$ ,  $K^{+}$ ,  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $Cl^{-}$ ,  $HCO_3^{-}$ , and Fe, Cu, Pb. The pH, temperature, electrical conductivities, acidity, alkalinity, total dissolved solid, and turbidity were determined. The cation, anion, and heavy element are majorly derived from leaching of the surrounding rocks and human activities influence as the mining activities in some of the villages does not contaminate or pollute its water, soil and wellbeing of the people living in Angwan mallam. The findings will be a benefit to Environmental Impact Assessment of Agwa mallam as the water in the area meets the National Agency for Food, Drug Administration and Control, Draft for National Standard for Drinking water, and World Health Organization guideline. @JASEM

The study area is part of the Basement Complex of Nigeria (Wright 1970), precisely within the Migmatite-Gneiss Complex. The area is accessible through a major road from Keffi to Akwanga, and through a new road from Kokona to Agwada, other numerous footpath serve as an access routes to rock exposure, streams, river channel and settlements in the area. The drainage pattern is dendritic in nature with the major river (River Antou) flowing southwest direction. Hydrochemistry of the area deals with the study of various elemental constituents that are contain in the water. This research focuses on the general occurrence of various constituent of the major cations, anions, and heavy element in the water. Chemical elements in water have a key function in helping plants and animals. The source of these elements is rock, which is transferred to the vegetations and the water. Failure to know the quantity of this element being consumed can become toxic and that is why the research is being carried out in other to be conscious of the elemental composition of the water in the area. Therefore, understanding the impact of mining on quality of water (ground and surface), establish relationship between hydrochemistry, and the rocks in the area which will help in evaluation of toxic in Angwan Mallam and its environs.

### MATERIALS AND METHODS

The Geology and hydrogeochemical mapping of the study area which lies between latitude N 08° 51', N 08° 45' and longitude E 007° 45', E 008° 00' of North Central part of Keffi, Nasarawa State, Nigeria was carried out. The methods of study involves desk study, field work and laboratory analysis. The

mapping was done with the aid of field equipment such as compass, measuring tape, Global Positioning System (GPS), masking tape and writing materials; Pacing and traversing were used in reaching outcrops through foot paths and river channels. Sample points (Table 1) and sample collections equipments such as plastic bottles (made of poly synthetic material), masking tape, and concentrated nitric acid ( $HNO_3$ ) were used. Two drops of concentrated nitrate acid ( $HNO_3$ ) were added in each of the water samples for homogenization and prevention of absorption of element to the walls of the plastic containers and also to prevent microbial growth in the samples. Eleven pairs of water samples were collected for physio-chemical analysis, two drops of concentrated trioxonitrate (v) acid, were added to a set of the eleven pairs of the sample and all (eleven pairs) of the samples were stored in the fridge before taken to laboratory for analysis to prevent chemical and microbial growth in the sample. The pair of sample with the drops of concentrated trioxonitrate (v) acid were used for the determination of cations  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^{+}$ ,  $K^{+}$  as well as the heavy metals Fe, Cu, and Pb while the remaining samples were used for the determination of of the anions  $SO_4^{2-}$ ,  $NO_3^{2-}$ ,  $Cl$  and  $HCO_3^{-}$ . The physical parameters pH, temperature, TDS (Total Dissolved Solid), electrical conductivities, acidity, alkalinity, and turbidity were also determined using pH meter, mercury thermometer, conditioning meter, titration, salinometer, and secchi disk.

### METHOD OF ANALYSIS

The samples were taken to UNICAM Solar 32 Data Station V7.03 Sheda, Abuja for analysis. Atomic

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Absorption Spectrometer (AAS) technique was used to determine the concentration of the metallic element in the sample. The cations ( $Mg^{+}$ ,  $Ca^{2+}$ ,  $Na^{+}$ ,  $K^{+}$  and  $Cu$ ) were determined in the sample (Table 2). Flame Atomic Spectrometer highly effective in atomization of element using hollow cathode lamp. The most current gas mixtures used are air/acetylene and nitrous-oxide/acetylene. Thus elemental compositions of the trace elements Pb, Cu, and Fe in the samples were analyzed.

*Calorimetric Method:* This method deals with rapid change in colour with gradual increase to excess in the reagent used. It was used to get a single set of colour standards that sufficed after the reaction of the reagent in excess. The colour of the element to be sought for becomes sharp at the excess application of the reagent (end point). Use of slide comparator kits including nine colour standards in permanent forms was prepared for easy routine analysis of the anion content in the sample. This method was used to determine,  $HCO_3^{-}$ ,  $Cl^{-}$ ,  $SO_4^{2-}$  and  $NO_3^{-}$

*X-Ray Fluorescent (XRF):* The four rock samples that was picked for analysis was crushed to an average grain size of a few millimeters to centimeter and then splitted to a few tens to hundred of grains. This small sample splitted was then grounded into a fine powder in order to make analysis easy for the method. Care was taken particularly at this step to be aware of the composition of crushing implements which can inevitably contaminate the sample to some extent. This fine powder was sieved to  $75\mu m$  (pre-analysis) was carried out in Nasarawa State University, Department of Geology and Mining Laboratory (1) after which it was conveyed to Centre for Energy

Research and Development, Obafemi Awolowo University for rock analysis. The analysis of major and trace elements in geological materials by XRF was made possible by the behaviour of atoms when they interact with X-radiation.

## RESULTS AND DISCUSSION

*Physical Parameters: Hydrogen Ion Concentration (pH):* pH in the water sample varied from 5.91 – 6.91. The lowest value of 5.91 was measured in well water (L9W), while the highest value of 6.91 (L5W) was surface water sample. Except sample L5W the other entire sample meet WHO and NAFDAC guideline. All the water samples have pH values below 7. The pH values of the mobile elements remain in solution in normal groundwater until they have been disturbed by groundwater movement. Most metallic elements are soluble, as cation in acid groundwater will precipitate as hydroxides (basic salts with an increase in pH). Above a pH of 5, aluminium ion are present in solution Offodile (2002) and since the pH measure of the water analyzed is more than 5, it may probably be a reason for the absence of aluminum (Table 3).

*Total Dissolved Solid (TDS):* Is the residue left when a certain amount of water is vaporized. The TDS in water sample can be represented by the sum of the ionic concentration of the major constituents which are usually  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^{+}$ ,  $Cl^{-}$ ,  $HCO_3^{-}$  and  $SO_4^{2-}$ . The TDS samples is having an average of 373.1 (mg/L) which makes it generally less than 500 (mg/L) – 1000 (mg/L). Sample L4W and L5W (580mg/L) and 909 mg/L still fall within the required standard of WHO.

**Table 1:** Sample location with Global Position System readings

Field Code	GPS			Water Source	
			Accuracy (m)		Elevation (m)
L1W	N08° 47' 0.42"		3	315	Surface
L2W	N08° 46' 56.55"	E008° 00' 08.6"	3	308	Surface
L3W	N08° 45' 50.1"	E007° 58' 20.10"	3	274	Surface
L4W	N08° 45' 59.1"	E007° 57' 58.5"	3	274	Sub surface
L5W	N08° 46' 36.7"	E007° 57' 48.5" E007° 57' 20.4"	3	280	Sub surface
L6W	N08° 45' 31.9"	E007° 57' 21.6"	3	277	Surface
L7W	N08° 45' 37.8"	E007° 56' 21.6:	2	247	Surface
L8W	N08° 49' 20.5"	E007° 59' 17.2"	2	287	Sub surface
L9W	N08° 49' 58.4"	E007° 59' 39.0"	3	270	Sub surface
L10W	N08° 46' 08.0"	E 007° 57' 30.0" E007° 55' 14.3"	3	245	Sub surface
L11W	N08° 45' 52.5"		3	278	Sub surface

**Table 2:** Result of water analysis which was carried out at the UNICAM solar 32 Data station v7.03, Sheda – Abuja.

Field Code	NO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Fe	Mg	Ca	Na	K	Cu	Pb	Zn
L1W	0.031	0.1170	0.271	0.620	-	11.719	29.3945	1.730	1.220	0.192	-	-
L2W	0.018	-	0.318	1.028	-	2.616	9.6092	0.779	0.755	0.145	-	-
L3W	-	-	0.274	0.793	-	2.5592	18.943	0.875	0.710	0.145	-	-
L4W	-	0.033	0.520	0.751	-	11.006	22.608	0.783	0.810	0.151	-	-
L5W	-	-	0.821	0.683	-	12.508	31.510	1.552	1.55	0.151	-	-
L6W	-	0.0330	0.482	0.759	1.994	4.4019	5.3966	0.774	8.441	0.161	-	-
L7W	0.027	-	0.229	1.109	1.1244	1.5735	5.9978	0.997	0.881	0.118	-	-
L8W	-	-	0.017	0.882	-	3.2615	16.2609	0.552	0.911	0.139	-	-
L9W	0.013	-	0.551	0.982	-	2.3594	9.5989	1.772	1.399	0.133	-	-
L10W	0.022	-	0.398	1.276	0.1781	8.6691	22.6230	2.443	2.020	2.168	-	-
L11W	-	-	0.369	0.479	-	1.8097	27.4750	0.832	0.911	0.147	-	-

= Below detection limit (0.001); Kokona (Pump) - L1W, Angwan Yorubawa (Dm) - L2W, Angwan Beshi (Stm) - L3W, Angwan Beshi (WL) - L4W, Angwan Mallam Magaji (MP) - L5W, Angwan Mallam (WL) - L6W, Angwan Kade (Rv) - L7W, Bokoko (HP) - L8W, Barrack (H.P) - L9W, Angwan Toni (WL) - L10W, Angwan Mallam (II) (WL) - L11W.

**Table 3:** Result of Physical Parameter of the water analyzed

Field Code	Temp (°C)	pH	TDS	Conductivity	Turbidity	Acidity	Alkalinity
L1W	28.4	6.18	283	0.354	0.06	0.13	8.18
L2W	29.1	6.06	264	0.329	305	1.92	4.64
L3W	28.7	6.06	260	0.338	36.61	0.15	0.180
L4W	28.9	6.63	580	0.737	13.67	0.11	1.80
L5W	29.0	6.91	909	1.148	0.99	0.12	2.50
L6W	28.7	6.30	218	0.275	0.13	0.25	0.02
L7W	27.8	6.41	321	0.327	30.88	0.05	0.13
L8W	28.5	6.10	300	0.378	13.92	0.09	0.19
L9W	28.0	5.91	269	0.336	1.82	0.06	0.12
L10W	28.4	6.75	454	0.566	42.21	0.15	0.20
L11W	27.8	6.47	246	0.403	2.92	0.34	0.025

**Temperature:** The temperature of water is an important characteristic which determine to a greater extent, change in water quality. Temperature is noted for its effect on the rates of chemical and biochemical processes significance in water. The measured temperature in the water samples ranges from 27.290C to 29.10C. The average temperature of the water samples is 28.50C. Consequently all the sample location can support the growth of microbial organism, taste, odor and corrosion problems may be increased.

**Conductivity:** Varied between 0.273  $\mu\text{s}/\text{cm}$  – 1.148  $\mu\text{s}/\text{cm}$ , the lowest value 0.293  $\mu\text{s}/\text{cm}$  was at L6W and highest 1.148  $\mu\text{s}/\text{cm}$  at L5W with an average value of 0.47  $\mu\text{s}/\text{cm}$ . The conductivities compared with total dissolved solid of the well water are about 25% higher with values of 218 – 909 (mg/L) (average 412.12 mg/l) and 0.2 – 1.148  $\mu\text{s}/\text{cm}$  (average 0.521  $\mu\text{s}/\text{cm}$ ) for TDS and conductivity respectively. This

may be as a result of increase in concentration due to ion exchange between the rocks and water.

**Turbidity:** Turbidity is an indication of clarity and is the optical property that causes light to be scattered or absorbed rather than transmitted in straight line through a water sample. Turbidity is caused by the presence of suspended matter, such as clay silt, finely divided organic and inorganic matter, plankton and other microscopic organisms. Turbidity is mainly a function of the suspended materials in the water which ranges from colloidal to coarse dispersion. The turbidity values recorded in the measured sample has the lowest of 0.06 NTU and highest of 305 NTU in L1W and L2W respectively. The sample with highest turbidity was due to clay reaction with water. It is clear that sample L1W, L5W, L6W, L9W and L11W satisfies Draft National Drinking Water guideline of 5 NTU. At these sampling locations, the water is clear and good for disinfections. For effective water

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disinfections, it is preferable that the turbidity must be below 1NTU. At location L2W, L3W, L4W, L7W and L10W turbidity are in excess of 5 NTU. They are physically noticeable and consequently may be objectionable to consumers.

**Sodium:** Sodium is readily soluble in water. High sodium in the soil is generally unfavorable to plant, because sodium ion can be exchanged with calcium and magnesium ion. It is the main constituent of evaporates and other types of rock salt. The concentration of sodium in the study area ranges from (0.5520 – 2.4430) mg/l with an average of 1.192 mg/l which makes it fall little below the permissible range of WHO Guidelines. Main source of sodium in water samples are gotten from soluble product from weathering of plagioclase feldspar by Davies et al (1970), atmospheric dust washed down by rain and exchangeable sodium from clay. The average value of cation  $\text{Na}^+$ ,  $\text{Ca}^+$  and  $\text{Mg}^{2+}$  of the analyzed water samples can be used to determine Sodium Absorption Ion Ratio (SAR) as parameter in classifying water for irrigation: (Unit in milli equiv/Lit) (Efeotor, 1983)

**Calcium:** Calcium rich soils are friable and easily cultivated. Such soils are favorable for irrigation as they allow easy infiltration and good drainage, facilitating plant growth; calcium chloride and calcium nitrate form the two minerals which are readily soluble in water. Hardness of water is as a result of carbonate and sulphate of calcium (temporal and permanent hardness). There is no health objection to high calcium content in water. The natural sources of calcium in natural groundwater are plagioclase, gypsum, pyroxene, calcite, dolomite and clay minerals (Dufer et al 1964). The source of calcium in the study area could be plagioclase, clay minerals and some mafic minerals. Concentration of calcium in the study area ranges from 5.9778 – 31.504 (mg/l), with an average of 18.1270 (mg/l). This is below 75 (mg/l) permissible ranges of WHO guideline. Calcium in this concentration has no effect on the health of human and animals.

**Magnesium:** Magnesium occurs as carbonates, hydroxide, oxide, phosphate and silicates. As carbonate, hydroxides, oxides and phosphate, the mineral is hardly soluble in water. Other compounds of magnesium are readily soluble; magnesium has the same effect on water as calcium, producing hard water. Like calcium, it improves soil fertility and is an essential constituent of plant chlorophyll. Generally, when the sum of magnesium and sulphate content of drinking water exceed 100 (g/l) most

people who use it experience laxative effects (Oteze, 1991). The probable source of magnesium in water of the study area is pophyritic granodiorite and Biotite gneiss. The concentration of magnesium in the study area has an average of 5.6839 (mg/l). This is below WHO and NAFDAC guideline. The magnesium concentration is safe for all purpose.

**Iron:** In a ferrous state is soluble, but exposure to the atmosphere during discharge, it oxidize to ferric, which is insoluble and is therefore precipitated to brownish residue, dissolution of clay minerals is also a natural source of iron. Iron hydroxides and clay minerals is leached under anaerobic. Three natural conditions that have been found to produce high levels on iron in groundwater (Ramesh, 1999) aquifers located over crystalline bed rock, swamps and organic materials interbedded with alluvial sediments located near areas of groundwater discharge. High level concentration of iron can give rise to iron bacteria which in turn can cause further deterioration in the quality of water by production of slims, stain laundry and fixtures. The likely source of iron in natural groundwater includes weathered magnetite, biotite, and ferromagnesian minerals. The possible source of iron in the study area is from weathered biotite and attributed to the presence of opaque minerals which are commonly found to be iron rich. The concentration of iron in the study area has an average of 0.2999 (mg/l) comparing this with WHO and NAFDAC (1999) guideline, the iron is within the permissible range.

**Potassium:** compounds except the silicates are readily soluble in water. It is a common constituent of most igneous rock. It is highly soluble in water, and it is less common in sedimentary rocks. Potassium, when leached from rocks, it easily recombines with other minerals resulting to its low concentration in groundwater. Sewage effluents may also be indicated by potassium due to their high content of potassium 20 (mg/l). Common sources of potassium in ground water are related to weathering of potassium feldspars. The average concentration of potassium of the analyzed water sample is 1.7408 (mg/l) having the highest rate of 8.441 (mg/l) and the lowest range of 0.710 (mg/l).

**Copper:** Is rarely found in natural water but it may enter water supply from the use of copper pipes. Copper is very toxic to fish but the traces obtained from copper pipes are rarely sufficient to affect human beings. Water containing about 1mg/l or less of copper can cause green stains on sanitary fittings. Lower concentrations can cause accelerated corrosion of other metals in the same system. 0.1mg/l of copper

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is sufficient to increase considerably the rate of corrosion of galvanized steel and as little as 0.02mg/l will cause pitting of aluminum in some water. The probable source of copper in the studied area are from the pegmatites due to high concentration of copper found in it, the average concentration of copper in the water samples analyzed is 0.3304mg/l with concentration ranging from 2.168mg/l – 0.117mg/l which makes the value little higher than NAFDAC water guideline of 0.05 mg/l.

*Lead/Zinc:* Is rarely present in natural waters. It is found mostly in tap water just like the lead (Pb) because of the use of galvanized iron pipe and tanks. Some water will readily take up zinc, especially in cooking process and zinc containers for food should not be used. Some water may attack the zinc of galvanized pipe, forming loose deposits of zinc carbonate and zinc in solution in such water, as supplied to consumer. Lead/zinc in water samples of the studied area are below a detectable limit (0.0001mg/l) which is below minimum allowable of WHO 2004.

*Nitrates:* Is an essential ingredient of plant nutrient. It occurs in soil and can be fixed by leguminous plants. Nitrate is an indicator of pollution in water, the presence of nitrate in the groundwater sample is therefore unrelated to any geological formation. It is reflection of human impact around sample locations. For example, the nitrate content in some locations such as L1W, L7W, L9W and L10W can be attributed to leachates from nearby septic tank/ pit latrine or fertilizer within the close vicinity of the sampling point. Nitrate contamination is high in sample L2W, possibility of fertilizer pollution is suspected since it was located at swampy surface area, The analyzed sample was characterized by very low bacterial count compared to nitrate concentration they both have a very low count on the result analyzed, Nitrate concentration varies from 0.013 – 0.031 (mg/l) with an average of 0.1110 (mg/l), based on WHO and NAFDAC any consumption of this anion can lead to methaemogloniaemia.

*Sulphates:* occurs mostly as calcium sulphate (CaSO<sub>4</sub>.2H<sub>2</sub>O) sodium and magnesium sulphate are readily soluble in water while calcium sulphate is less soluble; the sulphur content is useful in plant. Sources of sulphate include mineral deposits, sea water intrusion, industrial effluence from process such as tanning and pulp paper manufactured and could be pyrite or iron sulphide (FeS) minerals found in rock. Sulphate was noted only in three water samples of the location and it ranges from 0.0330 –

0.1170 (mg/l) having an average of 0.01664 (mg/l) which is below the minimum permissible level of the WHO and NAFDAC guideline.

*Chloride:* Chloride occurs mostly in the form of sodium chloride, it is generally soluble and essential to animals and man. However, in higher concentrations, it inhibits plant growth and can be harmful to man. Chlorine show lower water rock ratio than main rock forming element indicating that rock such as trachy – andesite and anhydride is obviously not the only source of chlorine and sulphide but can be found in water through human treatment for good drinking water. The major source of chloride in water include; fertilizer and air, it has little absorption in clay and highest occurrence in sea water. The major source of chloride in the study area could be from granite, fertilizer and air. From the result, chloride concentration ranges from 0.0170 – 0.8210 (mg/l) with an average of 0.3864 (mg/l) this range falls below the permissible range of NAFDAC (1999) guideline and Draft National Standard for Drinking water (2007). Chloride of this concentration causes no harm to the health of humans and animals.

*Carbonates:* occur mainly as carbonate of sodium and magnesium. Potassium carbonate of sodium and potassium are water soluble while those of calcium and magnesium are insoluble. Possible sources of carbonate in natural water are carbondioxide and organic matter this is most abundant anion in the water analyzed. Its concentration ranges from 0.4790 – 1.2760 (mg/l), which is probably due to the availability of atmospheric carbondioxide. The average measure of the carbonate is 0.9314mg/l which is below the minimum allowable range of NAFDAC 1999 water guideline.

*Conclusion:* Hydro-geochemical analysis shows how the ions are leached from the rock into the water of the study area. Water in the area meets the National Agency for Food, Drug Administration and Control, Draft National Standard for Drinking water, and World Health Organization guideline.

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