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# Groundwater X-Ray Fluorescence Analysis to Detect Solid Mineral Resources in Benue State, Nigeria

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## Abstract

*Three ground water samples were analyzed at Spectral Laboratory Services; Tudun Wada, Kaduna using XRF analysis to determine the elemental concentration of the samples. The physicochemical parameters of the water samples were also ascertained in the laboratory. This hydro-geochemical investigation was aimed at detecting economic mineral resources in Benue State, Nigeria. Geological, radioactive, biogeochemical, geo-botanical and hydro-geochemical prospecting techniques were highlighted as guides to discovery of ore minerals. The research failed to discover anomalous concentration of elements that would serve as indicator to the occurrence of a viable mineral deposit in the study areas. It may be said that there is no sharply increased content of any element; high above its threshold value in the sample results, that is indicative of higher than average content of the element in the soil, and possibly bedrock, which could serve as a pointer to a corresponding solid mineral deposit. From the study carried out, it is found that Ogyoma ground water has the best quality for drinking and other domestic uses. This is because the elements contained in the water are within permissible concentration levels as compared with WHO, EU and Nigeria standards for drinking water on table 8. This is in contrast to Kertyo groundwater with high content of undesirable elements, which makes it unsuitable for domestic uses.*

**Keywords**: X-ray Fluorescence, Mineral Resources, Physicochemical parameters, Surface alteration zones.

## Introduction

The investigation was aimed to expand knowledge of mineral resources of Benue State, and hence the potential contributions of the mineral resources availability and mining to the state and the nation's economy. Greater mineral resources production is aimed as a long term measure that targets among others, the minimization of Nigeria's poverty, economic and socio-political problems. Field work with further research in

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geological data bases would help to locate and delineate mineral bodies which will encourage employment and investment opportunities in the solid minerals sub-sector. Solid minerals development and mining is a basic industry like agriculture that produces raw materials upon which other industries depend for feedstock. Mineral resources availability, mining and mineral processing are technology-driven industries that bring about rapid industrialization and development to a nation. The following industries need a variety of industrial minerals: agriculture, construction, chemical, glass, paints, pharmaceuticals, textiles, paper, food, ceramics etc. There are known mineral occurrences in the country with potentials for being developed into mineral raw materials for existing local industries, new ones and even export. However, much exploration remains to be done in identification and delineation of commercially exploitable reserves of the minerals. Advancement in technology is moving from fossil-fuel cars to electric cars. Lithium mineral (Coltan) is used in the manufacture of lithium batteries to power cars. Nigeria has commercial quantities of lithium mined by artisanal miners in the states of Nasarawa, Kogi, Kwara, Ekiti, Cross River and Benue. Cars in millions will require lithium source energy to fire electric vehicles that will be in use across the world. Lithium battery-powered cars will safeguard the environment from hydrocarbon engine pollution.

Minerals are discovered by luck when hunters and farmers walk the forests and fields. Some mineral deposits have been found this way in Nigeria. Mineable mineral deposits are also found by act of tedious work involving extensive sampling either by digging pits and trenches, groundwater analysis, sampling rivers and streams, sand as well as gravel for placer mineral deposits, or expensive geophysical investigations (Wardell, 2008). Field exploration works trace geological units, such as local or regional structural patterns (fracture systems or alteration zones), known to host economic deposits. Minerals such as limestone, bentonite, gypsum, barite, copper, lead and zinc have been found by this means. Within mineralized belts, potential mining sites are commonly localized by intersecting fractures (faults and zones of weakness (Charles et.al, 2006); also, is surface soil search for veins and other features for possible indications of mineral deposits. Groundwater provides geochemical sample to use in the search for mineralized areas.

Hydro-geochemical method of prospecting has been successful in revealing uranium, molybdenum, zinc and copper deposits and they may subsequently help to find other metals and complex ores such as nickel, cobalt, vanadium, chromium, tin and gold. An increased concentration of metal in underground waters (as compared with the background value) is a direct guide.

Some dissolved mineral salts in groundwater are identified as nutrients and are beneficial for plant growth, while others may be phytotoxic or may become so at high concentrations. Specific elements Cd, Ni, Hg, Zn etc. are toxic to plants and affect their growth (morphology) or their physiological development. These indicator plants (botanical specimens) could be seen around or near water body sources. Analysis of such groundwater samples would reveal higher than average content of the element in the water and possibly also in the bedrock, which may serve as a pointer to a corresponding deposit. For the study of plants with toxic effects, preference should be given to plants with deep root system. This prospecting approach is based on the knowledge that plants absorb necessary, unnecessary elements (nutrients) and compounds mainly by their primary and secondary root systems in the soil and water where there is a specific elements (nutrients) and compounds mainly by their primary and secondary root systems in the soil and water where there is a specific element or assemblage of elements present in relatively large amounts. The abnormal growth of such plants may be universal or local indicators of elements or metals' presence in the growth environment. Certain species of both higher and lower plants (and even bacteria) are specific collectors of such elements as copper, zinc, lithium and manganese. Environment where Cu, Li, Hg, etc are present in high concentrations, they usually cause plant diseases, stunt growth etc. Specific plants developing with these conditions are important guides to mineralization (Ogah, 2010).

### Basic geology, as guide to detect mineral bodies, and mineral industrial uses.

There is need to understand the geological processes and the environment in which mineral commodities are formed. Minerals are formed from rocks, as well as remnants of volcanic eruptions such as lava and volcanic ash, others are sediments such as clay, sand and gravel all deposited on the Earth's surface or formed deep in the Earth's crust. At high temperatures some of the rocks melt and eventually form magma (molten rocks), where they start to cool and crystallize. During crystallization of magmas, economic minerals such as chromite, magnetite, nickel, and platinum and also massive sulphide occurences appear as bands in the magmatic rocks. These types of mineral deposits called magmatic deposits are a target for small scale miners. Many elements such as gold, tantalum, boron etc. crystallise in hot magma fluids (hydrothermal fluids) and flow into surrounding rock cracks. The cracks are gradually filled with quartz and with other elements such as tantalum forming tantalite mineral and boron forming tourmaline (rubelite) found in quartz veins. These types of deposits are collectively called magmatic hydrothermal deposits and are found close to igneous rocks commonly called granite (Tychsen et al., 2011). Diamond is a high-pressure form of the element carbon and has recently been found in Nigeria. Diamonds occur deep down at or below 150km in the crust. Kimberlistic magmas pick up diamonds to the surface by volcanic eruptions (Tychsen et al., 2011).

The other types are hydrothermal deposits without a relationship to magmatism. Outliving igneous activity, has been the rising of (juvenile) mineralizing waters and volatile materials, leading to the deposition of certain minerals, including sulphates, carbonates and flourides variously of iron, calcium, magnesium and barium etc. (Ogah$^2$, 2014). These deposits are formed from hot fluids that migrated through rocks, but have not been formed from crystallizing melt. The mineralized waters could be rain or groundwater (connate pore water) that percolated through the rocks for some time picking up elements of interest that can be gold, barium, copper, lead and zinc. Lead-zinc mineralization is attributed to the circulation of heated brines, leaching base metals from sediments and underlying basement. Barium elements would form barite that is very often associated with massive sulphide accumulation hosting copper-lead-zinc mineralization (Tychsen et al., 2011). High amount of zinc elements in a sample or environment may lead to discovery of zinc minerals, such as sphalerite and its associated minerals; galena and chalcopyrite. Zinc is used in metal alloys and as a raw material for producing corrosion-resistant paints, pigments, fillers, also used as corrosion protective countings on iron and steel. High concentration of copper elements could be an indicator or pathfinder to copper minerals: example chalcopyrite. Copper is used where high electrical or thermal conductivity is important. It is also used in a variety of alloys, brass, bronze and aluminium bronze. Lead (Pb) is the main element in Galena (Pbs). Lead is used in the manufacture of batteries, corrosion resistant pipes and linings, alloys, pigments and in radiation shielding. Aluminium silicate may lead to the discovery of bentonite minerals. Barium element may lead to the discovery of barium sulphate (barite).

### Surface alteration zones associated with Ore Surface deposits

At the time of ore deposition or formation of ore minerals, hydrothermal solutions invade the host or country rock, causing alteration of the country rock, due to changes in temperature, pressure and chemistry of the hydrothermal solution. Hydrothermal alterations are valuable indicators of possible distinctive assemblages of secondary minerals. At the time of the mineral deposition, the alterated country rock may not be extended to the surface of the ground, but later weathering, uplift and erosion can expose successively deeper alteration zones and eventually the ore body. Detection of surface alteration zones has yielded clues to the location of concealed mineral deposits (Charles et al., 2006 and Ogah[2], 2014). Flourite is discovered by scout searching for characteristics weathered features and textures, and these can be confirmed by trenching and or pitting where the deposit occurs near the surface of the crust.

Surface deposits are formed at or near the earth surface and not subject to high temperature and pressure, examples are limestone, marble, gypsum, bentonite, diatomite deposits, also placer gold found in fine quartz grains etc.

Calcium carbonate is sourced from carbonate rocks comprising limestone, dolomite and marble. Other associated minor minerals are siderite ($FeCo_3$), ankerite ($Ca_2MgFe(Co_3)4$) and magnesite ($MgCo_3$). These rocks and their derivative products are used as aggregates, fluxes, glass raw material, refractories, fillers, soil conditioners, etc.

Gypsum is formed in restricted basins, example; salt lakes where sediments such as clay were brought in by rivers. When the basins dry, calcium and sulphate are precipitated on the floor of the basins with the clay minerals and then pure gypsum layers are formed.

Bentonite is a clay mineral formed by surface weathering of ancient very fine grained volcanic rocks (MMSD, 2010). This can be found in active and ancient volcanic sites (volcanic ash, tuff).

Diatomite represents accumulations of algae (diatoms) which lived in lakes in tidal zones and oceans. When the diatoms die, they accumulate and are later compacted by sedimentation resulting in very light white stone.

Primary mineral deposits can be eroded, where the minerals are separated according to density. The deposits formed from erosion of continental rocks and primary mineral deposits are called placer deposits and are found in dry river beds as well as in rivers and streams, where the flow-velocity of such water bodies changes. Tantalite or cassiterite (tin ore –$SnO_2$) are found in old river and stream channels where the deposit source (primary deposit) can be traced somewhere upstream from the point where the grains are found. The lighter minerals from the river are washed down, leaving the heavy cassiterite mineral in the river bed along with other heavy minerals such as magnetite, ilmenite, tantalite and columbite.

To locate the primary deposit, the procedure is to collect samples upstream until no more grains are found. Then the deposit must be below the spot with no tantalite and cassiterite grains up the last sample point with many mineral concentrates.

## Radioactive and Biogeochemical prospecting Techniques

The products of alpha-decay of radioactive elements Radon (Rn), Thorium (Th) and Actinium (Ac) are inert gases referred to as radioactive emanations. Rocks give off part of their radioactive emanations into the gaseous or liquid environment. When a sharp (at least five-fold) increase in environment radioactive emanations is detected, it is considered an emanation anomaly of prospective interest. This method can be used in prospecting not only for radioactive minerals proper but also for many other minerals which possess slight radioactivity, lithium, beryllium, niobium, ilmenite and monazite placers, phosphorites, etc.

Niobium is found in columbite while tantalum is found in tantalite. High concentration of elements or gasses in soil or water above their threshold limit may lead to discovery of mineral bodies in and around sample locations. Tantalum is a key metal in every mobile phone also used in electronics. Tantalite often contains high amounts of highly radioactive uranium which produces radioactive gas radon (Ogah, 2010).

In gas prospecting, samples are analysed to determine the content of radioactive gases, mercury emanations or hydrocarbon gases in the search for oil and gas, also to determine the level of $Co_2$ and $O_2$ (in the oxidation zones of ore deposits) and lastly, of $SO_3$ and $H_2S$ ( in prospecting for sulphur deposits). The bacterial method may be mentioned here. It has been applied only to the search for oil and gas, in which the guides are the specific bacteria which oxidize hydrocarbons.

## MATERIALS AND METHODS

Three groundwater samples were obtained from two wells in Ogyoma and Adeke at depths of 20metres and 28metres respectively and a borehole 61metres below the surface at Kertyo-Makurdi. The three water samples labeled Kertyo, Adeke and Ogyoma were sent to Spectral Laboratory Services Laboratory in Kaduna for X-Ray Fluorescence (XRF) and Physicochemical analysis to determine the samples elemental and physicochemical contents.

### 1. XRF Procedure for elemental analysis of groundwater

The X-ray fluorescence Nitron 3000 was powered on and allowed to stabilise for five minutes after initialization. The Cu-Zn method was chosen which normally detect large amount of elements and sesquioxides due to its intensity. Sample was placed on the sample holder while the ray point was placed over it and the ray button was pressed to start taking the data. The data were collected in triplicates and this automatically takes the average. This procedure was followed for all the samples to get the percentage chemical composition in oxide and elemental forms.

### 2. Physicochemical Parameters Analysis of Water Samples

The parameters listed below were determined using Hanna Instrument (HI98129 model). The probe was checked and when found alright, then it was dipped into the samples and the key of each parameter were pressed from the machine then result was displayed in their respective unit.

**Table 1: Kertyo Sample Result**

| Layer | Component | Concn.$mg/cm^2$ | Error | Mole% | Error |
|---|---|---|---|---|---|
| 1 | $SiO_2$ | 21.822 | 4.616 | 20.644 | 4.367 |
| 1 | $V_2O_5$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $Cr_2O_3$ | 0.224 | 0.232 | 0.084 | 0.087 |
| 1 | $MnO$ | 0.301 | 0.179 | 0.241 | 0.143 |
| 1 | $Fe_2O_3$ | 1.908 | 0.211 | 0.679 | 0.075 |
| 1 | $Co_3O_4$ | 0.061 | 0.151 | 0.014 | 0.036 |
| 1 | $NiO$ | 0.113 | 0.141 | 0.086 | 0.108 |
| 1 | $CuO$ | 1.826 | 0.158 | 1.305 | 0.113 |
| 1 | $Nb_2O_3$ | 0.496 | 0.213 | 0.121 | 0.052 |
| 1 | $MO_3$ | 0.265 | 0.252 | 0.105 | 0.100 |
| 1 | $WO_3$ | 0.360 | 0.571 | 0.088 | 0.140 |
| 1 | $P_2O_5$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $SO_3$ | 1.693 | 1.174 | 1.202 | 0.833 |
| 1 | $CaO$ | 2.563 | 0.610 | 2.598 | 0.618 |
| 1 | $MgO$ | 8.343 | 94.332 | 100.00 | 133.033 |
| 1 | $K_2O$ | 6.937 | 0.988 | 4.186 | 0.596 |
| 1 | $BaO$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $Al_2O_3$ | 22.027 | 13.658 | 12.279 | 7.614 |
| 1 | $Ta_2O_5$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $TiO_2$ | 0.599 | 0.369 | 0.426 | 0.262 |
| 1 | $ZnO$ | 0.259 | 0.130 | 0.181 | 0.091 |
| 1 | $Ag_2O$ | 0.428 | 1.286 | 0.105 | 0.315 |
| 1 | $Cl$ | 26.939 | 1.674 | 43.189 | 2.684 |
| 1 | $ZrO_2$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $SnO_2$ | 1.417 | 3.144 | 0.534 | 1.186 |
| 1 | $RaO$ | 0.116 | 0.306 | 0.027 | 0.072 |
| 1 | $U_2O$ | 0.423 | 0.434 | 0.049 | 0.050 |
| 1 | $Th_2O_5$ | 0.882 | 0.380 | 0.02 | 0.040 |

**Table 2: Kertyo Elemental Result**

| Element | Line Code | Cond. Code | Intensity (c/s) | Error (c/s) | Conc. mg/cm$^2$ |
|---|---|---|---|---|---|
| O | Ka | 0 | 0.000 | 0.000 | 30.382 |
| Mg | Ka | 1 | 0.190 | 2.1443 | 5.032 |
| Al | Ka | 1 | 4.535 | 2.8119 | 11.658 |
| Si | Ka | 1 | 18.364 | 3.8849 | 10.201 |
| P | Ka | 1 | 0.000 | 3.4380 | 0.000 |
| S | Ka | 1 | 6.858 | 4.7552 | 0.678 |
| Cl | Ka | 1 | 304.399 | 18.9156 | 26.939 |
| K | Ka | 1 | 62.911 | 8.9623 | 5.758 |
| Ca | Ka | 1 | 27.350 | 6.5061 | 1.832 |
| Ti | Ka | 1 | 11.326 | 6.9660 | 0.359 |
| V | Ka | 1 | 0.000 | 7.5366 | 0.000 |
| Cr | Ka | 1 | 8.462 | 8.7563 | 0.153 |
| Mn | Ka | 1 | 16.359 | 9.7114 | 0.233 |
| Fe | Ka | 1 | 113.228 | 12.5214 | 1.335 |
| Co | Ka | 1 | 4.481 | 11.0904 | 0.045 |
| Ni | Ka | 1 | 9.843 | 12.3056 | 0.089 |
| Cu | Ka | 1 | 184.911 | 15.9863 | 1.458 |
| Zn | Ka | 1 | 29.339 | 14.6952 | 0.208 |
| Zr | Ka | 1 | 0.000 | 15.2801 | 0.000 |
| Nb | Ka | 1 | 35.258 | 15.1661 | 0.394 |
| Mo | Ka | 1 | 14.782 | 14.0654 | 0.177 |
| Ag | Ka | 1 | 3.035 | 9.1305 | 0.398 |
| Sn | La | 1 | 3.838 | 8.5163 | 1.116 |
| Ba | La | 1 | 0.000 | 6.5023 | 0.000 |
| Ta | La | 1 | 0.000 | 16.6901 | 0.000 |
| W | La | 1 | 10.545 | 16.7412 | 0.285 |
| Ra | La | 1 | 7.350 | 19.3326 | 0.109 |
| Th | La | 1 | 45.236 | 19.4732 | 0.752 |
| U | La | 1 | 19.124 | 19.6134 | 0.409 |

**Table 3: Adeke Sample Result**

| Layer | Component | Concn.mg/cm$^2$ | Error | Mole% | Error |
|---|---|---|---|---|---|
| 1 | $SiO_2$ | 40.811 | 4.984 | 39.836 | 4.865 |
| 1 | $V_2O_5$ | 0.066 | 0.180 | 0.021 | 0.058 |
| 1 | $Cr_2O_3$ | 0.087 | 0.132 | 0.034 | 0.051 |
| 1 | MnO | 0.090 | 0.101 | 0.074 | 0.084 |
| 1 | $Fe_2O_3$ | 2.642 | 0.153 | 0.970 | 0.056 |
| 1 | $Co_3O_4$ | 0.003 | 0.092 | 0.001 | 0.023 |
| 1 | NiO | 0.027 | 0.086 | 0.021 | 0.068 |
| 1 | CuO | 1.312 | 0.099 | 0.967 | 0.073 |
| 1 | $Nb_2O_3$ | 0.355 | 0.132 | 0.089 | 0.033 |
| 1 | $MO_3$ | 0.098 | 0.157 | 0.040 | 0.064 |
| 1 | $WO_3$ | 0.158 | 0.355 | 0.132 | 0.040 |
| 1 | $P_2O_5$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $SO_3$ | 0.770 | 0.977 | 0.564 | 0.716 |
| 1 | CaO | 6.077 | 0.523 | 6.356 | 0.547 |
| 1 | MgO | 10.558 | 77.779 | 100.00 | 113.181 |
| 1 | $K_2O$ | 2.281 | 0.562 | 1.420 | 0.350 |
| 1 | BaO | 0.000 | 0.000 | 0.000 | 0.000 |

**Table 3: Adeke Sample Result (continued)**

| Layer | Component | Concn.mg/cm$^2$ | Error | Mole% | Error |
|---|---|---|---|---|---|
| 1 | $Al_2O_3$ | 18.679 | 12.593 | 10.744 | 7.244 |
| 1 | $Ta_2O_5$ | 0.049 | 0.363 | 0.007 | 0.048 |
| 1 | $TiO_2$ | 0.753 | 0.225 | 0.553 | 0.165 |
| 1 | ZnO | 0.248 | 0.080 | 0.178 | 0.058 |
| 1 | $Ag_2O$ | 0.412 | 0.787 | 0.104 | 0.199 |
| 1 | Cl | 13.594 | 1.166 | 22.488 | 1.930 |
| 1 | $ZrO_2$ | 0.004 | 0.120 | 0.002 | 0.057 |
| 1 | $SnO_2$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | RaO | 0.181 | 0.187 | 0.044 | 0.045 |
| 1 | $U_2O$ | 0.252 | 0.266 | 0.030 | 0.032 |
| 1 | $Th_2O_5$ | 0.495 | 0.232 | 0.053 | 0.025 |

**Table 4: Adeke Elemental Result**

| Element | Line Code | Cond. Code | Intensity (c/s) | Error (c/s) | Conc. mg/cm$^2$ |
|---|---|---|---|---|---|
| O | Ka | 0 | 0.000 | 0.000 | 39.061 |
| Mg | Ka | 1 | 0.310 | 2.2808 | 6.367 |
| Al | Ka | 1 | 4.831 | 3.2567 | 9.886 |
| Si | Ka | 1 | 44.380 | 5.4200 | 19.077 |
| P | Ka | 1 | 0.000 | 3.9497 | 0.000 |
| S | Ka | 1 | 3.548 | 4.5022 | 0.308 |
| Cl | Ka | 1 | 192.715 | 16.5367 | 13.594 |
| K | Ka | 1 | 32.260 | 7.9506 | 1.894 |
| Ca | Ka | 1 | 106.569 | 9.1681 | 4.343 |
| Ti | Ka | 1 | 22.611 | 6.7603 | 0.452 |
| V | Ka | 1 | 2.517 | 6.8836 | 0.037 |
| Cr | Ka | 1 | 5.242 | 7.9201 | 0.060 |
| Mn | Ka | 1 | 7.708 | 8.7110 | 0.069 |
| Fe | Ka | 1 | 248.729 | 14.3613 | 1.848 |
| Co | Ka | 1 | 0.366 | 10.8946 | 0.002 |
| Ni | Ka | 1 | 3.617 | 11.7006 | 0.021 |
| Cu | Ka | 1 | 208.200 | 15.7671 | 1.048 |
| Zn | Ka | 1 | 44.059 | 14.1997 | 0.199 |
| Zr | Ka | 1 | 0.449 | 15.3072 | 0.003 |
| Nb | Ka | 1 | 41.059 | 14.1997 | 0.199 |
| Mo | Ka | 1 | 9.025 | 14.3925 | 0.065 |
| Ag | Ka | 1 | 4.873 | 9.2981 | 0.384 |
| Sn | La | 1 | 0.000 | 8.9152 | 0.000 |
| Ba | La | 1 | 0.000 | 6.2960 | 0.000 |
| Ta | La | 1 | 2.212 | 16.3047 | 0.040 |
| W | La | 1 | 7.291 | 16.3914 | 0.125 |
| Ra | La | 1 | 18.240 | 18.9137 | 0.169 |
| Th | La | 1 | 40.694 | 19.0672 | 0.423 |
| U | La | 1 | 18.258 | 19.2918 | 0.244 |

**Table 5: Ogyoma Sample Result**

| Layer | Component | Concn.mg/cm$^2$ | Error | Mole% | Error |
|---|---|---|---|---|---|
| 1 | $SiO_2$ | 54.937 | 4.156 | 58.472 | 4.424 |
| 1 | $V_2O_5$ | 0.055 | 0.111 | 0.019 | 0.039 |
| 1 | $Cr_2O_3$ | 0.074 | 0.080 | 0.031 | 0.033 |
| 1 | MnO | 0.100 | 0.062 | 0.090 | 0.056 |
| 1 | $Fe_2O_3$ | 1.278 | 0.084 | 0.512 | 0.034 |
| 1 | $Co_3O_4$ | 0.014 | 0.054 | 0.004 | 0.014 |
| 1 | NiO | 0.033 | 0.048 | 0.029 | 0.041 |
| 1 | CuO | 0.623 | 0.053 | 0.501 | 0.043 |
| 1 | $Nb_2O_3$ | 0.143 | 0.060 | 0.039 | 0.016 |
| 1 | $MO_3$ | 0.039 | 0.070 | 0.017 | 0.031 |
| 1 | $WO_3$ | 0.074 | 0.195 | 0.020 | 0.054 |
| 1 | $P_2O_5$ | 2.082 | 1.316 | 0.938 | 0.593 |
| 1 | $SO_3$ | 0.800 | 0.667 | 0.639 | 0.533 |
| 1 | CaO | 2.936 | 0.298 | 3.349 | 0.340 |
| 1 | MgO | 0.000 | 0.000 | 0.000 | 0.000 |

**Table 5: Ogyoma Sample Result (continued)**

| Layer | Component | Concn.mg/cm$^2$ | Error | Mole% | Error |
|---|---|---|---|---|---|
| 1 | $K_2O$ | 3.969 | 0.419 | 2.695 | 0.285 |
| 1 | BaO | 0.256 | 0.325 | 0.107 | 0.135 |
| 1 | $Al_2O_3$ | 21.198 | 8.576 | 13.295 | 5.379 |
| 1 | $Ta_2O_5$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | $TiO_2$ | 0.194 | 0.127 | 0.155 | 0.102 |
| 1 | ZnO | 0.208 | 0.045 | 0.164 | 0.035 |
| 1 | $Ag_2O$ | 0.123 | 0.334 | 0.034 | 0.092 |
| 1 | Cl | 10.437 | 0.784 | 18.826 | 1.414 |
| 1 | $ZrO_2$ | 0.012 | 0.056 | 0.006 | 0.029 |
| 1 | $SnO_2$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | RaO | 0.054 | 0.092 | 0.014 | 0.024 |
| 1 | $U_2O$ | 0.114 | 0.129 | 0.015 | 0.017 |
| 1 | $Th_2O_5$ | 0.247 | 0.114 | 0.029 | 0.013 |

**Table 6: Ogyoma Elemental Result**

| Element | Line Code | Cond. Code | Intensity (c/s) | Error (c/s) | Conc. mg/cm$^2$ |
|---|---|---|---|---|---|
| O | Ka | 0 | 0.000 | 0.000 | 43.249 |
| Mg | Ka | 1 | 0.000 | 2.2226 | 0.000 |
| Al | Ka | 1 | 10.541 | 4.2648 | 11.219 |
| Si | Ka | 1 | 106.159 | 8.0319 | 25.680 |
| P | Ka | 1 | 8.420 | 5.3239 | 0.909 |
| S | Ka | 1 | 5.684 | 4.7410 | 0.320 |
| Cl | Ka | 1 | 233.851 | 17.5605 | 10.437 |
| K | Ka | 1 | 94.287 | 9.9638 | 3.295 |
| Ca | Ka | 1 | 85.524 | 8.6940 | 2.099 |
| Ti | Ka | 1 | 10.246 | 6.7208 | 0.116 |
| V | Ka | 1 | 3.702 | 7.4458 | 0.031 |
| Cr | Ka | 1 | 7.944 | 8.4929 | 0.051 |
| Mn | Ka | 1 | 15.357 | 9.5169 | 0.078 |
| Fe | Ka | 1 | 215.790 | 14.2442 | 0.894 |
| Co | Ka | 1 | 2.966 | 11.3258 | 0.010 |
| Ni | Ka | 1 | 8.496 | 12.1893 | 0.010 |
| Cu | Ka | 1 | 185.317 | 15.8020 | 0.497 |
| Zn | Ka | 1 | 69.685 | 14.9029 | 0.167 |
| Zr | Ka | 1 | 3.016 | 14.4998 | 0.009 |
| Nb | Ka | 1 | 34.150 | 14.2671 | 0.114 |
| Mo | Ka | 1 | 7.511 | 13.3627 | 0.026 |
| Ag | Ka | 1 | 3.157 | 8.5645 | 0.115 |
| Sn | La | 1 | 0.000 | 16.4432 | 0.000 |
| Ba | La | 1 | 4.980 | 6.3116 | 0.229 |
| Ta | La | 1 | 0.000 | 16.4432 | 0.000 |
| W | La | 1 | 6.357 | 16.8526 | 0.058 |
| Ra | La | 1 | 10.628 | 18.2917 | 0.050 |
| Th | La | 1 | 39.993 | 18.4309 | 0.210 |
| U | La | 1 | 16.442 | 18.5086 | 0.111 |

**Table 7: Results of Physicochemical parameters of Water samples**

| ## | Time | User ID | Parameter | OGYOMA | ADEKE | KERTYO | Unit |
|---|---|---|---|---|---|---|---|
| 1 | 12:01:16 | Wahidat | pH | 7.5 | 7.2 | 8.1 | - |
| 2 | 12:04:11 | Wahidat | SALINITY | | | | mg/l |
| 3 | 12:09:25 | Wahidat | Electrical Conductivity | 0.00 | 0.00 | 0.00 | mS/cm |
| 4 | 12:12:02 | Wahidat | SULPHATE | 23.4 | 19.8 | 41.7 | mg/l |
| 5 | 12:17:07 | Wahidat | CHLORIDE | 8.2 | 11.7 | 79.8 | mg/l |
| 6 | 12:21:18 | Wahidat | NITRATE | 0.08 | 0.1 | 7.4 | mg/l |
| 7 | 12:27:21 | Wahidat | TURBIDITY | 1.96 | 2.35 | 82 | mg/l |
| 8. | 12:35:11 | Wahidat | CALCIUM | 23.1 | 29.4 | 52 | mg/l |
| 9. | 12:41:15 | Wahidat | MAGNESIUM | 43 | 39 | 67 | mg/l |
| 10. | 12:46:34 | Wahidat | HARDNESS | 66 | 68 | 119 | mg/l |
| 11. | 12:53:59 | Wahidat | IRON | 0.09 | 0.13 | 0.11 | mg/l |
| 12. | 12:57:09 | Wahidat | LEAD | 0.00 | 0.00 | 0.00 | mg/l |
| 13. | 13:04:01 | Wahidat | ZINC | 0.7 | 0.9 | 0.6 | mg/l |
| 14. | 12:10:13 | Wahidat | COLIFORM | 0.00 | 0.00 | 0.2 | mg/l |

**Table 8: World Health Organization (WHO), European Union (EU) Drinking Water Standards, and Nigeria Standard for Water Quality (NSWQ)**

| Parameter (Unit) | WHO | EU | | Quantity found in |
|---|---|---|---|---|
| pH | - | - | | fresh, surface and |
| Electrical Conductivity μs/cm | 250 | NSWQ | | groundwater |
| Aluminium (Al) mg/l | 0.2 | 6.5-8.5 | | 6.5 |
| Ammonium ($NH_4$) mg/l | - | 250 | | |
| Antimony (Sb) mg/l | 0.005 | 1000 | | |
| Arsenic (As) mg/l | 0.01 | | | |
| Barium (Ba) mg/l | 0.3 | 0.2 | 0.2 | 0.2 to 0.3mg/l |
| Berillium (Be) | - | - | 0.50 | |
| Boron (B) mg/l | 0.3 | 0.005 | - | |
| Bromate (Br) mg/l | - | 0.01 | 0.01 | <4μg/l |
| Cadmium (Cd) mg/l | 0.003 | - | | |
| Chloride (Cl) mg/l | 250 | - | 0.7 | <1μg/l |
| Cyanide (CN) mg/l | 0.07 | | - | |
| Coliform Bacteria ml | - | 1.00 | - | <1mg/l |
| Chlorine dioxide ($ClO_2$) mg/l | 0.4 | 0.01 | - | - |
| Chromium $Cr^{+3}$, $Cr^{+6}$ ) mg/l | 0.05 | 0.005 | 0.003 | <1μg/l |
| Copper $Cu^{+2}$ mg/l | 2.0 | 250 | 250 | |
| Fluoride (F) mg/l | 1.5 | 0.05 | 0.01 | |
| Sulphate ($SO_4$) mg/l | 500 | | | |
| Nitrate ($NO_3$) mg/l | 0.5 | 0in100 | | <10 for any 100ml |
| Nitrite ($NO_2$) mg/l | - | 0.05 | <2μg/l | |
| Hardness ($CaCO_3$) mg/l | 500 | | | |
| Iron $Fe^{2+}$ mg/l | 0.05 | | | |
| Lead (Pb) mg/l | 0.01 | | 1.0 | |
| Manganese ($Mn^{+2}$) mg/l | 0.5 | 1.5 | 1.5 | <1.5mg/l (up to |
| Mercury (Hg) mgHg/l | - | | 10) | |
| Molybdenum (Mb) mg/l | 0.07 | 250 | 100 | |
| Nickel (Ni) mg/l | 0.02 | - | - | |
| Selenium (Se) mg/l | 0.01 | 0.5 | - | |
| Silver (Ag) | - | - | 150 | |
| Sodium (Na) mg/l | 200 | 0.3 | 0.30. | 5-50mg/l |
| Inorganic tin (Sn) mg/l | - | | | |
| oxidisability | 5 | 0.05 | 0.01 | <0.5 μg/l |
| Turbidity NTU | - | - | | |
| (Nephelometric Turbidity unit) | 30 | - | 0.2 | <0.01mg/l |
| Calcium (Ca) mg/l | - | - | | |
| Magnesium ($Mg^{+2}$) mg/l | | - | 0.001 | <0.02-0.1mgNi/l |
| Dissolved Oxygen mg/l | - | - | | |
| Hydrogen Sulphide ($H_2S$) | 5.0 | - | - | |
| mg/l | | $5.0/O_2$ | 0.02 | <<0.01 mg/l |
| Zinc (Zn) mg/l | | - | | |
| | | -75 | - | |

## Result Analysis and Discussion

Groundwater has a direct bearing with mineral accumulation on earth. It is important as a source of freshwater for agricultural, industrial and domestic purposes and accounts for about 42%, 27% and 36% respectively (Adeyemi, Opeyemi & Olufemi, 2017). The quantitative distribution of elements in groundwater were obtained by XRF analysis from three sample locations namely kertyo in Makurdi, Ogyoma in Otukpo and Adeke in Gwer West Local Government areas of Benue State respectively for the purpose of mineral resources prospection. As a guide for the discovery of an economic orebody, the elements being sort must occur at much higher than normal concentration in the water. The elements associated with mineral deposits must have a concentration factor, ten times the normal or background value. That is to say, ten times the average abundance of these elements found in fresh, surface or groundwater for it to be a pathfinder or an indicator element of interest. It may be said that when there is a sharply increased content of some elements in the sample, it is indicative of a higher than average content of the element in the soil, and possibly also in the bedrock, which serve as a pointer to a corresponding mineral deposit.

The pH of the water samples is between 7.2 - 8.1 (table 7). This indicates alkaline condition which promotes more exchange ions per unit time that precipitate mineral soluble salts of sodium, potassium, calcium and several clay minerals (Kaolinic clay, bentonite, montmorrilonite) associated with calcium rich parent rocks such as anhydrite; $CaSO_4$, gypsum; $CaSO_4.2H_2O$, Calcite (limestone); $CaCO_3$, Dolomite; $CaMg(CO_3)_2$. Clay minerals occur in several parts of Benue State namely Ulayi, Gboko, Otukpo, Obi, Oju, Ukum, Ushongo, Moi-Igbo, Konshisha etc. Salt occurs in form of brine and incrustations in some sedimentary rocks in large parts of Benue soils, marshes and pools with high concentration in groundwater within and around Makurdi metropolis, Gwer West, Gwer East, Ado, and Ukum local government areas (Ogah, 2014). The Three XRF results show high concentration of chloride (Cl) of 27mg/cm$^2$ in Kertyo, 13.5mg/cm$^2$ in Adeke and 10mg/cm$^2$ in Ogyoma (tables 2, 4 & 6).

High amount of oxygen in water is necessary for formation of oxygen bearing compounds like carbonates ($Co_3$), Silicates ($SiO_2$), Nitrates ($No_3$), Sulphates ($SO_4$) and phosphate minerals ( Apatite; $Ca_5F(PO_4)_3$. From the three samples, the oxygen values are 30.4, 39.06, and 43.2 mg/cm$^2$ for Kertyo, Adeke and Ogyoma (tables 2, 4, 6 respectively). The abundance of oxygen accounts for chromite ($FeCrO_4$), ilmenite ($FeTiO_3$), magnetite ($Fe_3O_4$) and much silica (quartz) $SiO_2$ in the soil environments. The amounts of $SiO_2$ in the three water samples are 21.8, 40.8 and 55mg/cm$^2$ as shown in tables 1, 3 and 5 respectively. The solubility of $SiO_2$ increases with alkaline waters, hence in the dry season $SiO_2$ are removed through leaching leaving Aluminum (bauxite) $Al_2O_3$ or $Fe_2O_3$ as residual laterites. Hence we have abundance of Fe-Laterites rich in feldspar and feldspathoids derived from basalts and bauxites all over Benue State tropical soil. The levels of bauxite ($Al_2O_3$) in the water samples are 22.0mg/cm$^2$ for Kertyo, 18.7mg/cm$^2$ for Adeke, while it is 21.1mg/cm$^2$ in Ogyoma, tables 1,3, and 5. This shows high level of bauxite concentration in the sample areas' sub-surface.

High concentration of Radon (Rn) in surface or groundwater is an indicator of all types of Uranium deposit. The Radon XRF analysis result presented in tables 2, 4 and 6 show low level of Rn concentration of 0.109, 0.169, 0.050mg/cm$^2$ respectively and hence rules out the possibility of uranium radioactive deposit or any slightly radioactive mineral deposit in the study areas.

High amount of Manganese (Mn) element above threshold value could be a pathfinder element to vein and porphyritic deposits of copper (Cu), Barium (Ba) and Silver (Ag). In the similar vain, high above average value of Zn may serve as pathfinder element to Ag, Pb, Zn, Sulphide deposits etc. As well as high above maximum permissible concentration level of Be, Ta and Sn elements are indications of associated beryl, tantalite and cassiterite minerals respectively. Sulphates ($SO_4$) accumulation is an indicator to sulphide deposits. Subsurface waters that pass through sulphide bearing deposits can oxidize the sulphides and become anomalously charged with sulphate and thus indicate zones of sulphide mineralization for more intensified geochemical exploration. The average concentration values from the XRF analysis for the following elements are Mn=0.124, Cu=1.001, Ba=0.076, Ag=0.299, Zn=0.191, Ta=0.013 and Sn=0.372mg/cm$^2$ (tables, 2, 4 & 6 average). Kertyo water sample has the highest value of 41.7mg/l for $SO_4$ and an average of 33mg/L for the three water samples (table 7). These results compared with the values on table 8 column 4 show that the elements are below threshold values, that is within permissible concentration levels and do not serve as pathfinder (indicator) elements to their respective associated minerals.

From the result of the physicochemical analysis table 7, chloride concentration is highest in Kertyo water sample with a value of 79.8mg/l and an average of 33mg/l for the three samples. This value falls below maximum permissible level on table 8, but accounts for dissolved minerals salts in these areas under study. The high value of calcium and magnesium in Kertyo water sample is responsible for the water total hardness in the area. The high value of chloride, calcium and magnesium elements in Kertyo groundwater (table 7) makes the water to have salty taste and gives colouration to food, dissociates corn flour or semovita meals when used for cooking. It also erodes or fades away colours of clothes when used for washing. It is therefore, not suitable for drinking or domestic uses. The Ogyoma location has the highest abundance of groundwater with the highest value of silica (table 5) implying a highly permeable level of the groundwater.

The values for iron, lead and zinc elements on the physicochemical result sheet table 7, does not show that they are indicator elements as to warrant further investigations.

Turbidity in Kertyo water sample is high at 82mg/l (table 7). Groundwater turbidity harbor microorganisms that can entrap heavy metals, examples: Fe, Pb, Zn etc. and biocides affecting quality of water available.

Bacterial coliforms are due to potential presence of pathogens and organic substrate for microbial growth; this can bring bacterial re-growth in distribution systems and microbial fouling in water. The concentration of 0.2mg/l of coliform in Kertyo groundwater, table 7, as against the recommended concentration value of 0.00mg/l, makes it unsafe as drinking water except when boiled before drinking. However, the bacterial coliform value is not high enough to initiate the search for hydrocarbons (oil and gas) in this sampled location.

Deep rooted plants within and around the environment of the study locations were examined for effects of toxic quantities of elements on the manner of growth (morphology) or the physiological development of botanical specimens in these areas. No such plants as local indicators of high elements' presence or abundance in the environment were found, implying the absence of potential presence of any significant mineral deposit affecting plant growth.

## XRF Elemental Concentration Analysis for Domestic Water Uses in the three Sampled Areas.

The Nickel (Ni) value of Kertyo water sample is higher than the maximum permissible level of 0.02mg/l by 0.05mg/l which could cause possible carcinogenic health challenge in humans.

For all the water samples, the iron (Fe) content is higher than the maximum permissible concentration level for drinking water. It is higher by 1.0mg/l in Kertyo, 1.5mg/l in Adeke and 0.5mg/l in Ogyoma water samples respectively (tables 2, 4 & 6). This is an indication of abundant Fe-element in the geological environment arising from parent and country (host) rocks in these locations.

The Copper (Cu) content of Kertyo water sample is 1.5mg/l (table 2) against the permissible standard concentration level of 1.0mg/l. Excess of Cu in water can cause gastrointestinal disorder to consumers. Ogyoma and Adeke water Cu levels are within permissible concentration standard for domestic water uses.

Chromium (Cr), level of Kertyo groundwater in table 2 is 0.153mg/l slightly higher than the normal or standard concentration level of 0.05mg/l. The difference of 0.1mg/l in drinking water is dangerous to health and can cause cancer in humans.

## Conclusion

In all the elements and compounds in XRF analysis result, none has extremely anomalous concentration value of interest to further geochemical investigations that may lead to discovery of a probable mineral body. There is also the absence of geo-botanical evidence to locate a mineral deposit. Out of the three water samples analysed, Ogyoma groundwater has the least salinity, hardness and chloride concentration and it is the best in quality for drinking and other domestic uses. The next in quality for domestic purposes is the Adeke groundwater. The Kertyo groundwater is not suitable for drinking and other domestic uses due to high content of undesirable elements, Ni, Cu, Cr and high concentration of Fe in the water, as well as its hardness.

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